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Umer Rashid *Editors*

Biomass and Bioenergy

Applications

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Foreword

There are many global resources available to meet the growing energy demand. Global reserves of petroleum lie around 1.033.2 billion barrels, natural gas around 5.141.6 trillion cubic feet, and coal around 1.087.2 billion tons. The energy sources used for generating electrical power on global basis are nuclear (17.7 %), natural gas (14.8 %), coal (38.4 %), oil (9.3 %), hydro (18.4 %), and wood + refuse + renewable (1.4 %). The common renewables are solar, wind, biomass, energy from waste, geothermal, hydro, wave and tidal, and ocean thermal. Out of these energy sources, renewable energy is among the fastest growing. Annual turnover has reached 30 billion Euros or about 50 % of the world market. Recycling, energetic valorisation, prevention and organic valorisation are attracting great attention worldwide. One of the sources of renewable energy is biomass. In many developing countries these sources of fuel are a large proportion of the energy available.

A substantial increase in the production of bioenergy from biomass originating from different sources offers opportunities to reduce greenhouse gas emissions and helps to diversify use of resources in order to provide more secure energy supply. It can create additional income for agricultural land owners, thereby paving way for promoting new economic perspectives among rural communities. A greater production of bioenergy can provide incentives for greater use of agrilands as well as forests, which can counteract the aims of waste reduction policies. However, increase in bioenergy production can at the same time pose a risk of additional environmental pressure on plant diversity, soil use, and water resources. There are ways to overcome these disadvantages by growing low-impact bioenergy crops, forbidding ploughing of pastures, and bringing down the intensity of residue extraction depending upon the soil conditions. Application of sustainably fit environmental regulations is important if we want to increase bioenergy production. There is a great need for an assessment of economics and logistics in this direction.

This book provides detailed insight covering selected chapters on topics like non-wood renewable materials such as oil palm, bamboo, rattan, bagasse, and kenaf; upgrading of oil palm as added product a long-identified sustainable source of renewable energy which can reduce the dependency on fossil fuels as the main source of the energy supply; biodiesel synthesis using transesterification of triglycerides in the presence of catalyst and alcohol, and application of single-step process for biodiesel synthesis from microalgae; electrochemically active biofilms as fascinating biogenic tools for microbial fuel cells, nanomaterial synthesis, bioremediation, and bio-hydrogen production as synthesis of these nanoparticles as well as nanocomposites and bio-hydrogen production does not involve any energy input which make these approaches highly efficient; microalgal biomass as a source of renewable energy; critical analysis of the current situation and future needs for technological developments in the area of producing liquid biofuels from lignocellulosic biomass as a future alternative for bioethanol production; utilisation of sawmill by-product for making cellulose and its valuable derivatives which is normally used for direct combustion; ultimate valorisation of oil palm biomass in relation to biorefinery approach; polylactic acid-based kenaf biomass synthesised via ring opening polymerisation for a production of eco-friendly products which can replace the petroleum-based products; chemical functionalisation of natural cellulosic fibres through free radical-induced graft copolymerisation technique for green polymer composites applications so as to overcome the disadvantages associated with these fibres; recent applications of kapok fibre and its use as a desirable template material or supported candidate such as for catalyst carriers; abaca fibre as a renewable bioresource for industrial uses and other applications in environmental protection specifically for soil conservation and control of soil erosion as well as for the preparation of cellulose nanocrystals as components of the composites; recent advances in the realm of the extraction of nanofibrillated cellulose from lignocellulosic fibres as sustainable nanofillers with broad potentials use; termites from pest to biopolymer derivatives extractor as efficient converters of wood into sugars and for making numerous biochemicals and biofuels, with recent conversion methods of biochemicals from lignocellulosic biomass for application enablement and commercialisation, laying special emphasis on termite lignocellulolytic system; and last but not least applications of biomass-derived catalyst.

I am sure that the chapters presented in this book will encourage further discussion and research and development on biomass and biofuel production for human use, taking into account the environmental sustainability. It is a welcome addition to the existing information available on this topic. The main focus has been on Indonesia, Malaysia, Philippines, Thailand, Bangladesh, India, and Pakistan where large populations have been and are still using biomass as a source of energy. The authors and the editors of this book have done a good job in covering the diverse aspects of biomass/biofuel production and multiple uses of cellulosic materials.

Izmir, Turkey Münir Öztürk

Preface

Recently technological advances, consumer demands, and environmental consciousness lead to better application of available biomass for environmental sustainability. Biomass is abundantly available worldwide as a cheap and extremely important renewable energy source of materials for producing energy which can be used for different applications at the cost competitive rates. In recent years, the use of biomass and bioenergy has been widely adopted worldwide to produce biofuels, biogas, biocatalyst, bio-composites, bioplastics, green chemical products, cellulose textiles, etc. However, there are still important issues and applications of biomass to be explored. The number of biomass energy applications is expanding rapidly which motivated us to work in this area to compile resources in the form of the present book.

This volume (second of the book series *Biomass and Bioenergy*) attempts to give an overview of the current applications of biomass and bioenergy to scientists, researchers, and industrial people in the field of material science, chemical engineering, forestry, and mechanical engineering to understand where and how biomass and bioenergy can be utilised, how it works, and the advantages as well as the limitations. Overall, biomass is seen as a potential material, and this book covers the utilisation of biomass in different applications such as hydrogen production, bioethanol, biodiesel, biofuel, bioenegry, biofilms, renewable energy, nanocellulose, green composites, and catalysts. With this book we tried to provide some new insights into the readers about applications of biomass and bioenergy, which were not explored in previous published works.

We are highly thankful to all the contributors from around the world, who helped us to shape our idea in the form of a much needed volume by following our instructions and feedback. We greatly appreciate their commitment.

We thank Springer-Verlag team for initiating and supporting our book idea and their unstinted cooperation at every stage of the book production.

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Dr. Umer Rashid, Ph.D. is working as a Senior Fellow Researcher at Universiti Putra Malaysia, Malaysia since 2011. He has obtained his M.S. in Chemistry in 2003, from the University of Agriculture, Faisalabad, Pakistan and then completed his Ph.D. degree also from the University of Agriculture, Faisalabad, Pakistan in 2009 in the field of Analytical Chemistry. During his Ph.D. he worked as a Visiting Scientist in the Food and Industrial Oil Research Group at the USDA in Peoria, IL, USA. He is also the recipient of 2007 The Industrial Oil Products Division Student Excellence Award by Industrial Oil Products Division of the American Oil Chemist's Society (AOCS), USA. He completed his Post Doctorate in the field of Green Chemistry from Universiti Teknologi PETRONAS, Malaysia from 2010 to 2011. The focus of his research has been on the production and characterisation of novel feedstocks for biodiesel production. He has produced 92 research papers in internationally recognized ISI journals, including five book chapters with international publishers. Currently, he is working on the synthesis of heterogeneous catalyst from carbon based sources for the utilisation of high free fatty acid feedstocks for biodiesel production.

Chapter 1
Non-wood Renewable Materials: Properties Improvement and Its Application

Rudi Dungani, H.P.S. Abdul Khalil, Ihak Sumardi, Yoyo Suhaya, Endah Sulistyawati, Md. Nazrul Islam, N.L.M. Suraya, and N.A. Sri Aprilia

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Abstract Plant biomass are woody and non-wood materials (e.g., oil palm, bamboo, rattan, bagasse, and kenaf) and are abundant and renewable resource. Unfortunately, the heavy reliance on this resource is a threat to forest ecosystems and a recipe for accelerated land resource degradation. Due to the increasing scarcity of wood resources, many rural communities have shifted to utilization of crop residues for many different applications. The non-wood biomass is readily available, environmental friendly, and technologically suitable, and therefore, an excellent raw material for the future. The non-wood materials like bamboo, rattan, oil palm, and bagasse have superior properties and durability, which can be further prolonged by the modification treatment. The modification treatments increase the performance of the non-wood and could make it suitable for applications in many fields ranging from construction industry to automotive industry. This chapter deals with the properties improvement techniques of the selected non-wood biomasses and evaluates its applications for various purposes. The new developments dealing with the improvement of non-wood properties have also been presented in the chapter. The performance of non-wood biomass materials has been compared to the wood-based materials. Recent studies pertaining to the above topics have also been cited. Finally, the advanced applications of the improved non-wood biomasses have been highlighted.

Keywords Non-wood biomass • Biocomposites • Properties improvment • Fibers

1.1 Introduction

Fossil resource-based industry has serious negative impact on the global environment due to the increase in the atmospheric concentration of carbon dioxide, along with a number of other pollution problems. Non-wood biomass (agricultural waste) is the most abundant resource and one that is also renewable. However, it also has various advantages of a techno-economical. Utilization of non-wood biomass has been based on the paradigm of a fossil resource-based society, and thus, it is critically important to establish sustainable production and utilization system for material, especially those in tropical regions where resources and biodiversity are plentiful.

In subtropical and tropical region, non-wood biomass are natural resources which plays very important role in the daily life of millions people. Traditionally, the main uses of non-wood biomass in ropes and twines mainly produced through cottage industries. Non-wood, especially, in a form of fibers is converted into yarn, string, ropes, floor mats, bags, floor and wall coverings, and different handicrafts. Meanwhile, the modern processing techniques have considerably extended their usefulness. Non-wood biomass are very promising alternative material because it is economical, renewable, and processable material that has been shown to exhibit equal or better physical and mechanical properties and comparable to some commercial wood species. Therefore, it is becoming more important to establish sustainable and renewable resources for societies. In addition, establishment of basic science and technology dealing with lignocellulosic materials, including bamboo, oil palm, rattan, and bagasse, is indispensable to the promotion of non-wood industries of tropical countries.

Polymers and reinforcing fibers from renewable resources, e.g., annual plants or non-wood, is one way to produce renewable and biodegradable composite materials for various applications such as furniture, automotive components, structural, and others. In the composite industry, non-wood fibers are used to produce a wide variety of products with different properties: fiber as filler reinforcement, biofiller, fiber for polymer composite, upholstery material, packaging materials such as board and corrugated board, and fluff products for diapers.

The declining supply of raw material causing concern and in this context the natural fiber material can be seen as a good alternative material for the local timber industry to produce value-added biocomposite product in tropical countries. Biocomposite product needs further development as a long-term strategy to develop the tremendous wealth of non-wood (natural plant) fiber that is currently under utilized. Interest in using non-wood biomass, which is predominantly lignocellulosic materials, in the production of biocomposites has gained momentum in recent years. The non-wood biomass has not been fully exploited as source cellulosic fiber, principally to biocomposites technology development. Lignocellulosic, in this context, is referring to a non-wood biomass fibers which have different properties due to differences in chemical composition and morphological of fibers (Abdul Khalil et al. 2012).

Malaysia and Indonesia produce total of over 90 % of lignocellulosic material from oil palm industry only (Yuliansyah et al. 2009). Other lignocellulosic source mentioned was sugar cane bagasse, bamboo, rattan, and natural fibers (kenaf).

1.2 The Overview of Selected Non-wood Biomass

The biomass development through intensification use of non-conventional raw material (kenaf, oil palm, bamboo, rattan, bagasse, and another non-wood) was technically and economically feasible. They can play an important supplementary role, especially in the form of fibers. The non-wood materials were identified suitable for the production of paper, composites, and engineered material. There are several non-wood fiber sources other than those of agricultural residue origin. While some of them are of forest origin, others are cultivated in view of their suitability for biocomposites production. Malaysia and Indonesia are world's largest producers of oil palm. But the situation is not as impressive with regard to their utilization.

The most important properties of fiber in utilization to biocomposites product are fiber dimension (length, thickness, and width), crystallinity, and permeability. Therefore, fiber produced by agricultural waste (oil palm waste and bagasse), and natural fiber plants (kenaf, jute, pineapple, abaca etc.) are seen as promising lignocellulosic raw material for the manufacturing of natural fiber reinforced/filled composites for different application. These fibers have tremendous variations in chemical and physical properties as compared to wood fiber. Products produced using natural fiber improved their homogeneity and quality (Abdul Khalil et al. 2012). Non-wood biomass offers numerous advantages; they are abundantly available, have high specific mechanical properties, low in cost, low density, safe to handle, not a threat to environment, and also renewable and biodegradable (Abdul Khalil et al. 2008a; Bachtiar et al. 2011). Oil palm, bamboo, bagasse, rattan, and kenaf biomass which used as raw material to produce fibers are shown in Fig. 1.1.

1.2.1 Properties of Non-wood Biomass and Fibers

The properties and characteristic of physical fiber, chemical (lignin, hemicellulose, and cellulose) content of various non-wood and agricultural residues were examined to assess their suitability for biocomposites production. The fundamental characterization and properties will not only help in open up a new avenue for this fiber, but also emphasize the importance of this biomass as future material. In order to determine the applicability of biomass as raw materials for the production of biocomposites, the properties of the raw materials have first to be examined and determined.

The physical, mechanical, and morphological properties on performance of non-wood fibers depend on cellulose content, fiber orientation, crystal structure, and diameter/cross-section area of the fiber. The fiber cross-section area strongly influences the evaluation of fiber strength. Hence, as a natural material, non-wood biomass fiber is strongly influenced by the strength of its constituent cells, namely affected by thickness of fiber wall (Rowell et al. 2000).

1.2.1.1 Chemical Properties

The major chemical component of non-wood biomass and fiber is composed of cellulose and hemicelluloses that are combined with lignin with lesser amounts of extractives, protein, starch, and inorganics. The three-dimension polymeric components determine most of the properties of non-wood biomass and fibers (Ndazi et al. 2006). The distribution of chemical components pass through the cell wall which is composed of primary and secondary wall layers. Variation and contribution of chemical composition from non-wood biomass to other non-wood biomass are different from parts of the same non-wood biomass. Table 1.1 shows the chemical composition of different non-wood biomass and fibers.

1.2.1.2 Physical and Mechanical Properties

The physical properties of non-wood fiber are important to know in order to reach its highest potential in the utilization. As depicted previously, the physical properties of fibers such as defects, strength, fiber dimensions, variability, crystallinity, and structure are some of the important considerations in utilization for production of high-performance structure fiber/polymer composite.

Oil palm waste Oil palm fibers

Bamboo waste Bamboo fibers

Bagasse Bagasse fibers

Rattan Rattan fibers

Kenaf Kenaf fibers

Fig. 1.1 Non-wood biomass fibers

Table 1.1 Chemical composition of some non-wood biomass and fiber

Type of biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Extractive (%)
Oil palm	14.3–65.2	12.5–38.7	17.3–26.5	2.0–3.5	0.9–3.0
Bamboo	20.3–61.5	19.3–21.4	11.1–32.2	1.7–5.1	1.3–2.8
Bagasse	55.6–57.4	23.9–24.5	24.35–26.3	1.5–5.3	2.65–3.25
Rattan	35.6–52.9	22.8–34.7	21.0–22.0	1.3–2.0	0.3–2.0
Bast kenaf	44.3–57.8	15.6–19.2	22.0–23.2	2.0–5.0	0.1–0.25
Core kenaf	37.5–49.6	15.1–21.4	18.0–24.3	2.3–4.3	0.12–0.3

Sources: Law et al. (2007), Abdul Khalil et al. (2006), Shibata (2012), Wang et al. (2010), Muniandy et al. (2012), Hemmasi et al. (2011), Zaini et al. (2013), Li et al. (2007)

Table 1.2 Dimension of selected non-wood biomass fibers

Type of fiber	Fiber length (mm)	Width fiber (μm)	Width lumen (μm)	Wall thickness (μm)
Oil palm	0.33–50.31	8.3–20.5	7.90–17.3	1.8–8.3
Bamboo	2.98–5.63	12.9–42.5	1.6–31.1	2.4–13.3
Bagasse	1.22–1.59	19.35–20.96	9.12–9.72	4.95–5.62
Rattan	1.23–1.92	1.04–2.13	0.8–1.12	1.9–3.8
Bast kenaf	2.27–2.51	25.74–26.59	13.05–13.75	6.35–6.42
Core kenaf	0.72–0.88	36.10–36.78	23.58–27.48	4.31–6.60

Sources: Abdul Khalil et al. (2008a), Sreekala et al. (2004), Tamizi (2010), Abdul Khalil and Suraya (2011), Phukringsri and Hongsriphan (2013), Shibata (2012), Hemmasi et al. (2011)

Non-wood biomass of bamboo, rattan, and oil palm in the form of stem have different physical and mechanical properties which are affected by variety of species, age, and locality. The fiber length and width is very important in non-wood biomass-based fiber composites as it give an indication of possible strength properties (Rowell et al. 2000). The fiber characteristics of biomass indicate a wide range of fiber length, width, and thickness. The average values are obtained by different workers on each type of biomass (Tamizi 2010). The dimensions of some common non-wood biomass fibers are shown in Table 1.2.

On the other hand, fiber strength can be an important factor in selecting a specific non-wood biomass fiber for a specific application. Non-wood biomass fibers also vary in mechanical properties depending on what part of the plant the fiber came from and the age of the plant. The variation of value for mechanical properties shows that results reported by researchers are not identical because of variation in the type fiber and also the irregular sectional area which fluctuates along the length of non-wood biomass fiber (Virk et al. 2012). Table 1.3 gives data on physical and mechanical properties of several non-wood biomass and fibers. It can be seen that physical and mechanical properties vary widely depending on the type of non-wood biomass and fiber.

1.2.1.3 Morphological and Fiber Ultrastructure

The lignocellulosic of fibers non-wood biomass, multi-cellular with single cells embedded in a matrix composed of non-cellulosic matters, and lignin constitutes one of the main components in the system. The fiber will change in physical properties

Table 1.3 Physical and mechanical properties of selected non-wood biomass and fibers

Type of non-wood biomass and fiber	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)	Density (gr/m^3)
Oil palm	227.5–278.4	2.1–5.0	2.7–3.2	0.7–1.55
Bagasse	257.3–290.5	6.2–8.2	15–18	0.31–1.25
Bamboo	330.5–400.3	15.4–30.0	45.6–65.5	0.51–1.13
Rattan	280.3–500.5	19.32–31.3	40.9–66.4	0.25–0.59
Bast kenaf	895.1–930.3	1.46–1.76	49.3–56.2	0.22–0.40
Core kenaf	898.5–938.7	1.43–1.69	50.5–56.8	0.10–0.20

Sources: Muniandy et al. (2012), Tamizi (2010), Abdul Khalil and Suraya (2011), Abdul Khalil et al. (2008a), Gassan et al. (2001), Hemmasi et al. (2011)

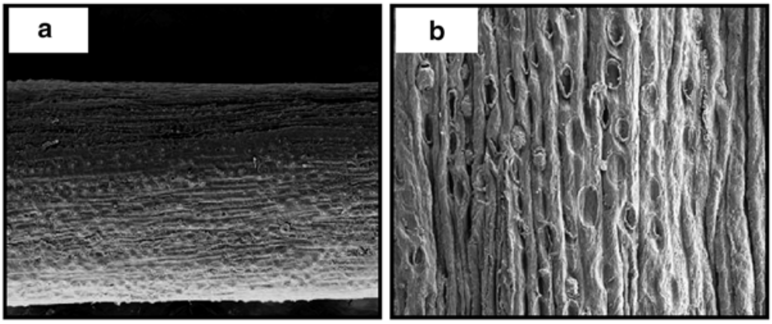


Fig. 1.2 Scanning electron micrograph of oil palm EFB fiber: (**a**) Longitudinal surface view at magnification 500× (*photo by* Abdul Khalil et al. 2006); (**b**) Surface of oil palm fiber with silica bodies (*photo by* Bhat et al. 2011)

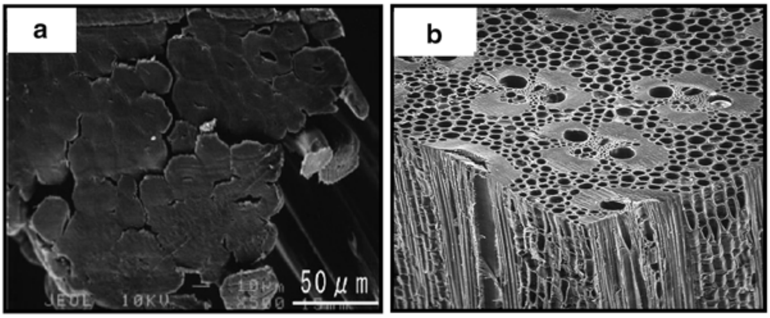


Fig. 1.3 Scanning electron micrograph of bamboo fiber: (**a**) Cross-section structure bamboo fibers (*photo by* Shibata 2012); (**b**) vascular bundle of bamboo fibers (*photo by* Liese 2004)

because of differences in its morphology. The ultrastructure of non-wood biomass fibers by scanning electron micrographs (SEM) is shown in Figs. 1.2, 1.3, 1.4 and 1.5. Generally, the natural fiber has major differences in structure (density, cell wall thickness, tracheid length, and diameter) that result in differences in physical properties (Rowell et al. 2000).

Figure 1.2a shows the longitudinal surface view at magnification 500× and Fig. 1.2b shows closer and clearer view of silica bodies on oil palm fiber. As depicted

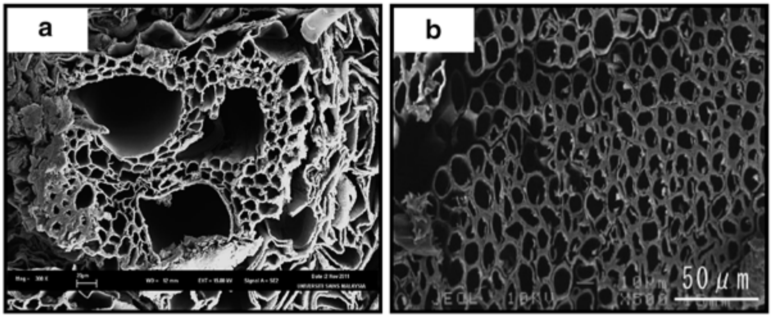


Fig. 1.4 Scanning electron micrograph of a bagasse fiber: (**a**) bagasse fiber at magnification, 300×; (**b**) Cross-sectional structure bagasse fiber (*photo by* Shibata 2012)

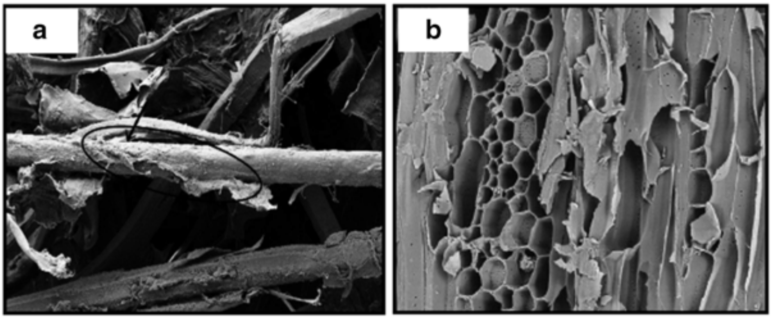


Fig. 1.5 Scanning electron micrograph of kenaf fiber: (**a**) bast kenaf fiber (*photo by* Abdul Khalil and Suraya 2011); (**b**) longitudinal section of core kenaf fibers (*photo by* Abdul Khalil et al. 2010c)

in Fig. 1.2b, silica bodies are found in great numbers on oil palm EFB strand (Law et al. 2007). Furthermore, Law et al. (2007) reported that, silica bodies seem to attach themselves to circular crater which spread relatively uniform over the strand's surface. They also investigated that the silica bodies looked like rounded-shape and are measured about 10–15 µm in diameter.

The bamboo fiber is often brittle because their fibers contain higher lignin compared to other natural fibers. The lignin components are covering in fibers resulting in great difficulties in delignification (Okubo et al. 2004). Therefore, it is impossible to remove the lignin clearly. The fiber morphology for each species has a different measure of size in terms of fiber length, fiber diameter, lumen diameter, and wall thickness. Study by Tamizi (2010) showed that there were differences in fiber dimensions of bamboo at different locations (node and internode) and positions (outer, middle, and inner layer) in the same species. He observed fiber length was found to be longer at the internode. However, the middle layer has the longest fiber length compared to the outer and inner layer (Fig. 1.3).

Figure 1.4a, b show cross-section structure of bagasse fiber under SEM. Bagasse fibers were found to be porous in structure (Shibata 2012). The structure of the bagasse fibers has a fairly high length (1,590 µm), an acceptable wall thickness (5.64 µm), and

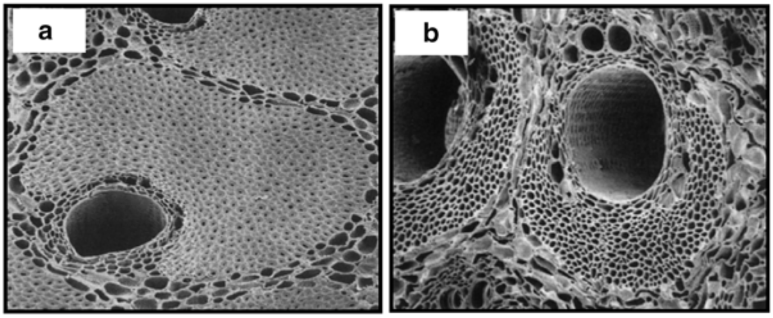


Fig. 1.6 Scanning electron micrograph of rattan: (**a**) Vascular bundle of *C. thwaitesii* with thicker-walled fibers in the periphery and thinner-walled fibers (*photo by* Bhat et al. 1990); (**b**) Vascular bundle of C. *thwaitesii* with thicker-walled fibers in the center of basal internode (*photo by* Bhat et al. 1990)

small cell diameter (20.96 μm). The ratio cell length to diameter is around 75.85 (Hemmasi et al. 2011). It is very well suited for papermaking. The comparison of length fiber showed that the bagasse fibers are shorter than bamboo (Deniz and Ates 2002).

In Fig. 1.5a, it can be seen that the diameters of kenaf fibers ranged from 20 to 90 μm (Abdul Khalil et al. 2006). The individual fibers showed smooth surface and the fiber diameters reduced to an average value of 11 ± 3 μm after bleaching (Zaini et al. 2013). Longitudinal section at tangential surface of core with very small pits in the fibers and parenchymatous cells is shown in Fig. 1.5b. Kenaf fibers have similar cell dimensions to jute fiber; however, the cells in kenaf fiber are much longer (range 20–25 mm). In the cross-sectional area, the single kenaf fibers are much finer than those of jute (Rowell and Stout 2007).

The percentage of wall thickness and fiber of rattan decrease significantly from the basal to the top internodes of the stem and from the periphery to the center at a given internode. Phukringsri and Hongsriphan (2013) suggested that, the increasing of wall thickness will increase stem density due to the deposition of additional lamellae. They considered that, difference of the number and thickness of lamellae in a fiber wall often vary from fiber to fiber even within a given vascular bundle. As depicted in Fig. 1.6a, b, the structure of rattan at transverse section consisted of scattered vascular bundles and ground parenchyma cells.

1.2.2 *Availability of Non-wood Biomass and Fibers*

The establishment of wood industries has to be based on availability of raw materials. Specifically, raw materials from natural forests that are utilized for products with high value-added function, raw materials from non-wood materials (bamboo and rattan) are utilized to replace wood from natural forests and agricultural wastes (postharvest fruits for oil palm and sugarcane production) and natural fiber utilized to replace wood fiber or wood particle otherwise obtained from natural forests.

1.2.2.1 Oil Palm

Oil palm waste is among the most abundantly non-wood biomass all over the world. Oil palm plantations are established primarily in tropical regions, where they are produced in 42 countries worldwide on about 27 million acres (Abdul Khalil et al. 2010a). Oil palm production has nearly doubled in the last decade, and this plant has become the world's foremost fruit crop, in terms of production, for almost 20 years. Biomass of oil palm includes empty fruit bunches (EFB), oil palm trunks (OPT), oil palm fronds (OPS), palm shells, and palm oil mill effluent palm (POME). Malaysia and Indonesia are two main countries which produced roughly around 85 % of the world oil palm.

Sumathi et al. (2008) reported that the oil palm industry in Malaysia, with its six million hectares of plantation, produced over 11.9 million tons of oil and 100 million tons of biomass. The amount of biomass produced by an oil palm tree, inclusive of the oil and lignocellulosic materials, is on the average of 231.5 kg dry weight/year. Prediction based on a planted area of 4.69 million ha and a rate of production dry oil palm biomass of 20.34 tons per ha per year shows that the Malaysian palm oil industry produced around 95.3 million tons of dry lignocellulosic biomass in 2009 (Abdul Khalil et al. 2012). Meanwhile, Indonesia produced 143 million tons of the oil palm biomass annually (Yuliansyah et al. 2009; Hambali et al. 2010).

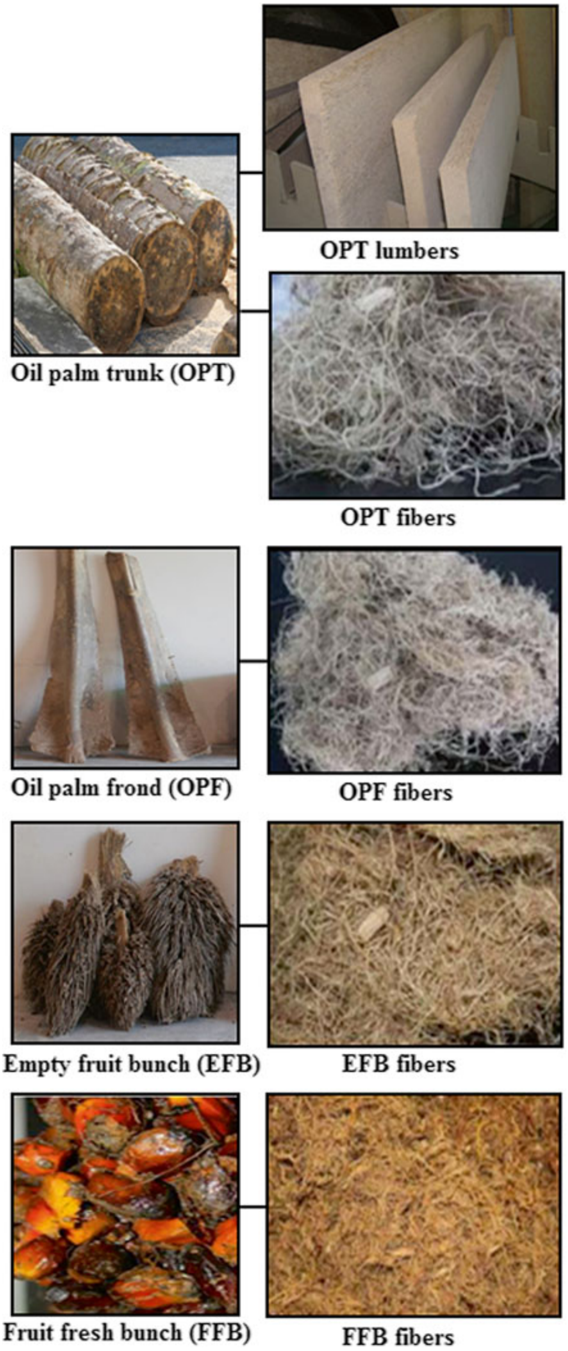
Therefore, oil palm biomass in the form of lumber or conventional composites such as plywood (Abdul Khalil et al. 2010b), oriented strainboard (Hashim et al. 2011) and medium density fiberboard (Ibrahim et al. 2013), and polymer composite (thermoset and thermoplastic) (Abdul Khalil et al. 2008b) can be produced from the parts of oil palm trunk and their fibers. Figure 1.7 showed lumber and fibers product from oil palm biomass as raw material.

A great potential has been depicted by oil palm wastes fibers as a reinforcing material in polymer composites. Many researchers reported the good physical and mechanical properties of this fiber have led to diversify in its applications in the composites material area. Oil palm-producing countries can generate revenue out of this waste and this utilization can also reduce the disposal problem facing by many industries.

1.2.2.2 Bagasse

Bagasse is biomass fiber remain after sugarcane stalks are crushed to extract the juice. It accounts for 9–18 % of the stalk weight in commercial variety (Fig. 1.8). Normally 30 % of bagasse fiber are produced from a sugar factory out of total crushing. The researcher study has attempted to use bagasse as a renewable raw material for power generation and for the production of non-wood biomass material (Mustafa Al Bakri et al. 2013). Typically, the processing of one ton of sugarcane yields about 300 kg of bagasse (Vandamme 2009). In the producer countries, the utilization of sugarcane bagasse becomes more important as it is utilized for manufacturing paper, board or panels, and fuel sources that supply electricity and steam for consumers and mill boiler. World's top producer of sugarcane is Brazil which earns billion

Fig. 1.7 Oil palm biomass waste



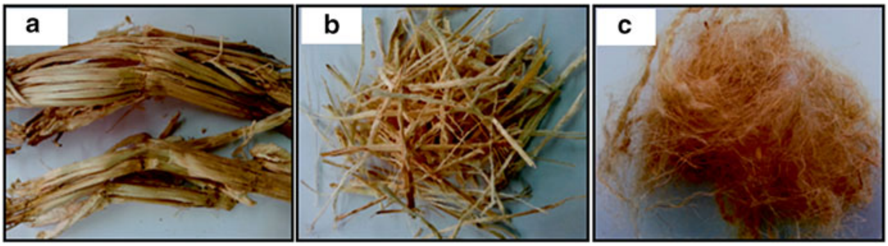


Fig. 1.8 Bagasse waste: (**a**) raw material; (**b**) flakes; (**c**) fibers

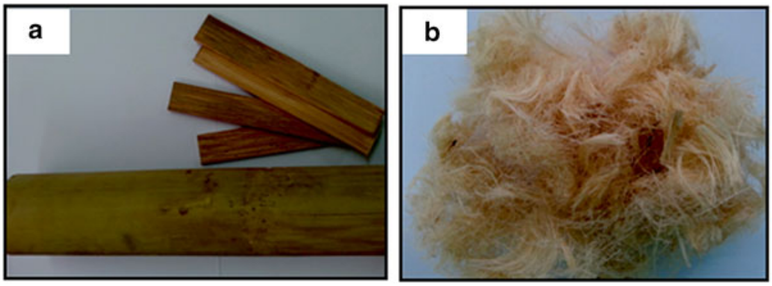


Fig. 1.9 Bamboo biomass: (**a**) Culm and strips; (**b**) fibers

dollars annually by producing sweeteners, ethanol, and alcohols. Fermentation of sugarcane bagasse is the main process in the ethanol production. During this process, sugar or sugar-based ethanol production is a solid residue generated in the form of a dried pulp known as sugarcane bagasse. For example, 28 billion liters of Brazilian ethanol production will yield around 350 million tons of bagasse (Alves et al. 2012). Bagasse are widely utilized and become more important in many industries such as paper and board manufacturing, polymer composites, and also as fuel sources that supply electricity. Many research and development efforts have been done towards the technologies to reduce the pollution and cost of value-added products by the use of agricultural wastes.

The present review by Verma et al. (2012) reported the use of bagasse fibers as reinforcements in polymer matrix. This review reports some selected works in the field of bagasse fibers.

1.2.2.3 Bamboo

Bamboo fiber is also a good candidate for non-wood fibers and can be exploited for the design and development of polymer composites (Fig. 1.9). This material is the most important material for socio-economical status of society and it takes several months to grow up. Traditionally, various living facility such as floor mats, bags and different handicrafts has been use from bamboo, mainly produced through cottage industries. Their properties is brittle compared to other natural fiber because of the

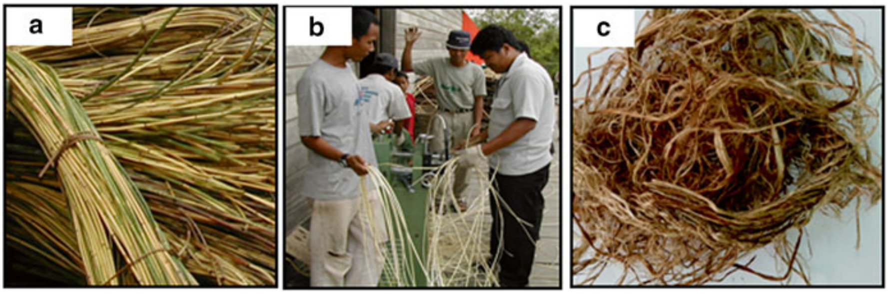


Fig. 1.10 Rattan: (**a**) raw material; (**b**) fibers preparation; (**c**) fibers

high lignin content which covering the bamboo fibres, but still possessed better in mechanical properties (Abdul Khalil et al. 2012). It can also be used in manufacturing reinforced composite for application in building construction.

Six countries in Asia, which are India, China, Indonesia, Philippines, Myanmar, and Vietnam, occupied largest area of bamboo. Almost 11.4 million hectares are from India and 5.4 million hectares are from China and two million hectares are from Indonesia. India and China are reported as the largest area which approximated 70 % of total area of bamboo in Asia. The bamboo area in Asia has increased by 10 % over the last 15 years, primarily due to large-scale planting of bamboo in China and to a lesser extent in India (Lobovikov et al. 2007).

1.2.2.4 Rattan

Rattans are climbing palms belonging to the palm family (Palmae or Arecaneae). Rattans have about 610 different species belonging to 13 genera found in the world and these are mainly distributed in Southeast Asia and its neighbouring areas. There are about 20 species distributed in Africa and China. The rattan canes being aesthetically beautiful materials, malleable yet strong and durable, are in great demand particularly in the furniture and handicraft industries and are used either in whole or round form, especially for furniture frames, or split, peeled, or cored for matting and basketry. Rattans were also cultivated for edible shoots production in a past few decades, especially in Thailand and Laos. It is because planting is spreading rapidly without needing special policy support because shoot-producing plantations offer a rapid and proven return on both the domestic and export markets (Fig. 1.10).

1.2.2.5 Kenaf

Kenaf is one of the most widely used as non-wood fibers in various applications. Kenaf (*Hibiscus cannabinus* L) is a warm season annual fiber crop. It is among the most versatile, natural, ecofriendly, antistatic non-wood fiber available, durable, and spread widely in many countries such as Africa and Asia (Summerscales et al. 2010). Kenaf plant has an outer fibrous bark surrounding the core and an inner

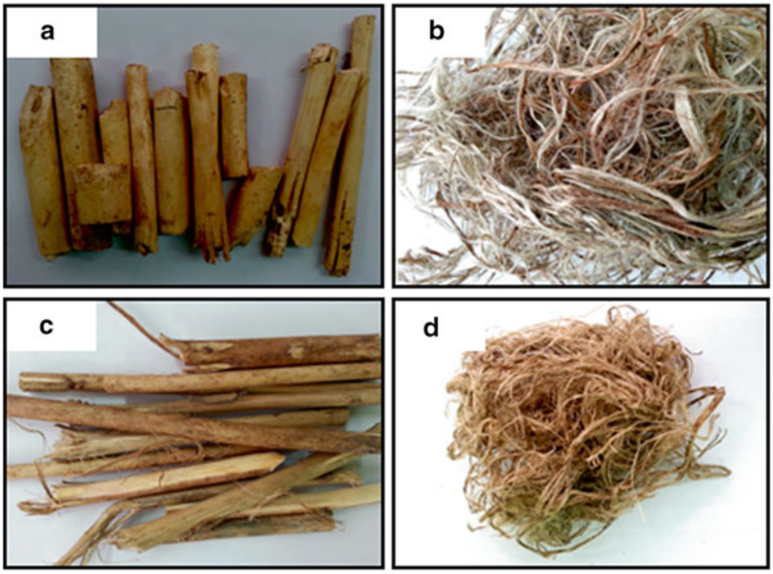


Fig. 1.11 Kenaf biomass: (**a**) Core; (**b**) core fibers; (**c**) bast; (**d**) bast fiber

woody core. The kenaf comprises 35–40 % and 60–65 % by weight of the stalk in bast fiber and core fibers, respectively (Ishak et al. 2010) (Fig. 1.11). Interest is strong on kenaf being shown in worldwide as it is fast growing and local climate can yield twice per year. For example, kenaf plant can yield a dry weight of 6,000–10,000 kg/ha/year, while Edeerozey et al. (2007) reported that new varieties of kenaf plant may reach 30,000 kg/ha/year.

1.3 Improvement of Properties

The non-wood biomass modification can make up the defects of non-wood material in the processing and use, which could effectively improve the quality of non-wood products and the use value, and also could provide a strong technical support to improve the non-wood biomass processing and utilization. The modification non-wood aims to alter the absorptive behaviour of non-wood materials and fibers and thus gives an advantage in terms of dimensional stability.

1.3.1 Physical Modification

Physical modification is one of the methods used to modify the surface properties of natural fiber. It is among the effective method to improve the fiber–matrix interaction in composites. Ultraviolet (UV) treatment and electric discharge such as corona and

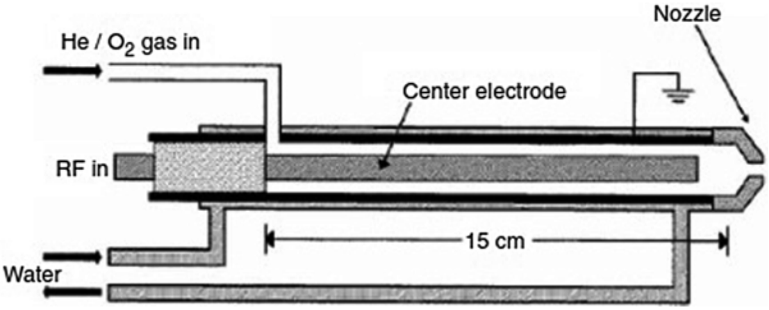


Fig. 1.12 Schematic of the atmospheric pressure plasma jet (Mukhopadhyay and Fangueiro 2009)

cold plasma are among the example of physical modification. UV treatment altered the polarity of the natural fibers, while plasma treatments increase the polarity and change the water absorption capacity of the fibers. Plasma in low-temperature is a useful technique to increase the surface characteristics of the non-wood fiber and resin by utilizing ingredients such as electrons, ions, radicals, and excited molecules. The corona treatment is most interesting techniques for surface oxidation of fiber. Treatment of this process result changes the surface of the cellulosic fibers, which in turn affects the melt viscosity of composites (Mukhopadhyay and Fangueiro 2009; Mohanty et al. 2005). Figure 1.12 shows the schematic of the atomospheric pressure plasma jet.

There is also potential for physical methods to produce dimensional stability of the binderless board as shown by Widyorini et al. (2005) by using steam/heat treatment in kenaf and sugarcane bagasse. Many researchers have investigated chemical change in the raw material and board in non-wood lignocellulosic material with physical treatment. Widyorini et al. (2005) reported that, mild steam-injection treatment caused significant degradation of hemicelluloses, lignin, and cellulose in the kenaf core. They also reported that decrease in hemicellulose, cellulose, and lignin by steam-injection pressing was able to produce kenaf core binderless board of relatively good quality. One of physical modification, which has piqued the interest of scientists, is thermal modification (Razak et al. 2004). Heat treatment of bamboo using virgin coconut oil and effects on the resistance of against the subterranean termite have been studied by Manalo and Garcia (2012). They reported that heat treatment significantly improved bamboo's resistance to termites based on mass losses and visual observations.

1.3.2 Chemical Modification

Chemical modification of lignocellulosics is defined as any chemical reaction between the parts of a cell wall polymer and a chemical reagent with or without catalyst that results in the formation of a covalent bond between the components (Rowell 2006). The mechanism and efficiency of stress transfer between the fiber and matrix often determine the performance of the composite, and this transition region is called the interface. Interfacial properties between both components are an important factor to determine physical and mechanical properties and this could be enhanced by chemical modification methods.

Alkaline treatment is among the most commonly used method in chemical modification of natural fibers. This treatment removes a certain amount of lignin, wax, and oils on the external surface of fiber and could depolymerize cellulose (Mohanty et al. 2000). NaOH is used as a swelling agent in alkaline treatments which will change the orientation of highly packed crystalline cellulose order and transforms it to more amorphous region, thus providing more access of matrix and chemicals penetration (Xue et al. 2007; Leonard et al. 2007).

The esterification method for acetylation treatment involves the grafting of acetyl groups onto the cellulose structure. The reaction will replace the hydrophilic hydroxyl group with acetyl groups to be more hydrophobic of cellulose fiber. Thus, the hydrophilic nature of the fiber decreases leading to improvement in dimensional stability of the composites (Sreekala et al. 2000). The study by Abdul Khalil et al. (2001) showed that the bagasse fiber to treatment with acetic anhydride through acetylation process causes the bagasse fiber to become more hydrophobic. Furthermore, the fiberboards made from acetylated fiber had an equilibrium moisture content of about one third that of controls. They also reported that internal bond strength of acetylated fiberboards was higher; however, modulus of rupture and elasticity were slightly lower. To accelerate the reaction, fibers should be soaked in acetic acid, then immersed in acetic anhydride in certain reaction time and temperature. The result of this treatment is rough surface topography with less number of void contents that give better mechanical interlocking with the matrix (Tserki et al. 2005; Xue et al. 2007) and produce the short length crystallites (Mohanty et al. 2000).

The other method in chemical modification of natural fibers is benzoylation treatment. This treatment use benzoyl chloride to decrease the hydrophilicity of the fiber and improvement of fiber matrix adhesion, thereby increasing the strength of the composite. Besides, thermal stability properties of the fiber increase after benzoylation treatment due to activated hydroxyl groups of the fiber (Xue et al. 2007).

Coupling agent such as silane is also used to modify fiber surface. Several stages are involved in this treatment such as hydrolysis, condensation, and bond formation. Silanols are forms in the presence of moisture and hydrolysable alkoxy groups during this reaction. It will react with cellulose hydroxyl group of the fiber and will improve fiber matrix adhesion to stabilize composite properties (Xue et al. 2007). Bifunctional siloxane molecules will act as siloxane bridge between the cellulose fiber and the matrix, thus improving the compatibility between them.

Peroxide treatment can also improve the interfacial properties between fiber and matrix in polymer composites. One of example of this treatment is the peroxide-induced grafting of polyethylene adheres onto the fiber surface. As a result, good fiber matrix adhesion occurs and this treatment also decreases moisture absorption tendency by the fiber and improves thermal stability (Wang et al. 2007; Kalaprasad et al. 2004). Figure 1.13 shows illustration of principle of chemical modification.

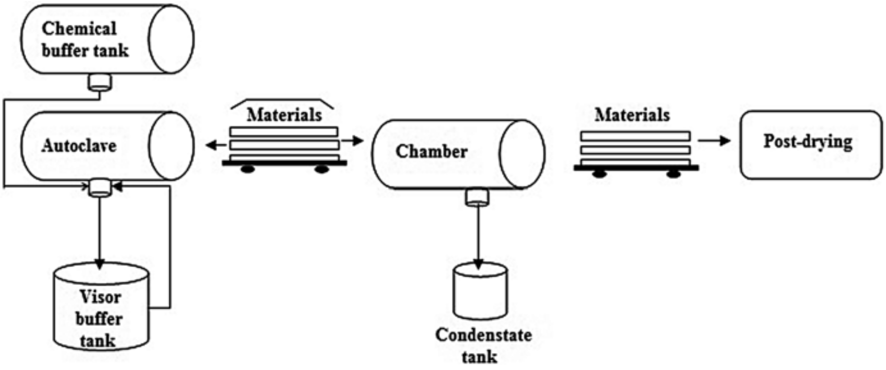


Fig. 1.13 Schematic drawing of the chemical modification process

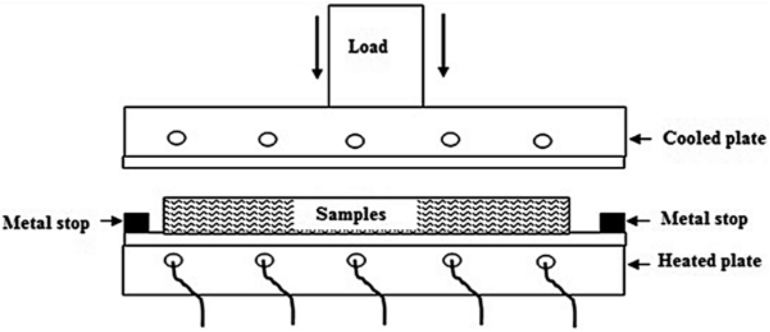


Fig. 1.14 Schematic drawing of the densification using heated plate

1.3.3 Mechanical Modification

Compression of modification is intended to enhance the properties of both wood physical and mechanical properties such as density, hardness, and the shear strength and improve dimensional stability of non-wood. The product is called densified wood. Compression method is one of mechanical modification, namely, densifying by compression. This method may modify the properties of non-wood under plastic conditions without damaging their cell structure. Fixation is the final stage of the compression process.

Many attempts have been done to fix the compressed deformation of wood permanently by the combination resin treatment and chemical modification. Heat treatment or heating wood under dry conditions is another effective method of fixing (Dwianto et al. 1998). Hartono (2012) investigated the permanent fixation of the compressed deformation of oil palm trunk by compregnation with phenol formaldehyde. This treatment significantly improves the physical and mechanical properties. Figure 1.14 shows illustration of compressed deformation with heat treatment.

1.3.4 *Others*

There are other types of non-wood modification besides physical and chemical modification which involved thermal as an agent or medium of modification. Thermal treatments are controlled pyrolysis of non-wood biomass being heated (>180 °C) in absence of oxygen (O_2) inducing as such chemical changes. By applying heat some of the non-wood structures are broken down, influencing negatively the strength properties, and new water-insoluble polymers are formed.

In study by Amouzgar et al. (2010), in microwave drying method, the moisture content of oil palm trunk (OPT) core part reduces from 294 to 12–15 %. The core part of OPT which contains less vascular bundles and more produce improved permeability of OPT core part. Furthermore, they suggest that the microwave drying is effective for drying oil palm trunk core due to less time usage and better removal of moisture as well as defects free OPT. Meanwhile, the study by Torgovnikov and Vinden (2005) reported that microwaves drying can produce dried wood with uniform and less moisture content and more permeability.

1.4 Wood Versus Non-wood Materials: Similarities and Differences in Various Applications

The non-wood fibers can play an important supplementary role, especially for the production of paper, composites, and engineered material. Given the different properties of these different non-wood fibers, these fibers can be used as a reinforcing agent with other fibers for the production of high-quality composites.

1.4.1 *Morphological and Chemical of Fiber Wood and Non-wood*

The natural wood material has very high difference of properties compared to non-wood and natural fibers. The among species, trees of the same species, and between pieces from the same tree has different wood properties. Therefore, wood material cannot match composite products though it has the uniformity and range of properties that can be controlled.

Wood fibers are hollow and have a layered structure with primary and secondary walls. The primary wall is thin compared to the secondary walls and consists to a large extent of lignin. In the secondary walls, lignin and hemicellulose are reinforced by cellulosic fibrils. In the thick S2 layer the fibril orientation is close to parallel to the fiber axis, while fibrils in the thinner S1 and S3 layers have a clear off-axis orientation (Salmen and Burgert 2009). The inner (S3) layer surrounds lumen, the hollow center of the fiber. As a consequence of the fibril orientation in

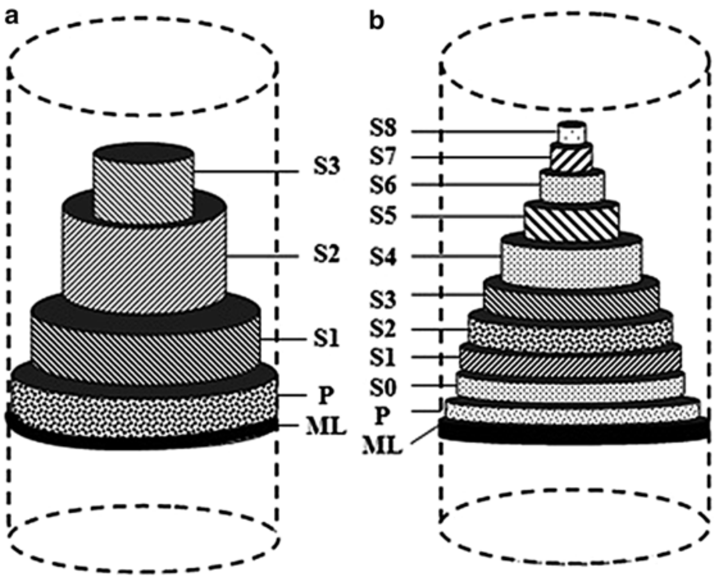


Fig. 1.15 Model of cell wall architecture of single fiber: (**a**) wood fiber; (**b**) non-wood fiber (bamboo). *ML* middle lamella, *S* cell wall layer

the layered structure, the wood fibers are anisotropic with different properties in longitudinal, radial, and tangential directions.

Non-wood fiber such as bamboo that have the secondary wall varies from S1 to S*n*, where *n* depends on the number of lamellae in the cell. This can be compared with the cell wall structure of wood in which the secondary wall consists of three main layers (S1, S2 and S3). The wood and non-wood fiber wall structure is illustrated in Fig. 1.15.

There are two general classifications of non-wood-producing natural fibers: primary and secondary. Part of primary natural fiber are those grown for their fiber content, while secondary non-wood plants are those where the fibers come as a by-product from some other primary utilization. Jute, abaca, pineapple, and kenaf are examples of primary natural fiber, while bagasse, bamboo, oil palm, and rattan are examples of secondary non-wood plants.

Madsen and Gamstedt (2013) reported that softwoods generally offer long (~2–3 mm) and flexible fibers, while hardwood fibers are shorter (~1 mm) and stiffer. They suggested that the hardwood fibers is typically used for making composites with characterization inplane isotropic, and non-specific (random) in fiber orientation (Madsen and Gamstedt 2013). Meanwhile, they also observed lignocellulosic fibers from non-wood (e.g., kenaf) are long fibers (5–50 mm), and these fibers are used for making composites with anisotropic properties for specific fiber orientation composites.

Table 1.4 Similarities and differences of wood versus non-wood fibers

Wood fibers	Non-wood fibers
• The secondary wall consists of 3 main layers (S1, S2, and S3)	• The secondary wall has many layers (S1 to S*n*), where *n* the number of lamellae in the cell
• Primary wall is thin compared to secondary wall	• Primary wall is thin compared to secondary wall
• Softwood fibers are long and flexible and hardwood fibers are shorter and stiffer	• Relatively long fibers
• High luminal area	• Small luminal area mean excellent mechanical properties of fibers
• High hemicellulose and lignin and low degree of cellulose crystallinity	• High cellulose content, and degree of cellulose crystallinity
• High microfibril angle	• Low microfibril angle

On the other hand, Abdul Khalil et al. (2008a) reported that, the fibers from EFB are thread-like bundles under SEM analysis. However, this fiber has long and short length as well as diameter of about 50–60 μm, 10–30 μm, and 200 μm, respectively, after processing. Meanwhile, the luminal area in wood fibers is around 20–70 % of the fiber cross-sectional area (Madsen and Gamstedt 2013). These value, if the compared with non-wood fiber, is higher, where in the non-wood fibers the luminal area is in the range 0–5 %. The content of wood fibers in the hemicellulose and lignin is higher than non-wood fiber (Mussig 2010). Furthermore, the wood fibers have lower cellulose crystallinity (55–70%w/w) than non-wood fibers (90–95 % w/w) (Madsen and Gamstedt 2013). The cellulose content, wood and non-wood fibers similar, increased after treatments (Madsen et al. 2007). Because this treatment could remove of non-cellulose residues of the fibers.

The microfibril angle (MFA) of microfibril cellulose in the middle layer of the secondary wall S2 forms a right-handed spiral which makes an angle with the cell axis. The MFA in wood fibers is in the high range 3–50° (Anagnost et al. 2002). Meanwhile, Gassan et al. (2001) reported that, the MFA in non-wood fibers is in the small range 6–10°. Several studies also investigated MFA in wood, the type, and location of the fiber affect on MFA. Inspite of the difference, wood and non-wood fibers have more in similarity. Some similarities and differences of wood and non-wood fibers were shown in Table 1.4.

1.4.2 *Wood and Non-wood in Composites Applications*

There are two lignocellulosic fiber composites, that is, fiber of wood composites and fiber of non-wood composite. The fibers of wood composites contain wood elements in a matrix material, in which less than 60 % of product mass is wood elements. The basic element in wood-based composites can be made in a variety of sizes and shapes such as particles, flakes, chips, excelsior, veneers, laminates, or lumber, and fiber (Fig. 1.16).

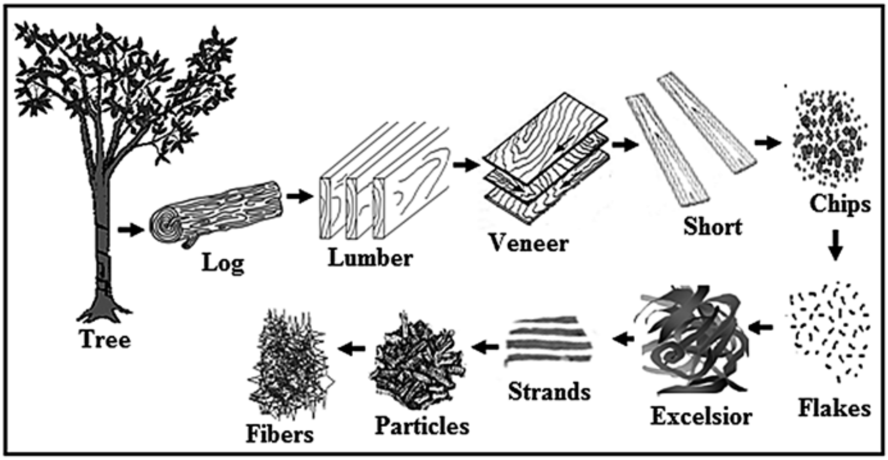


Fig. 1.16 Wood elements used in the production of wood-based composites

The primary component of conventional wood-based composites often 94 % or more by mass is the wood element. These wood elements include veneers, strands, particles, flakes, and fibers. In other word, the conventional wood-based composites needed only a few percent resin and other additives. A number of nonstructural and structural applications are uses from conventional wood-based composites, such as panels interior and exterior, furniture, and support structures in buildings.

The non-wood fibers from plants are materials to reinforcement in polymer-based composites. According to several studies, natural fiber is the most popular (Abdul Khalil et al. 2012) and effective (Bachtiar et al. 2011). Based on recent literature, it has been found that several advantages from natural fiber such as high cellulose content delivers a high tensile strength (Shah et al. 2013) and can thus be used to produce high-grade composite (Abdul Khalil et al. 2012).

There has been a lot of research done on non-wood fibers in polymer composites (Abdul Khalil et al. 2012; John and Thomas 2008). One of the successful researches is EFB fibers for various wood-based polymer composites (Abdul Khalil et al. 2012) and pulp and paper (Wanrosli and Law 2011). The fibrous strands of the trunks and fronds are suitable for manufacturing pulp and paper, chipboard, and cement/gypsum-bonded particleboard. The raw materials of all non-wood biomass are mainly used as fibers reinforced biocomposites with thermoplastic and thermoset polymers for application of automotive, construction, furniture, sport good, electronics, and cosmetics (Fig. 1.17).

Biocomposite can be produced from the parts of non-wood biomass. Palm lumber or conventional composites such as plywood (Abdul Khalil et al. 2010b), bamboo epoxy composite (Shin and Yipp 1989), kenaf polyester composite (Ishak et al. 2009), bagasse-fiber-reinforced composites (Acharya et al. 2011), rattan powder-filled polypropylene composites (Balakrishna et al. 2012), etc. Despite these advantages, natural fibers suffer from some drawbacks due to the presence of hydroxyl groups (OH) in the fiber. These hydroxyl groups attract and hold water molecules through hydrogen bonding, which leads to fiber swelling and causes the

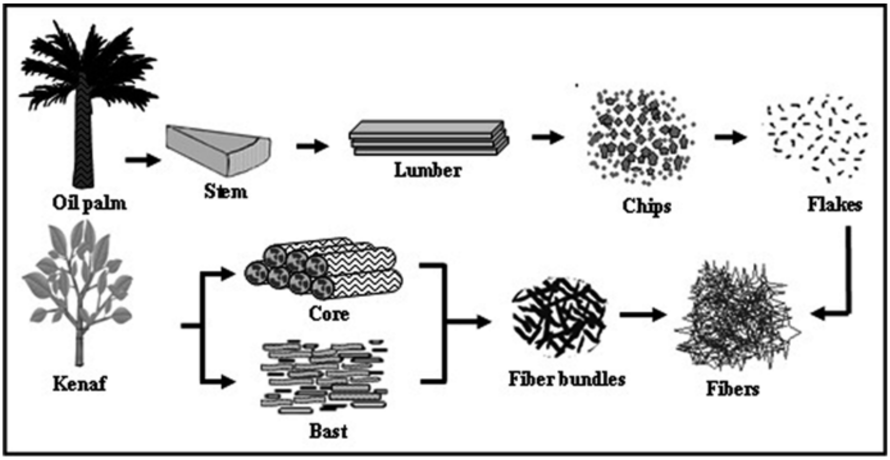


Fig. 1.17 Type of raw materials of non-wood composites

presence of voids at the composite interface, resulting in deterioration in mechanical properties (John and Thomas 2008) and loss in dimensional stability (Rahman and Khan 2007) of its fiber and composites. In composite processing, the addition of hydrophilic natural fiber to hydrophobic plastics results is not good mechanical properties of composite because of non-uniform fiber dispersion in the matrix and inferior fiber-matrix interphase (John and Thomas 2008).

1.5 Various Application of Modified Non-wood Products

Green technology has been boosted by utilization of these renewable materials as natural fibers to non-wood biomass-based products in various application (such as light construction, furniture, food packaging, automotive components, etc.). In general, non-wood biomass was made as composite for almost all utilization, and some of those still used as traditional application (solid biomass). Some examples of the variety of products and applications for non-wood-based biocomposite industry in the world are shown in Table 1.5.

1.5.1 Structure Application

Several researches have used non-wood biomass as raw material for structural application. Result of their studies provides a strong technical support to improve the non-wood biomass processing and utilization. The utilization of bamboo and oil palm fronds in form fiber by the construction industry has resulted in a product of cement board (Araujo et al. 2011). Through several technologies-based biocomposites from

Table 1.5 The utilization of non-wood raw material for various application

Type of non-wood raw material		Utilization	Type of products
Oil palm	Trunk	Utilized to replace wood otherwise obtained from natural forest – Furniture – Core plywood – Light structure	
	Fiber	Utilized to replace wood fiber or wood particles otherwise obtained from natural forest – Automotive component – Food packaging – Biocomposites	
Bamboo, rattan	Culm/stem	Used to substitute wood in many aspects – Flooring – Furniture – Light structure – Handcraft	
	Fiber	Fibers for the production of high-performance structural fiber/ polymer composites – Biocomposites	
Postharvest (bagasse)	Fiber	Utilized as alternate raw materials for many wood-based industries – Food packaging – Biocomposites	
Natural fibers (kenaf)	Fiber	Utilized to replace wood fiber or wood particles otherwise obtained from natural forest – Biocomposites – Automotive component – Roofing – Upholstery material	

bamboo have been developed like advanced polymer biocomposite (Mahdavi et al. 2012). They reported that, the bamboo-reinforced composites has high performance (mechanical properties), similar with commercially wood products. Moreover, the use of rattan as reinforcement in portland cement concrete has been studied extensively by Akinyele and Olutoge (2011).

The considerable investigations have been made in kenaf fibers as a reinforcement in polymer matrix. The kenaf fibers-reinforced composites had gained much attention in structural applications (Abdul Khalil and Suraya 2011). Additionally, the oil palm waste as fibers-reinforced composites is reported by Abdul Khalil et al. (2012) for structural application.

1.5.2 Furniture Application

With increasing developments of newer bio-composites into the furniture industry, the use of non-wood fiber biocomposites in furniture making could support the concept of reducing waste. Composite conventional can be manufactured from non-wood biomass (oil palm, bamboo, and rattan). It is lighter than composites manufactured from normal wood. The physical and mechanical properties indicate that biocomposites from non-wood material is suitable for non-load bearing applications, such as paneling and furniture applications. The natural fibers can be used for the manufacture of biocomposite advanced (Abdul Khalil et al. 2012).

1.5.3 Sport Goods

Among the most successful of these have been carbon fiber composites. Some of the largest volume users of composites for sport good are carbon fiber composite, such as for the manufacture of golf shafts, racquets, skis, snowboards, hockey sticks, fishing rods, and bicycles. The use of carbon fiber reinforced polymer for almost 20 years which it has steadily displaced traditional materials. Recently, advanced composites are found in products used for seven of the top ten most popular outdoor sports and recreational activities (Lee 2010).

1.5.4 Automotive

In automotive applications, the most common system used today is thermoplastic polypropylene and unsaturated polyester, particularly for nonstructural components (Ayrilmis et al. 2011) so the advantage to their use is limited. Non-wood fiber-reinforced polypropylene composites have achieved commercial attraction in automotive applications. Because they have specific properties of these non-wood materials (such as high-stiffness, high-strength, and low-density as compared to metals) this material is highly desirable in primary and secondary structures of automotive application (Begum and Islam 2013).

Kenaf has already been used in commercial applications such as composite boards, automotive panels, insulation mats, and geotextiles. Major global corporations such as Toyota Motor Corporation and Panasonic Electric Works have taken the lead in the global kenaf industry. Toyota has developed kenaf fibers for automotive interior applications, and Panasonic, a structural wall board to replace timber-based plywood. Similarly, in 1996 interior automobile panel from kenaf fiber has applicated for Ford Mondeo. Similarly, the hybrid kenaf/glass-reinforced composites have been studied by Jeyanthi and Rani (2012) for utilization in passenger car bumper beam.

1.5.5 Others

Non-wood biomass also has been explored in food and beverage packaging applications (Verma et al. 2012). Kenaf/plastic compound pellets can be molded into commercial food packaging and virtually any other product now made of plastic (Sanchez et al. 2005). They considered that kenaf/plastic compound become an excellent barrier against gas and vapor transmission.

Many researchers are concerned to produce carbon black and activated carbon from non-wood raw material, and it can be used for many applications, such as applications of carbon black reinforced elastomer composites to manufacture component of automotive such as tires, gloves, V belts, hoses, and complex-shaped mechanical goods. Currently, utilization of bamboo as carbon black filler as replacement of burned fossil fuels in natural rubber polymer matrix creates greener tires (Suhaily et al. 2013).

1.6 Conclusion

With the wood resources being limited for the developing countries, the technology of non-wood biocomposites will continue to develop at a rapid rate. This, along with the rapid rise in demand for biocomposite products, represents a major potential market for suppliers to wood industry. In order to promote some non-wood fibers and to develop their composites, it is necessary to understand their properties. One of all properties of non-wood fiber, the mechanical properties are very important in the composites production. In general, the wood and non-wood fiber has mechanical properties based on their physical, chemical, and morphological properties and include fiber orientation, cellulose content, crystal structure, and diameter/cross-sectional area of the fiber. Futhermore, the lignocellulosic raw materials used in wood-based industries are abundantly available and renewable resource in tropical regions. The fact is that the agricultural waste and natural fiber are comparatively superior for the development of wood-based industries. Since the availability of non-wood biomass and increase the research in development of biocomposite, therefore, necessary for how the ensuring the sustainability of non-wood biomass management to future. It is due to the fact that the livelihoods of about millions people in tropical region depend on this natural resource.

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Chapter 2
Jatropha curcas L.: A Future Energy Crop with Enormous Potential

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Abstract Jatropha (Jatropha *curcas* L.) is a member of Euphorbeaceae family with multiple attributes and enormous prospective. Jatropha is now being credited as the most promising biofuel crop. It has been documented as the most suitable oil-producing plant due to its variety of potential attribute among lots of oil seed-bearing species. The oil can be extracted from the seeds of Jatropha plant and used as feedstock for bio-diesel production and other use of jatropha oil is for making soap, adhesive, foam, composite, surface coating, coloring agents, etc. Jatropha roots, shoot latex, leaf, and kernel oil have curative characteristics. Fruit shell and seed cake can be used as organic fertilizer as well as animal feed upon detoxification because they are rich in N, P, and K. Jatropha can save cost of fuel import, create employment opportunity, reduce environmental pollution, and improve the financial condition of rural peoples. Research is required to know the actual potentiality of jatropha products. Much more research on variety development and cultivation technology is needed to be done to increase seed yield of Jatropha which will enhance its economic sustainability.

Keywords Physic nut • Nonedible oil • Agro-technology • Breeding • Alternative fuel • Biodiesel • Economic sustainability

2.1 Introduction

The world is being paid modernization and industrialization day by day and results in increasing demands for transports and engines. Oil is the major source of energy for the entire world as it is convenient to handle and store. An alarming scarcity is already highlighted in the production of crude petroleum oil for energy generation. So, the energy sources are becoming limited and situation leads to seek an alternative fuel.

2.1.1 The Needs for Renewable Sources of Energy

Biofuels are getting worldwide attention as an alternative source of energy due to ever-increasing requirements for energy and depletion of petroleum reserve (Becker and Francis 2003). Renewable energy sources are introduced on a large scale around the world. Most sources are producing electricity or mechanical energy (solar cells, wind energy, hydropower), heat (biomass, solar collectors), or gas (anaerobic digestion). However, there is also a need for the production of bio-liquids like petrol or diesel for diesel engines to produce mechanical power. Therefore, biodiesel (bio-liquids) is increasingly catching global interest as a promising alternative to the expensive petroleum fuels (GEXSI 2008). Biodiesel is known as a substitute fuel for diesel engine and believed to be an eco-friendly, biodegradable, low cost, renewable, and nontoxic clean alternative. Biodiesel exposed to have healthier emissions than conventional petro-diesel (Evenson and Gollin 2003). Biodiesel is an alternative to petroleum fuel and produced from renewable sources such as vegetables oils and animals fats (Barn Wall and Sharma 2005). Biodiesel is agriculture-oriented and decreases harmful air contaminants such as chemicals, particulate matters, CO, SO_2, NO_2, and toxic air pollutants.

2.1.2 Food Security and Biodiesel Production

Countries which have tropical climate have produced many species of edible and nonedible oil crops. Use of nonedible vegetable oil in the production of biodiesel production can be one of the circumstances for fuel security without hindering the availability of food materials. For example, the usage of palm oil as a feedstock for biodiesel production becomes the most recent environmental issue in South and South East Asia. Palm oil contributes about one third of world requirements of vegetable oils. Most of the Asian countries can get energy sustainability benefit from biodiesel who are still importing oil and other petroleum product (Evenson and Gollin 2003), which is believed as the strategy for clean development mechanism (CDM). Some countries have large surplus of food crops but in other countries millions of people are facing the shortage of food. In Asia, the demand for food and energy is high due to its high population (>60 % of the world population). Selection of feedstock for biodiesel production mainly depends on geographical distribution (Knothe 2005). Major sources of bio-diesel feedstock among different countries include rapeseed (USA, Germany, France), soybean (USA and Brazil), Oil palm (Malaysia), sunflower (Bulgaria, Greece, Spain), wheat (Germany, Denmark, France), and Jatropha (Nicaragua and South America) (Jayasingh 2004, www.biomassfutures.eu).

Alteration of edible oil or food crops into bio-fuel will possibly fetch severe crisis on food scarcity (Msangi et al. 2006; Rajagopal and Zilberman 2007) for human consumption and demand in the world market (Biomalaysia 2009). Use of nonedible jatropha seed oil as biodiesel feedstock will keep away from falling into the debate of energy vs. food (Srinivasan 2009). On the other hand, production of biodiesel from jatropha seed oil releases less air pollutants compared to petro-diesel (Prueksakorn and Gheewala 2006).

2.1.3 Nonedible Oil as Biodiesel Feedstock

Biodiesel production by using nonedible oil as feedstock has anticipated added interest particularly for vegetable oil net importer countries (FAO 2009). On the other hand, it will impact on the inconsistency in food price and food security. Sustainability of biodiesel production can assist by utilizing nonedible oils as a feedstock and reduces the impact on inconsistency of world food supply. Jatropha (Jatropha *curcas*), karoch (*Pongamia pinnata*), polanga (*Calophyllum inophylum*), neem (*Azadirachta indica*), rubber (*Hevea bransiliensis*), and mahua (*Madhuca indica*) are most important nonedible oil plants with significant prospects as a biodiesel feedstock (Azam et al. 2005). Jatropha is one of the promising feedstocks for biodiesel production to alleviate the energy crisis all over the world (Charlene et al. 2004; Kaushik et al. 2007). Jatropha biodiesel showed improved performance compared to fossil fuel (Ghosh et al. 2007; Mandpe et al. 2005). Goldman Sachs, an US leading investment Company, had reported that Jatropha biodiesel will be the cheapest one among the potential alternatives (Peterson 2008).

2.2 Description of the Jatropha Plant

Jatropha (*Jatropha curcas* L.) has stirred up interest all over the tropics as a potential biofuel crop. It is a multipurpose shrub under the family Euphorbiaceae with a number of features and huge potential (Jones and Miller 1991; Martin and Mayeux 1985; Openshaw 2000; Pant et al. 2006; Takeda 1982). Jatropha has been recognized as the most important oil plant due to its diverse characteristics such as wider adaptive quality, drought resistance hardy structure, survivable capacity with inadequate nutrients supply, shorter maturity time as well as high recovery percentage of seed oil (Gui et al. 2008; Jones and Csurhes 2008; La Koh and Peterson 2008; Salimon and Abdullah 2008). The uses of different parts of Jatropha range from conventional medicine to living fence and recently established prospects as an alternative of petroleum fuel (Openshaw 2000).

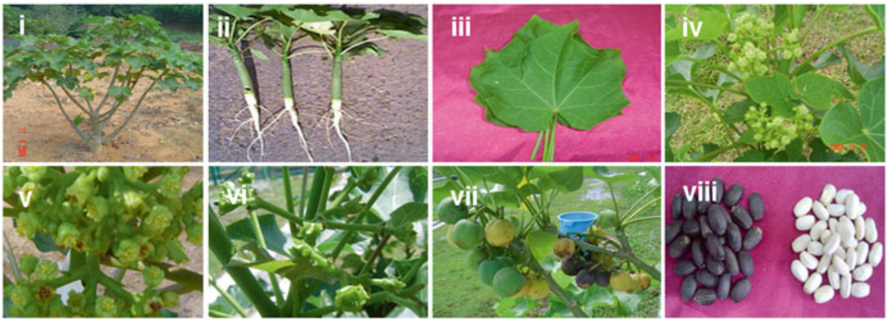

Fig. 2.1 Jatropha plant parts: (*i*) whole plant, (*ii*) seedlings, (*iii*) fresh leaves, (*iv*) inflorescence, (*v*) male flower, (*vi*) female flower, (*vii*) branch with *green* and mature fruits, (*viii*) seeds and kernels

2.2.1 Identity of Crop **Jatropha curcas**

Jatropha (*Jatropha curcas* L.) is a diploid species with chromosome number $2n = 22$ (Dahmer et al. 2009; Sasikala and Paramathma 2010). There are around 170 species of the plant identified to have under the genus Jatropha (Dehgan 1984; Katembo and Gray 2007) but the term "Jatropha" usually refers to the species *Jatropha curcas*. Jatropha grows to a height of approximately 6 m and is a deciduous shrub (Fig. 2.1). It is a small perennial tree and can continue to grow until 40–50 years depending upon soil and environmental conditions (Foidl et al. 1996; Openshaw 2000). The plant takes about 6–36 months to commence flowering (Islam et al. 2010a) and 4–5 years or more to come to the complete fruit-bearing stage. The bark of Jatropha is smooth, gray in color, branches are strong, and leaves are pale green, thick feathery. Normally one tap root with four lateral roots are formed from seeds (Fig. 2.1) and cuttings do not develop tap root (Heller 1996 Islam et al. 2010b). The color of Jatropha seed is black and average 100-seed weight is around 50–75 g (Islam 2011).

2.2.2 Origin and Distribution

Jatropha is a miracle plant which grows relatively quick, lives, and can produce seeds for more than 50 years. Jatropha is indigenous to Mexico and Central America and was introduced for cultivation in tropical and subtropical countries of the world (Heller 1996; Kumar and Sharma 2008). Recent information demonstrates that cultivation of jatropha has been extended mostly in the arid regions of Central and South America, Africa, and Asia (Fig. 2.2) (Anonymous 1965; Shui 2005).

Fig. 2.2 Jatropha growing areas around the globe (*Source*: Jongschaap et al. 2007)

2.2.3 Vernacular Names of Jatropha

Jatropha is commonly known as physic nut or purging nut (English), Barbados nut and often referred to as biodiesel plant. There are other names which also vary per region or country (Heller 1996). For instance, Jatropha is locally known as *jarak pagar* (Salimon and Abdullah 2008) and *jarak budeg* in Indonesia (Jakarta 2006; Jones and Csurhes 2008), *tubatuba* in the Philippines (Perino 2006), *sabuda*m in Thailand, *lohong kwang* in Cambodia, *jamalgota* in Bangladesh and *ratanjut* in India (Siddharth and Sharma 2010), *purgeernoot* in Dutch, *purgiernuss* in German, *safed arand* in Hindi, *butuje* in Nigeria, *bagani* in Ivory Coast, and *hab el meluk* in Arabic, *galamaluca* in Mozambique, *tempate* in Costa Rica, *piñon* in Guatemala, *purgeira* in Portuguese, *pourghère* in French, *mundubi-assu* in Brazil and *piñoncillo* in Mexico (Sharma et al. 2012).

2.2.4 Climate and Soil

Jatropha can be grown in low to high rainfall areas (250 to over 1,200 mm per annum) either in the farms as a commercial crop or as a hedge to protect fields (Katwal and Soni 2003). It is found mainly at the altitudes of 0–500 m with average annual temperatures of 20 °C or above, but can grow at higher altitudes and stands against little frost. It cannot grow in the areas under extreme environment. Jatropha can be easily grown on soils with good aeration and good drainage system (Islam et al. 2010a). It is also well adapted to marginal soils and can be grown on degraded lands. A soil with moderate fertility is favorable for commercial cultivation of Jatropha. Flowering and fruit bearing of Jatropha is induced during rainy season

Table 2.1 Asian countries qualified for Jatropha cultivation as fuel crop

Sl. no.	Name of the country	Sl. no.	Name of the country	Sl. no.	Name of the country
1	Malaysia	7	Laos	13	Mongolia
2	India	8	Vietnam	14	Sri Lanka
3	Indonesia	9	Myanmar	15	Syria
4	Bangladesh	10	Nepal	16	Maldives
5	China	11	Pakistan	17	Yemen
6	Thailand	12	Philippines		

with decreasing of temperature. More than 80 countries around the world reported to be qualified for Jatropha cultivation as fuel crop; among them 17 are Asian countries (Table 2.1).

2.2.5 *Cultivation of* Jatropha curcas

The agro-technology of Jatropha beneath diverse climatic conditions is not fully documented yet (Openshaw 2000). Before exploiting Jatropha for commercial cultivation for industrial applications, it is essential to obtain all information about its biology, agro-technology, and all other uses so that maximum potential of the plant could be exploited (Kumar and Sharma 2008). There is a scarcity of information regarding the effect of different aspects of agro-technology and their interactions on seed production. Jatropha can grow well to marginal lands but may not achieve commercial yield. If the plantation is not raised with proper agro-techniques, it will result in the establishment of a plantation giving poor yield (Hon and Joseph 2010). To increase seed production of Jatropha, it is imperative to develop high yielding variety and its agro-technology that produces the maximum seed yield with the minimum amount of input.

Many countries have started large scale cultivation of Jatropha, but there is little information about its favorable and unfavorable effects on the large scale production (Parawira 2010). Recent published information on low production were mostly applied to young Jatropha plantations of 1–2 years old (Jongschaap et al. 2007; Parawira 2010). So, there is a need of research about the performance of different jatropha genotypes, its management interventions, influence of various factors related to its cultivation, and their interactions on seed yield (Parawira 2010). Research also needed to select elite Jatropha genotypes for agronomic optimization, propagation, and their genetic improvement.

2.2.6 *Varietal Evaluation and Yield Components*

The success of the genetic improvement program depends on the genetic diversity present in the population and selection of genetically diverse parents for further breeding program. More information is needed about genetic variation of Jatropha genotypes or accessions around the world which can help to develop high yielding variety of Jatropha for diverse ecological regions. Seed yield and oil content variation in initial materials help to select better types that is candidate plus plants (CPPs) for the development of high yielding variety of Jatropha (Islam et al. 2011b). Selection and multiplication of elite germplasm will be the key to the success of Jatropha biodiesel program. Varieties comprise favorable traits such as seed yield, oil content, resistance to pests and adaptability to diverse agro-climatic conditions should be an arena that needs to be exploited for genetic improvement of *Jatropha curcas*. Seed yield of Jatropha has been significantly affected by genetic and environmental factors (Ginwal et al. 2004; Jongschaap et al. 2007).

Kaushik et al. (2006, 2007) reported the preponderance of ecological features over genetic attributes. Several literatures were reported the presence of significant variation among the populations, bushes, and clones of Jatropha for vegetative growth, branches per bush (no.), seed yield per bush, seed size, and oil content of seed (Prabakaran and Sujatha 1999; Ginwal et al. 2004; Pant et al. 2006; Kaushik et al. 2007; Sunil et al. 2008; Popluechai et al. 2009). Variation was also reported in morphology of seed, germination of seed, and growth behavior of seedling (Ginwal et al. 2005; Islam et al. 2009a, 2013a). A large number of evaluations of germplasm have been carried out by exploiting samples gathered from candidate plus plants (CPPs) of various countries and propagated through seeds or stem cuttings (Singh et al. 2009). Selection of candidate plus plant is the foremost essential part in any plant improvement program through breeding (Tewari et al. 2001). The selection of candidate plus plants (CPPs) can be done based on different traits linked with the species in concern. In case of Jatropha, yield per plant, oil content of the kernel, and branches per plant might be more significant in contrast to other characters (Francis et al. 2005; Becker 2008; Islam et al. 2009b). Jatropha is a monoecious and cross-pollinated plant, which means once genetically identical materials have been identified, asexual propagation of superior phenotypes will yield superior progeny. This progeny will help to create new Jatropha variety suitable for various environmental regions.

Jongschaap et al. (2007) and Montes et al. (2008) reported low genetic diversity among Indian and African genotypes of Jatropha, but higher genetic diversity among Latin American genotypes. Basha et al. (2009) also observed genetic variation among Mexican accessions and no variation in the 72 accessions collected from 13 countries. Latest research on molecular markers also supported high levels of genetic uniformity among Jatropha accessions collected from China (Sun et al. 2008) and only little amount of genetic variability in Indian accessions (Basha and Sujatha 2007; Ranade et al. 2008).

Ginwal et al. (2004) reported significant immense variability in 10 Indian genotypes which attributed >80 % of total phenotypic variation. Higher genotypic variability was found for plant height, number of branches per plant, number of seeds per plant, number of fruits per plant, number of leaves per plant, 100-seed weight, and seed and oil yield per plant of Jatropha (Gohil and Pandya 2009; Islam et al. 2011b). More than 90 % heritability was observed for seed oil (%) and 100-seed weight (g) along with high genetic advance in Jatropha. High yielding varieties of the

Table 2.2 Seed yield of Jatropha (kg/ha) per year depends on the age of plantation and water availability

Seed yield	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7–10
Without irrigation	–	250	1,000	2,000	3,000	4,000	6,500
With irrigation	250	1,000	2,500	5,000	8,000	12,000	15,000

Source: Openshaw (2000), Peterson (2007), Islam et al. (2011a)

plant require genotypic characterization towards identifying breeding lines (Popluechai et al. 2009). *Jatropha curcas* genotypes differed significantly with respect to male flowers per inflorescence, female flowers per inflorescence, fruits per bush, and various physiological parameters (Jubera 2008). The variation in number of male flowers per inflorescence was low compared to female flowers per inflorescence (Kumar et al. 2008). The extent of genetic variability can be broadening by introduction of genetically diverse genotypes or by interspecific hybridization (Basha and Sujatha 2007; Achten et al. 2010). Six species of Jatropha found in India display remarkable genetic variability suggesting potential of improving *J. curcas* by interspecific hybridization. Interspecific hybridization between *J. curcas* and five other species available in India has been successfully carried (Basha and Sujatha 2007).

2.2.7 Seed and Oil Yield

Jatropha plants produce flowers six months after sowing (Islam et al. 2010a). Globally, seed yield in Jatropha varies from 550 to 14,000 kg/ha/year under good crop management, irrigation availability, soil productivity, and absence of disease from mature stands (Francis et al. 2005; Openshaw 2000) and for fruits 7.5 t/ha/year (Openshaw 2000). But recent report by Kashyap (2007) states for India that yield is limited to maximum 1.5 t/ha/year under rainfed conditions. Seed yield varies from 0.4 to 10 kg/pl/year on the age of plant, soil, and climatic conditions around homesteads, gardens, and fields (Verma and Gaur 2009). A single full-grown plant can produce around 4 kg seed per year under favorable environment (Parawira 2010). Studies have found that the seed yields vary (Table 2.2) with the age of Jatropha plantation and water availability (Henning 2000).

The seed oil content of Jatropha reported in the literature makes it difficult to estimate its profitability to grow under commercial cultivation. Seed oil content of Jatropha varies depending on genetic materials (Islam 2011). The oil content in seeds ranges from 35 to 40 % (Gubitz et al. 1999, www.jartropha.org) and the kernels from 50 to 60 % (Azam et al. 2005; Henning 2000; Li et al. 2006; Islam et al. 2013b). The seed oil content varies from 27.8 to 38.4 % among Indian accessions (Wani et al. 2006). The seed oil content of Jatropha has been reported to around 47 %, but the acceptable oil content is around 40 % (Achten et al. 2008; Gressel 2008; Sujatha et al. 2008). Maximum seed oil content is close to 50 % in the kernel which is higher than that of seeds because oil-free shells have been removed

(Islam et al. 2011b). Achten et al. (2008) reported seed oil content of dry seeds is about 34 % including shell which corresponds to 0.68–17 t/oil/ha. Jatropha species such as *J. pohliana*, *J. gossypiifolia,* and *J. curcas* is found to produce seeds with high oil contents (Oliveira et al. 2009).

2.2.8 Harvesting and Processing

Jathropa curcas starts to bear fruits within 6–8 months after planting (Islam et al. 2010a). Fruits mature in 3–4 months after flowering. Fruits are ready for harvesting when the fruit turns yellow, but the best time for harvesting is when fruit color changed from yellow to black. Seeds are separated from the fruits after collection, cleaned and sun dried. Seeds for further plantation should be dried in the shade to avoid harmful effects of sun on seed viability and germination. Dried and black seeds of Jatropha are normally used for oil extraction. Approximately 30 kg of fruits can yield 18 kg of seed.

The seed oil of Jatropha can be extracted by two main methods: (1) chemically by solvent (n-hexane) extraction and (2) mechanically either by a manual ram-press or by power-driven expeller. On the other hand, enzyme extraction is done by organic solvents which offer a nonhazardous substitute of common method of extraction of oil from kernel (Shah et al. 2005). Pant et al. (2006) reported oil extraction from dry seed using steam distillation method. Solvent extraction by n-hexane yields the maximum seed oil of about 60 % by weight (Islam 2011). Mechanical extraction from dry seed by power-driven expeller can yield 30–40 % oil (Forson et al. 2004). This process of oil extraction is easy and more suitable especially in the village region.

2.3 Use of Various Plant Parts of Jatropha

The seed oil of Jatropha has a variety of uses such as production of soap, insect repellent, drug, cosmetics, etc. apart from it being utilized as bio-diesel (Shanker and Dhyani 2006). Jatropha plant produces many useful products as shown in Fig. 2.3, especially the seed, from which oil can be extracted and converted into biodiesel (Mandpe et al. 2005). The oil is used to stimulate hair growth and also used as lubricant. Tropical countries can produce Jatropha seed oil in a sustainable manner without affecting saving environment and society (Francis et al. 2005). Crude protein content is higher in kernels than in seeds (Makkar and Becker 1997). Karaj and Müller (2010) reported that the moisture content of Jatropha seed kernels was lower than the seeds. The kernels contain more inorganic substances compared to seeds as ash content of kernels was higher than the seeds. Jatropha plant has been planted as a fire barrier because of higher moisture content in its branches, stems, and leaves (Meng et al. 2009). Being a woody plant, it can be used to support other climbing

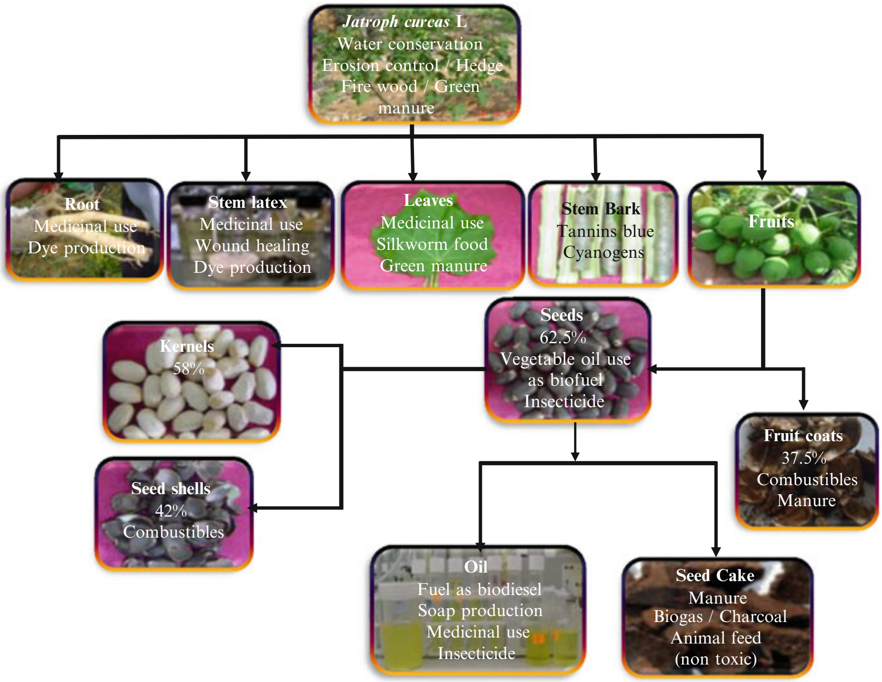

Fig. 2.3 Various uses of *Jatropha curcas* plant parts (Islam et al. 2010a)

plants like vanilla and paper (Eijck 2006). The leaves can improve soil fertility and add organic matter in the soil when it drops down. Jatropha flowers can attract bees and can be used for honey production. Information available in different literatures on various aspects of Jatropha uses has been described in this section as follows:

2.3.1 Improve Soil Properties, Protect Soil Erosion and Crop from Farm Animals

Traditionally, Jatropha plant has been grown as a hedge crop since 1980s. Cultivation of Jatropha has several benefits on soil protection, soil restoration, and management. It is an important multipurpose crop to reduce desertification, deforestation, and soil degradation (Grimm 1996; Kheira and Atta 2008; Rockerfeller Foundation 1998). It has the capability of growing on marginal land, at the same time it can help to reclaim problematic soils. It can serve as a bio-fence to protect soil erosion, agricultural crops from wind erosion and farm animals (Heller 1996; Kumar and Sharma 2008). This plant can also act as a barrier to avert spread of pests and diseases in the crop field (Li et al. 2006). This plant is selected for this purpose due to its easy propagation by stem cuttings and it is not browsed by cattle.

2.3.2 Components of Herbal Medicine

Jatropha is widely known as medicinal for a range of disease treatment. Various parts of Jatropha plant such as roots, fresh leaf, outer layer of stem, fruits, seeds, and oil are utilized in conventional drug and veterinary purposes (Dalziel 1955; Duke 1985, 1988). Effective cardiovascular, anthelmintic, antidiabetic, antiulcer activity of methanol extract of fresh leaf in animals have been demonstrated by several researchers (Sharma et al. 2012). Latex of Jatropha plant is effective against bleeding of wounds and skin diseases such as scabies, wet eczema, and dermaties with benzyl benzoate emulsion (Heller 1996; Marroquin et al. 1997). The tender twigs of Jatropha plant are used to clean-up teeth, relief tooth-ache, and reinforce gums. Stem extract shows anti-cancerous activities as it contains organic compounds like jatrophine, jatropham, and curcain (Thomas et al. 2008). The roots are reported as a remedy for snake bites. Activity of Jatropha root extract against diarroheal, inflammation, and snake bites has confirmed through several investigations (Mujumdar and Misar 2004; Sharma et al. 2012) on albino mice. The fruits of Jatropha have anti-fertility, abortion activity, and fetal resorption activity (Sharma et al. 2012). The seed oil is also used in the treatment of skin diseases, rheumatism syphilis (Marroquin et al. 1997). Investigation is under process to find out the potential of Jatropha plant against HIV.

2.3.3 Jatropha Oil as Bio-Pesticides

The pesticidal activity of jatropha extracts from roots, latex, bark, leaves, fruit, seed, and oil against insects and microorganisms even animals has been reported by several researchers (Grainge and Ahmed 1988; Consoli et al. 1989; Meshram et al. 1994; Jain and Trivedi 1997). Jatropha plant extracts possess activity as pesticide, rodenticide, fungicide, bacteriocide, moluscucide, and cytotoxin. It also shows undesirable effects on human, rodent, poultry, cows, and sheeps (Agaceta et al. 1981; Goel et al. 2007; Ye et al. 2009; Rakshit et al. 2010). The kernel oil and extracts of Jatropha plant parts have prospect as a pesticide. Kaushik and Kumar (2004) reported the insecticidal effects to control cotton bollworm, a serious pest of cotton including harmful insects of pulses, potato, maize, etc. The pesticide from a blend of neem oil, jatropha oil, and turpentine oil (extracted from pine trees) has been used to control the damage caused by rats in seedling, fruit bunches of oil palm, and rhinoceros beetles in oil palm seedlings and insect in flower (Sivakumaran 2008).

2.3.4 Raw Materials for Coloring Agent

A dark blue dye has been reported to produce from bark of Jatropha which is utilized for dying clothes, fishnets, fishing-lines, etc. (Misra and Misra 2010). The coloring agent is extracted from young shoots, fresh leaf, and condensed to

Table 2.3 Biogas production efficiency of Jatropha residues

Jatropha residue	Inputs (amount)	Biogas yield
Press cake	800 kg	360 m^3 biogas
Oil residue	800 kg	360 m^3 biogas
Fruit shell (fresh)	3 t	100 m^3 biogas
Vegetative parts	–	–

Sources: Foidl and Eder (1997), Gunaseelan (2009)

greenish fluid or desiccated to brown mass. The dye pass on to cotton relatively faster as tinted shade of coffee. The dye obtained from leaves and stem of Jatropha plant is reported to be used to color domestic threads, ropes, and clothes during ceremonial occasions (Srivastava et al. 2008). Further research in this regard can open up enormous potential.

2.3.5 Firewood and Input for Charcoal Production

Jatropha seed cake is an excellent fuel for cooking, particularly when turned into briquettes. High-quality charcoal can be produced from seed cakes which have the prospect to get good market price. But it is better to apply as nutrient supplement to improve soil properties to increase crop production (Benge 2006). The fruit shells and other plant parts can be used as fuel. Jatropha wood burns too quickly and not good as a fuel wood. Due to its soft, hollow, and light properties, Jatropha wood would not be of high value either as charcoal or as fire wood (Benge 2006).

2.3.6 Materials to Generate Biogas

Biogas is a methane-rich fuel gas and good source of energy for cooking and lighting. Seed cake, fruit shell of Jatropha, and vegetative plant parts can be utilized as raw materials to generate biogas (Table 2.3). Jatropha seed cake which is leftover after extraction could be transformed into biogas through fermentation in a tank along with cow dung, leaves, fruit shell, etc. The residues of biogas tank still retain some nutrients which can be used as manure. Foidl and Eder (1997) used seed cake as a single digestion input for biogas production. Biogas production efficiency of Jatropha residues is summarized in the table:

2.3.7 Use for Human Consumption

Jatropha is reported to be toxic to humans and many cases of poisoning are found in the literature (Siegel 1893; Becker 1996). Jatropha plants remain edible for the first 3 months when grown from seeds. Seeds of Jatropha can be edible only after dissecting the embryo (Levingston and Zamora 1983). However, it is suggested to avoid eating Jatropha seeds. On the other hand, nontoxic variety which does not contain toxic phorbol esters is reported to be found in Mexico and Central America (Makkar et al. 1998a, b). The roasted seeds, steamed or stewed young leaves of nontoxic plants, can be safely eaten (Delgado Montoya and Parado Tejeda 1989). It could be a prospective source of cooking oil for human being and seedcake as an excellent nutrient resource for farm animals (Makkar and Becker 1997, 1999; Aregheore et al. 2003).

2.3.8 Fuel for Stove or Lamp

Jatropha seed oil has prospect to be used as fuel for cooking and lighting because of its comparable properties with kerosene. But high ignition temperatures and viscosity (240 °C and 75.7×10^{-6} m^2/s) of Jatropha oil compared to kerosene (50–55 °C and 2.2×10^{-6} m^2/s, respectively) makes it difficult to use directly in traditional stoves or lamps. On the other hand, due to high ignition temperature and viscosity crude Jatropha oil blocked the pipes and nozzles of stove or lamp. Therefore, oil lamps and stove requires modification with very short wick in order that the flame is very close to the surface of the oil. More investigation is needed to design such unique stove or lamp for Jatropha seed oil (Mndeme 2008).

2.3.9 Oil as a Biodiesel Feedstock

Jatropha seed contains high amount of nonedible oil and can be transformed into biofuel (Subramanian et al. 2005; Islam et al. 2013b). At present, it is credibly very much encouraged as nonedible vegetable oil plant around the earth. Jatropha plants have been studied by several scientists for prospects of its seed oil, biodiesel, or mix together with diesel (Augustus et al. 2002; Pramanik 2003; Reddy and Ramesh 2006; Tiwari et al. 2007; Rao et al. 2009). Jatropha seed oil can be directly used in diesel engine or can be used by blending with conventional diesel (Gubitz et al. 1999). Jatropha seed oil was used as an alternative of diesel since World War II (Agarwal and Agarwal 2007). The physico-chemical properties and fuel performance makes Jatropha seed oil a good substitute of diesel fuel (Table 2.4).

Physio-chemical properties of seed oil may be affected by the climate and soils of the area where it is grown (Islam 2011). The oil properties also affect biodiesel production process by transesterification as well as combustion process during use. Limited informations are available on physical, chemical, and fuel characteristics where seeds are collected from different regions (Islam et al. 2013b). Oliveira et al. (2009) suggested that supplementary research on agro-technology is needed to improve the yield and physiochemical properties of Jatropha seed. The biodiesel obtained from Jatropha after transesterification meet up the standard of ASTM D

Table 2.4 Comparative physio-chemical characteristics of standard diesel, seed oil, and converted biodiesel of Jatropha

Physio-chemical characteristics	Standard diesel	Jatropha oil	Jatropha biodiesel	Limits
Specific gravity	0.82–0.89	0.90–0.92	0.85–0.90	0.86–0.90
Viscosity@ 40 °C	3.7–5.8	24.5	5.2	1.9–6.0
Cetane number	46–70	23–41	57–62	47 min
Sulphur (%)	<1.0–1.2	0.13–0.16	<0.02	20 max
Density at 15 °C (g/cm^3)	0.84–0.89	0.92	0.87	0.87–0.89
Cloud point (°C)	5.0	11.0	8.20	–
Pour point (°C)	−20	4	2	–
Iodine number	60–135	90.8–112.5	95 to 106	100–120
Neutralization number (mg KOH/g)	≤0.8	0.92	0.24	–
Flash point (°C)	68	225	135	130 min
Calorific value (MJ/L)	42.25	39.66	42.67	35 min
Peroxide value (meq/kg)	–	4.6	–	–
Saponification value (mg KOH/g)	–	196	–	–
Refractive index	1.32	1.46–1.61	0.92–1.46	–
Acid number (mg KOH/g)	0.104	1.0–38.2	0.40	0.80 max
Solidifying point (°C)	−14	2.0	−10	–
Boiling point (°C)	248	286	255	–

Source: Gubitz et al. (1999), Kumar and Sharma (2005), ASTM (2006), El Kinawy (2010), Raja et al. (2011), Islam et al. (2013a)

975-09 (USA) and EN 590:2009 (EU) (Azam et al. 2005; Tiwari et al. 2007). The Jatropha oil cannot use directly into diesel engine due to its high viscosity and CN number during winter season (Pramanik 2003; Fairless 2007).

Several authors have studied *J. curcas* oil and the biodiesel obtained from this oil, which are available in the literature (Azam et al. 2005; Kumar and Sharma 2005; Zhu et al. 2006; Modi et al. 2007). El Diwani et al. (2009) calculated the yield of biodiesel and obtained 97.6 % (wt) biodiesel after transesterification of 100 kg seed oil using methanol and NaOH as catalyst. A reaction of 100 kg seed oil with 10 kg catalyst will produce 100 kg biodiesel and 10 kg glycerol after transesterification process.

2.3.10 Seed Oil for Soap Production

The possibility of making the soft and durable soap from the Jatropha oil was reported in literature (Openshaw 2000). The by-product (glycerol) from transesterification process of Jatropha seed oil finds the application in soap manufacturing. IPGRI estimated that the mechanical extraction can yield 3 L of oil from 12 kg seeds and transformed into 4.76 kg soap. Economy of soap manufacturing was reported by Henning (2000) and showed a net profit of 1.43 USD from the

Table 2.5 Nutrient composition of Jatropha seedcake compared to other organic manure

Nutrient elements	Jatropha seedcake (%)	Jatropha root (%)	Cowdung (%)	Neem cake (%)	Poultry litters (%)
N	4.10–4.75	1.97	1.26	5.00	3.10
P	2.00–2.60	0.11	0.78	1.00	2.98
K	1.18–2.30	1.99	1.19	1.50	1.47
Humidity	3.95	–	8.57	–	9.25

Source: Eijck (2006), www.jatropha.pro

production of 28 white soaps, each with 170 g using oil from 12 kg of either Jatropha seed alone or in combination with other oil seeds. Benge (2006) also reported the economy of soap production from Jatropha oil.

2.3.11 Cosmetic and Pharmaceutical Emulsion Products

Glycerol by-products of biodiesel production process can be utilized to produce variety of products such as lipsticks, eye shadow, perfume, makeup, adhesive, preservative fluids, tube joint glue, tonic for cough, etc. Johannsen (2001) relates to a one shot fat composition obtained from the different plant spices including Jatropha with the emulsion used in cosmetic industry. The invention claims that the prepared fat composition was dermatologically safe and can act as: (1) an emollient, (2) stabilizer, (3) consistency imparting agent, and (4) coemulsifier in cosmetic and pharmaceutical emulsion products used for skin care applications (Masanao et al. 1985; Kouichi 1979). High amount (36 %) of linoleic acid (C18:2) present in Jatropha seed oil makes it potential for cream production.

2.3.12 Seedcake Use as Organic Manure

Jatropha seedcake is rich in several essential elements of plant like N, P, K, Ca, Mg, Zn, Fe, Cu, Mn, B, and S (Kumar and Sharma 2008). So it can be used as potential organic manure and soil conditioner (Staubmann et al. 1999; Gubitz et al. 1999). Seedcake can also be used as supplement of fertilizers as it contains NPK similar to neem oilcake, castor oilcake, cowdung, and poultry litter (Table 2.5). Nitrogen content of Jatropha seedcake varies from 3.2 to 3.8 % (Juillet et al. 1955; Moreira 1979; Vöhringer 1987; Delgado Montoya and Parado Tejeda 1989). GTZ project report in Mali showed that pearl millet yield increased up to 1,366 kg/ha in Jatropha seedcake (5 t/ha) treatment compared to manure (5 t/ha) and mineral fertilizers (100 kg ammonium phosphate and 50 kg urea/ha). This trial was appreciated by the farmers of Mali since costs of Jatropha seedcake were much less compared to mineral fertilizer (Henning et al. 1995). On the other hand, leaves of Jatropha add plenty of organic matter in the soil and increase the microbial activity including earthworms (Gubitz et al. 1999).

2.3.13 Feed for Farm Animals

Seedcake of Jatropha can be used as feed for farm animals after detoxification because it contains 11 % oil, 50–60 % crude protein, and trace amount of amino acids. On the other hand, seedcake of nontoxic varieties might be supplied directly as animal feed. High-quality protein concentrate as feeds for farm animals and aquaculture species can also be produced from seed cake after processing and detoxification (Makkar et al. 2008; King et al. 2009). Nontoxic varieties of Jatropha have been found in Mexico and Central America and are not available in Asia and Africa.

2.3.14 Seed Oil Use to Produce Plastics

Thermoplastic material is produced by reacting unsaturated or hydroxyl-group-containing fatty acids or their esters with bi-functional ester or amide-forming compounds (Rainer et al. 1994). The oil from the seeds of Jatropha contains mainly oleic, linoleic, and palmitic acids as an ingredient of FFA. FFA composition of Jatropha seed oil can be used as one of the material to produce plastics.

2.3.15 Use of Jatropha by-Product as Bio-Adsorbent

The various industrial activities such as tanneries, papermaking, refining ores, etc. are introducing heavy metal ions into the aqueous streams which pose a serious threat to the environment (Dhiraj et al. 2008). The elements such as Ni, Cr, Hg, Cr, Se, Zn, Pb, etc. can cause danger to human life. The bio-accumulation and toxicity are the major concerns from the aforementioned metals. The by-products generated after the biomass processing have gained the attention to exploit them as bio-adsorbents due to lower price, maximum efficiency, and easy regeneration process of bio-absorbents. Garg et al. (2007, 2008) investigated various agricultural waste including jatropha oil cake for the adsprotion of cromium (Cr) and cadmium (Cd) from aqueous solutions under various experimental conditions. Seedcake of Jatropha showed improved adsorption efficiency compared to corn cob and bagasse.

2.3.16 *Thermal Stabiliser*

The effect of Jatropha seed oil as a thermal stabiliser on polyvinylchloride (PVC) has been investigated by Okieimen and Sogbaike (1996). Thermal degradation of PVC was carried out at 170, 180, and 190 °C under oxidative and non-oxidative conditions in the presence of Jatropha seed oil. The viscosity measurements and the estimates of unsaturation levels in the degraded polymer showed that the oil soaps of Jatropha have good stabilizing effect on thermal degradation of PVC under oxidative and non-oxidative conditions.

2.3.17 *Herbicides*

In the past, the weeds have been killed by using garden tools or stones or metals or by means of physical pulling from the ground. But in recent years some useful chemicals (e.g., glycophosphates) have been used to kill the weeds. Glycophosate is a general purpose herbicide which is translocated through the plant to the root system. The invention WO2008080163 (Jones 2008) revealed an herbicidal composition and method of using the same for killing unwanted plants. In specific, the invention relates to the use of fatty acids and esters of fatty acids in herbicidal compositions as herbicidal agent. The invention claims that the esters of fatty acids obtained from Jatropha seed oil in addition to other plant oils could be utilized in herbicide preparation.

2.3.18 *Jatropha as Agroforestry Crop*

Jatropha has multipurpose potential as industrial, agricultural, pharmaceuticals crops. It is a potential and money-spinning agroforestry crop due to its easy cultivation technology, short gestation, and long productive period (Gubitz et al. 1999). Jatropha can ensure utilization of wasteland, rural man power, water and financial resources, traditional energy, and enhancing investment in rural areas. *Jatropha curcas* has several characteristics which make it suitable for multifunctional agroforestry species (Achten et al. 2010).

2.3.19 *Bio-Polyol*

The petroleum-derived polyols have been employed in the manufacturing of polyurethane. Utilization of renewable materials in the production of polyurethane including other polymer materials is increasing day by day due to elevated GHG (green house gas) emission and declining petroleum reserve. The natural oil polyols are used to make polymers such as polyurethanes, polyesters, polycarbonates, etc. Among many available natural oils, Jatropha oil can also be used as raw material to produce natural polyols (Timothy et al. 2007). Polyol made from vegetable oil has advantage over polyols made from petroleum (petrochemicals) because of being biodegradable, abundant, and renewable (Harjono et al. 2012).

2.3.20 Tanning Agent

The chemical compound employed to assist the tanning process is known as tanning agent and the process of converting rawhides to leather is known as tanning process. The tanning of bark, wood, roots, or berries has been traditionally used from the pre-historic period (Okuda 1995). Tanning component removes the water from interveining space between the protein fibers and cement of the fiber of hides. Chromium (III) sulfate [$Cr_2(SO_4)_3.12H_2O$], a mineral tannin agent, is predominantly used in tanning industry. Due to the ecological safety concern chromium salts and other mineral tanning systems, there is need for an alternative tanning agents. The bark of Jatropha contains tannin. The research reported use of *Jatropha curcas* seed oil as co-stabilizing agent for skins and hides in tanning process. Jatropha tannin agent is eco-friendly in nature and can find the application in leather processing, textile, and coating industries (Sundar et al. 2013).

2.4 Current Research on Jatropha Plantation

Research on Jatropha has started more than 20 years ago, but characterized more by sporadic action than by continuous work (Grass 2009). A study carried out by GEXSI (2008) provided a first overview on *J. curcas* L. projects on a global scale. There is a lack of in-depth and long-term information on Jatropha production systems, i.e. acreage, seed yield, and its agro-technology (propagation, agronomy, management, etc.). The current plantation practices are mainly based on data from experimental plots and small scale experience. Seed yield is possibly the greatest uncertainty when conferring the potential uses of Jatropha as a biofuel. Seed yield can even vary considerably within a plantation because of genetic diversity (Basha and Sujatha 2007). Different oil yields and energy contents for *Jatropha curcas* were noted by several researchers (Openshaw 2000; Augustus et al. 2002; Pramanik 2003; Francis et al. 2005; Herrera et al. 2006; Vyas and Singh 2007), all notes showed such inconsistencies (Islam 2011). Therefore, proper plant selection is crucial for the development of a high yielding Jatropha crop.

Genetic studies provide basic information for the development of new varieties and improvement of any crop through breeding program (Burley and Wood 1976). Genetic diversity of Jatropha accessions or native gene pools was reported by many scientists and found to be low and insufficient for various countries (Basha and Sujatha 2007; Pamidimarri et al. 2008; Ranade et al. 2008; Sun et al. 2008; Achten et al. 2009, 2010). Variations present in the base population for seed yield per plant and oil content (%) can help to select better types for developing high yielding variety of Jatropha. Systematic classification and assessment of available germplasm can provide information to develop high yielding variety through further breeding program. Therefore, selection and multiplication of elite germplasm will be the key to Jatropha biodiesel program. Studies on genetic control of yield contributing characters have not yet been carried out by including Jatropha accessions from its center of origin (Islam 2011). So emphasis should be given to estimate genetic diversity among the available genetic resources, select elite accessions, and multiply them for further improvement program (Kaushik et al. 2007). Propagating large quantities of *Jatropha curcas* is not a complicated task, provided that proper techniques are being used.

2.5 Jatropha Initiatives in Malaysia

The Malaysian government encourages and supports all initiatives towards the development of the biofuel industry (Mustapha 2008). But government does not have any instant plant to interrupt national palm oil plantation to break equilibrium of resources (Peterson 2008). Malaysian government has approved license to 91 biofuel manufacturers, but only four have started production of biodiesel due to high market price of crude palm oil (Nagarajan 2008). The majority of the industries that started with Jatropha do not have plantation and mainly focused on research and development, and marketing of biodiesel. Asian countries like India, China, and Indonesia are in advance in research on Jatropha technology compared to Malaysia from cultivation to biodiesel production even by-product development. Pusat Asiatic Genom Teknologi Sdn Bhd (PAGT), a local company, has started plantation and research on various aspects of genomics of Jatropha. About 40,000 ha of land has been planted with Jatropha in Sabah and Sarawak by 2008, but all are scattered as small scale plantation. No exact statistics are available about the area of Jatropha plantation in Sarawak, but plantation trend is increasing day by day (Mail 2009). A pilot project on Jatropha plantation has been started by the local government of Sabah to reclaim waste land or to utilize its fallow lands (Star Newspaper 2007). Malaysian Rubber Board, Malaysian Palm Oil Board, and National Tobacco Board of Malaysia are carrying performance test and breeding of Jatropha to find out its potentials (Peterson 2008). Mission Biotechnology has made an agreement to plant Jatropha in 80,000 ha of lands and was expected to increase up to 1,000,000 ha. About 1,500,000 ha of marginal land are available throughout Malaysia which has potential for planting Jatropha (Peterson 2007). The Federal Government of Malaysian does not want to lose any profit from Jatropha; at the same time does not want to overemphasize on its plantation. That’s why speed of development of Jatropha biodiesel industry is nearly moderate.

Ark Bio Sdn Bhd, a member of Cosmo Biofuel Group, is trying to develop superior planting materials of Jatropha including other oil-producing plants and their large scale propagation which could be used in biodiesel industries (Arkbio 2009; Khoo 2008, 2011). This company is collaborating with other research organizations for the development of agro-technology, plantation management, and farm automation. Cosmo Biofuel Group is intensely associated with the development of Jatropha plantation, biodiesel production, by-product development, and commercialization of the products in South East Asia. This group also established its pilot project on Jatropha plantation in Kuala Pilah on 2006 and several product development projects with its counterparts in China, Thailand, Cambodia, Indonesia, and Vietnam (Jatroleum 2009; Peterson 2008). Cosmo Biofuel Group also established about 10,000 ha Jatropha plantation in Cambodia with an NGO. In 2008, this Company commenced a pilot plantation of Jatropha for business purpose on 1,000 ha in the Fujian Province of China. Bionas Agropoliton Technology Corridor Development Sdn Bhd is engaged with marketing of Jatropha planting materials and seed oil. This company supports local farmers to business enterprise in Jatropha plantation and assured them buyback value agreement of RM 0.85/kg of seeds (Peterson 2008).

Two governments (Malaysia and Indonesia) have signed an agreement to develop Jatropha technology for future biodiesel under the domain of renewable energy which will cover R & D related to agro-technology, high yielding variety, and product development (Bernama 2008). Among several aspects of Jatropha cultivation superior planting material is one of the most important concerns for the plantation and production of seed. One Malaysian researcher (Luhat 2009) developed fourth-generation planting material “Superbulk” through breeding program using a pure line seed of Nicaraguan Jatropha. Superbulk is recommended as superior planting materials for East Malaysia which can give early and high seed yield. Recent initiatives have been taken to develop dwarf variety with high seed yield capacity and lower male and female flower ratio (Luhat 2009; Islam 2011).

2.6 Constraints of Jatropha Technology

Jatropha technology has several shortcomings even though it can survive with inadequate nutrient condition. Firstly, lack of high yielding variety. Secondly, uneven fruit ripening which need lots of labor to harvest from the plant (Peterson 2008). Thirdly, as a single crop, Jatropha can be harmful as a noxious weed for other economic crop (IANS 2008). Fourthly, it can dislodge position for animal browsing (Jones and Csurhes 2008). It is a hardy and almost pest-free plant, but for plantation as a single crop it is getting several difficulties of insect and disease infestation. Three pest insects have been reported to attack Jatropha plant: (1) leaf miner (*Stomphastis thraustica*), (2) the leaf and stem miner (*Pempelia morosalis*), (3) brown soft scale (*Coccus hesperidum*), (4) shield-backed bug (*Calidea panaethiopica*), (5) mealy bug (*Paracoccus marginatus* Williams), and (6) Termites (*Odontotermes*

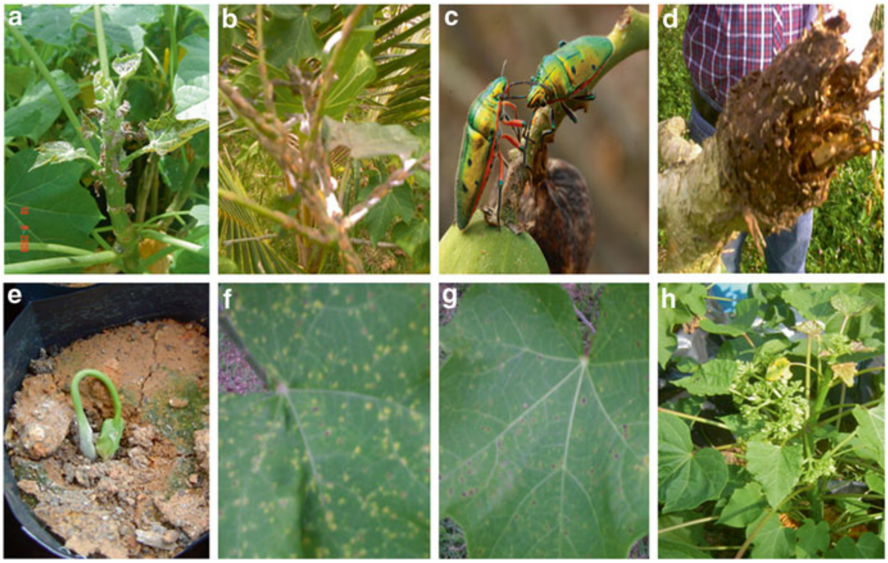

Fig. 2.4 Showing (**a**) seedlings infested by mealy bug, (**b**) brown soft scale, (**c**) shield-backed bugs, (**d**) termite, (**e**) foot rot, (**f**) leaf spot, (**g**) leaf rust, (**h**) virus-infected plant

formosanus Shiraki) which can cause flower and fruit abortion (Terren et al. 2012). These insects cause damage of leaf, dropping of bud and fruit as well as abnormal seed formation (Fig. 2.4). Toxicity and insecticidal properties of Jatropha fail to protect against the attack by insects and diseases. These attacks affect the plant's productivity. Grimm (1996) estimated that an 18.5 % loss in harvest potential is caused by Heteropteran and Lepidopteran insect. Jatropha also reported to be infected by root rot (*Clitocybe tabescens*), leaf spot (*Colletotrichum gloesporioides*), leaf deterioration (*Phakopsora jatrophicola*), and viral diseases (Perino 2006). There is a little published information about the crop management and fertilizer requirements of Jatropha. Other constrains of Jatropha technology are the presence of toxic subsrtances in different parts of the plant and phorobol ester in seed oil. The oil of Jatropha seed is nonedible or toxic to human being and animals due to the presence of phorobol ester (Gubitz et al. 1999; Kaushik et al. 2007; Kureel 2006; Martin and Mayeux 1985; Menezes et al. 2006; Openshaw 2000).

2.7 Cultivation Scope and Future Outlook

"*Jatropha is a bonus plant, and you only plant it where you can't plant other good crops. It is not an alternative to oil palm, which can give better yield*" (Peterson 2008). Jatropha is becoming an economically feasible alternative to fast-depleting fossil fuels due to its easy cultivation and market demand. Reclamation of wasteland, arid land, and marginal soil could be possible by substantial plantation of Jatropha. Jatropha is a novel addition to agricultural farming but not a substitute of plantation.

2.8 Conclusion

Jatropha is a multipurpose plant with enormous prospects for the countries of tropics and subtropics. It can be cultivated on marginal land and retrieve waste land, desert, and plants that are attacked by a small number of pests and diseases. Research on downstream uses has already been done by several researchers throughout the world. But more research on upstream activities such as improvement of yield-related traits and management practices, development of high yielding variety, mechanization in harvesting, and postharvest processing are essential to know the exact potentiality of Jatropha. Potential in biodiesel production, possible manufacturing of many by-products, erosion control, bio-fence, medicine, etc. makes Jatropha attractive to plantation industry. By-products from the biodiesel production process give additional profit which makes Jatropha cultivation more attractive to the business people. Energy value of remaining portion of jatropha fruit is twice than that of biodiesel. This industry is still in its infant stage; however, lots of initiatives have been taken to sustain Jatropha technology. Moreover, additional investigation is required to explore all the potentiality of Jatropha including its marketing system.

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Chapter 3
Upgrading of Oil Palm Empty Fruit Bunch to Value-Added Products

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Abstract As the second largest producer of palm oil in the world, Malaysia generates a substantial amount of oil palm biomass as agricultural wastes in the forms of empty fruit bunches, shell and fiber, fronds, leaves, and trunks. This biomass feedstock has long been identified as a sustainable source of renewable energy which could reduce the dependency on fossil fuels as the main source of the energy supply and thus lead to reduction of greenhouse gases emission. This chapter highlights the application of oil palm biomass as value-added product and specifically demonstrates the capability of empty fruit bunch as renewable source in generating bio-oil which later could be upgraded as biofuel. Green extraction technique known as supercritical fluid extraction using supercritical CO_2 (SC-CO_2) was implemented in this study. Effects of two extraction conditions were investigated which includes temperature (60–80 °C) and CO_2 flow rate (3–6 mL/min). The extraction was conducted for 2 h using 10 g of OPEFB within particle size 0.15 mm. The crude bio-oil obtained in this study was diluted in 10 mL dichloromethane (DCM) for analysis using gas chromatography-mass spectrometry (GC-MS). Hexadecanoic acid (palmitic acid, C_{16}), dodecanoic acid 1, 2, 3-propanetriyl ester (glycerol trilaurate, C_{39}), and 6 octadecanoic acid (stearic acid, $C_{18:0}$) were identified as the major compounds.

Keywords Bio-oil • Oil palm empty fruit bunch • Supercritical CO_2 • Palmitic acid (C_{16}) • Glycerol trilaurate (C_{39}) • Stearic acid ($C_{18:0}$)

3.1 Oil Palm Industry in Malaysia

Malaysia is a country located in south east of Asia experiencing tropical climate which is suitable for growing of oil palm. The seed which is originated from West Africa was introduced by British in early 1871 and its first commercial plantation is in 1917 at Tennamaran Estate of Selangor (Basiron and Weng 2004). Today, the plantation covers 5 million ha of land in Malaysia which make the country as one of the largest exporters of palm oil in the world. Figure 3.1 indicates the production of crude palm oil (CPO) from peninsular Malaysia from 2004 until 2011. The production is relatively kept increasing which indicates the stability and sustainability of the sector.

The oil palm trees that have been planted in Malaysia are mainly from the type of *tenera,* which is the hybrid seed of *dura* and *pisifera.* The ripe oil palm fruit is reddish in colour which grows in large bunches. The fruit is made up of mesocarp fiber layers that enclosed the palm kernel and most of the oil is extracted from both parts, known as CPO and crude palm kernel oil (CPKO) (Sumathi et al. 2008). It is able to bear fruits after 30 months and produce 4–5 tons of CPO each hectare every year. The tree could be productive for 20–30 years and only require 0.26 ha of land to produce 1 ton of oil compared to soybean, sunflower and rapeseed which required 2.22, 2, and 1.52 ha of land, respectively (MPOC 2012). Sumathi et al. (2008) state that oil palm is energy-efficient crop since it requires less energy to produce 1 ton of oil. Figure 3.2 illustrates the ratio of energy output to input for several commercially grown oil crops which indicates that oil palm output is three times greater than the others (Sumathi et al. 2008).

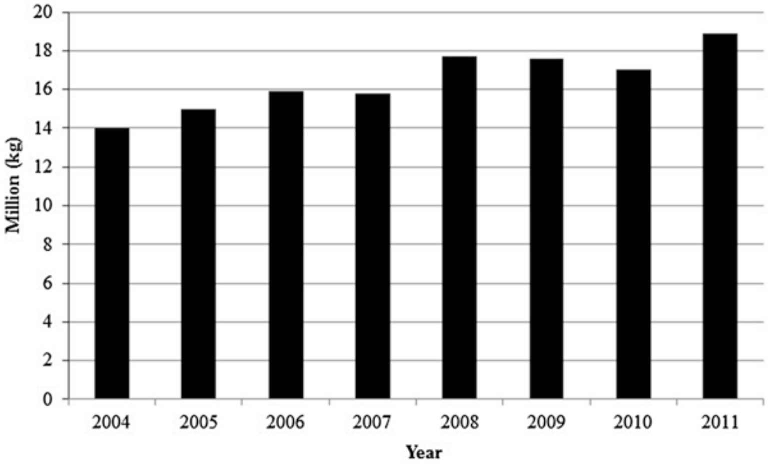

Fig. 3.1 Production of crude palm oil from peninsular Malaysia (Malaysian Palm Oil Council 2012)

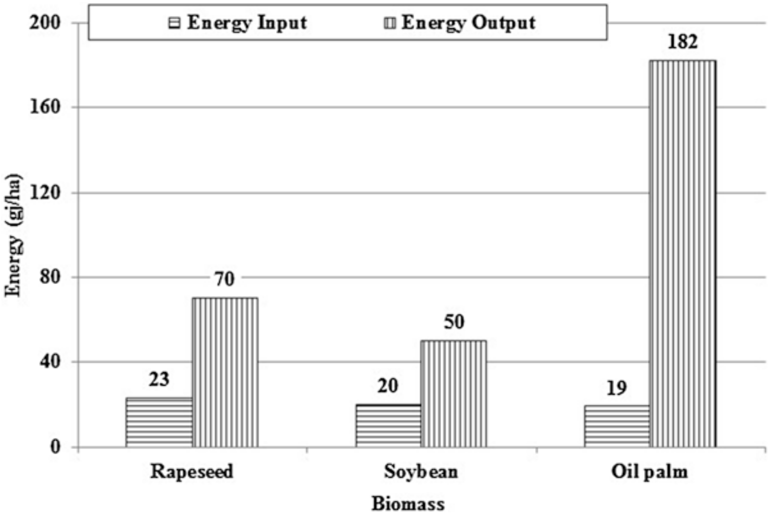

Fig. 3.2 Input and output energy consumption of several biomass (Sumathi et al. 2008)

Figure 3.2 demonstrates the staggering amount of waste generated which currently is still underutilized. For instance, it is estimated that 37 million tons of oil palm biomass had been generated in 2008 which consisted of 22 % OPEFB, 13.5 % fruit press fiber (FPF), and 5.5 % palm kernel shell (PKS) (Mazaheri 2010; MPOC 2012). Figure 3.3 illustrates the general mass balance involved in palm oil mill which indicates that pure oil only contributes 21 % of a fresh fruit bunch and left almost 50 % waste including OPEFB as the biomass (Mazaheri 2010; Umikalsom et al. 1997; MPOC 2012). Yusoff (2006) states that OPEFB is one of the main by-products and wastes produced from the mill. As described in Table 3.1, EFB is the highest amount of biomass generated in the mills compared to fiber and shell in 1997 for an estimated plantation hectare of 148 palms/ha (Yusoff 2006).

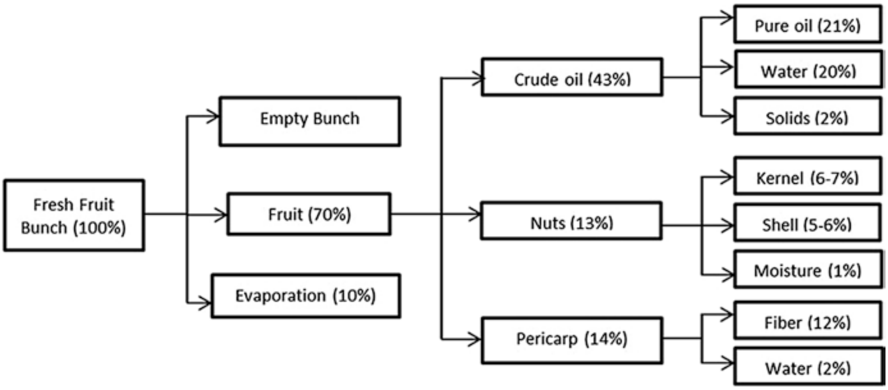

Fig. 3.3 Composition chart of palm oil mill (Mazaheri 2010; Umikalsom et al. 1997; MPOC 2012)

Table 3.1 Amount of biomass generated by palm oil mills in 1997 (Yusoff 2006)

Biomass	Quantity (million tons)
Empty fruit bunch	10.6
Fiber	6.6
Shell	2.7
Pome	32

3.2 Waste to Value-Added Product

Renewable energy is environmental friendly since it does not emit CO, CO_2, SO_x, NO_x, and particulates during combustion compared to fossil fuels including oil, gas, and coal (Tan et al. 2009; Sulaiman et al. 2011). It has been one of the main agenda for Malaysian Government although the country is rich with primary energy resources. Utilization of renewable energy resources, particularly oil palm wastes, has been increased since it is a strategically sustainable energy resources and able to reduce agriculture disposal problem in an environmental friendly manner (Sulaiman et al. 2011). In 2006, biodiesel which is a blend of palm oil (5 %) and petroleum oil (95 %) was promoted through National Biofuel Policy. The policy ensures the quality of the biodiesel to meet the industrial standard and to support biodiesel pumps at selected stations. It also encourages the establishment of biodiesel plants in Malaysia. In addition, Malaysia has implemented National Renewable Energy Policy and Action Plan in 2010 which is aimed to branch the utilization of local renewable energy resources towards electricity supply and socio-economic development (APEC 2013). Figure 3.4 represents several major crops that have been used as the natural renewable sources for respective biofuels.

Oil palm biomass is a promising renewable energy source due to rising price of crude petroleum. Therefore, converting oil palm biomass into biofuel is not only able to reduce the petrol crisis, but also helps to protect the environment by reducing CO_2 emission (Shuit et al. 2009). According to Sulaiman et al. (2011)

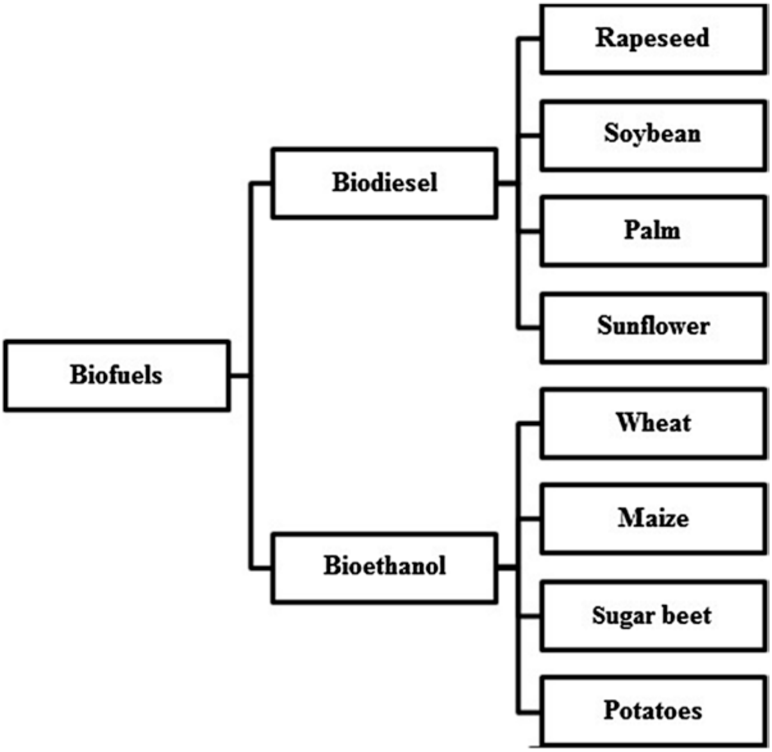

Fig. 3.4 Crops for biofuels production (Demirbas 2007)

oil palms waste has been used to produce steam for mills and electricity generation. It was reported that more than 300 palm oil mills are operating using self-generated electricity using oil palm waste which is also sufficient for surrounding remote areas (Sulaiman et al. 2011). Generally, biomass is a lignocellulosic material which is made up of hemicellulose, cellulose, lignin, and minor amount of extractives. Biomass material is eligible to be converted to energy by applying thermochemical or biological processes (Demirbas 2007). Tan et al. (2009) mentioned that liquid fuel such as bio-diesel is one of the global extensively researched renewable energy resources. Biodiesel is mono-alkyl esters of long-chain fatty acids which is derived from trans-esterification reaction of triglycerides from the feedstock presence of alcohol, forming esters and glycerol (Tan et al. 2009).

By implementing several conversion technologies as shown in Fig. 3.5, biomass is able to be converted into biofuel. One of the most interesting thermochemical conversion technologies is biomass gasification due to its high combustion efficiency compared to pyrolysis. Gasification is believed to cause the carbon to become less reactive and forming stable chemical structure which consequently increased the activation energy as the conversion increased (Demirbas 2007). Biomass gasification occurs at higher temperature than pyrolysis and is able to produce

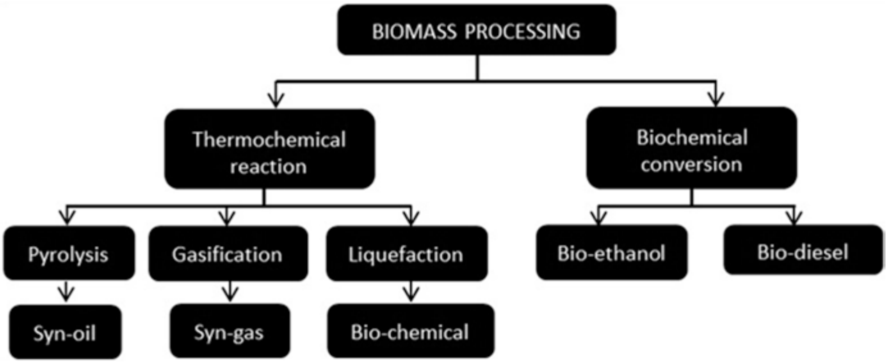

Fig. 3.5 Conversion technologies applicable to biomass (Demirbas 2007)

mixture gases including H_2 at 6–6.5 % concentration (Demirbas 2007). These gaseous products are able to be converted into clean fuel gases or known as biofuel (Demirbas 2007). Oil palm biomass is able to produce many types of biofuel including bio-ethanol, bio-methanol, bio-briquettes, hydrogen gas, and pyrolysis oil (Shuit et al. 2009).

It is well known that biofuel is able to reduce the emission of CO_2. For instance, biofuels such as bioethanol, biomethanol, and biodiesel can help reduce the emission of this greenhouse gas by almost 80 % compared to petroleum diesel (Shuit et al. 2009). Shuit et al. (2009) also claimed that CO_2 emission was reduced by 1,040 thousand tons when diesel was replaced with biogas to generate electricity. Empty fruit bunch, mesocarp fibers, and palm kernel are the main oil palm wastes that have been used to provide steam for electricity generation. Currently, Malaysia has 300 palm oil mills which self-generated electricity by using these wastes and this figure is increasing. Small Renewable Energy Program (SREP) has been launched in 2004 and 62 projects have been approved which include 25 projects that are implementing oil palm biomass as the fuel source (Shuit et al. 2009). PKS also has been applied as fuel in the boiler of some cements company which is believed to reduce CO_2 emission by 366.26 thousand tons in 2006 (Shuit et al. 2009; Sulaiman et al. 2011). Therefore, biomass is an option for renewable energy which can reduce the greenhouse effect compared to current fossil fuel (Sulaiman et al. 2011; Shuit et al. 2009).

Oil palm waste is also able to generate hydrogen, which currently has been regarded as synthetic fuel obtained from fossil fuels (Sulaiman et al. 2011). Via gasification, various parts of oil palm such as EFB fiber, shell, trunk, and frond can be converted into biohydrogen which is diversely applicable in transportation or power generation. Hydrogen as transportation fuel is efficient for the engine and environment due to its zero emission (Sulaiman et al. 2011). Besides, oil palm biomass is also rich in sugar and lignocellulose which makes it a perfect candidate for production of bio-methanol and bio-ethanol. Bio-methanol has high octane rating which makes it suitable for spark ignition in the engine (Shuit et al. 2009). It is prominently converted through gasification which involves vaporization of biomass

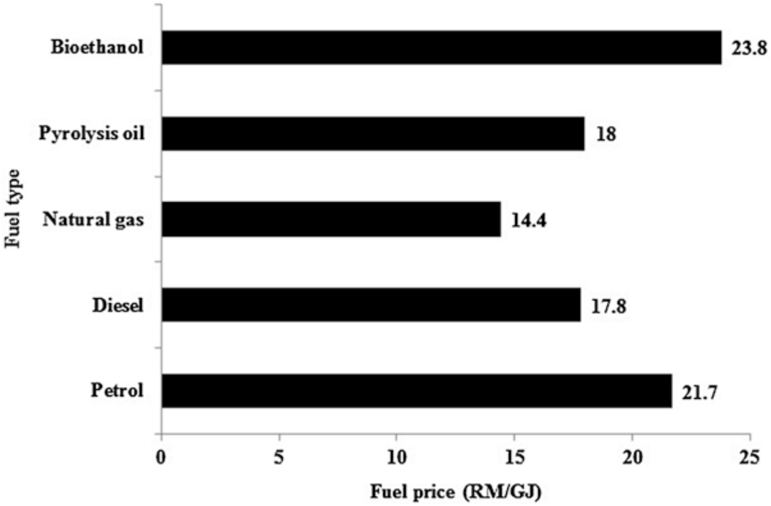

Fig. 3.6 Cost of producing various fuels in Malaysia (Shuit et al. 2009)

at high temperature and removing impurities from the hot gas before being converted to bio-methanol using catalyst (Shuit et al. 2009). Inversely, bio-ethanol is produced via fermentation process and is mostly applied as fuel additive to reduce emission of CO and smog. According to Shuit et al. (2009), xylose from EFB is produced via acid hydrolysis and can further be utilized as second generation bio-ethanol. Brazil, US, and European market have provided the flexible-fuel vehicle which can run on mixtures of gasoline and up to 85 % bio-ethanol (Shuit et al. 2009). Figure 3.6 compares the production price of various fuels in Malaysia. About 46 % of the cost for bio-ethanol production is due to the feedstock which could be further reduced throughout the year since the feedstock is abundantly available and cheap (Shuit et al. 2009). Therefore, biofuel is achievable to replace the fossil fuel.

Bio-oil is also one of the products from biomass conversion. The term bio-oil refers to liquid fuels made from biomass material including agricultural crops, municipal waste, and agricultural and forestry by-product via bio-chemical or thermochemical processes (Demirbas 2007). Bio-oil normally has pungent odour, is brown in colour, and contains fragments of cellulose, hemicelluloses, lignin, and extractive (Sulaiman et al. 2011). Bio-oil is also known to be high-density oxygenated liquid and can be used to run diesel engines partially in blend, turbines, or boilers (Sulaiman et al. 2011; Demirbas 2007). The yield of bio-oil is about 70 and 15 % charat temperatures around 500 °C together with short vapor residence times (Sulaiman et al. 2011). Bio-oil is considered as relevant technologies in both developing and industrialized countries due to energy security reasons, environmental concerns, foreign exchange savings, and rural sector of socio-economic issues (Demirbas 2007).

3.3 Conversion of Oil Palm Empty Fruit Bunch to Bio-Oil via Supercritical Fluid Extraction

The liquid fuel or commonly known as bio-oil could be further upgraded to other value-added compounds such as gasoline and diesel. Recently, it was reported that a promising route to convert biomass to liquid fuel is via supercritical fluid extraction (SFE). It is one of the thermochemical reaction techniques that can be applied to extract bio-oil from biomass other than combustion, pyrolysis, and gasification (Qian et al. 2007; Demirbass 2000; Xu et al 2011; Naik et al. 2010; Minowa et al. 1998). The technique is able to obtain liquid fuels with low molecular weight from the biomass by converting the solid compounds under supercritical fluid conditions. Compared to conventional fast pyrolysis method, supercritical fluid liquefaction is advantageous since drying the feedstock is not necessary and therefore it is simpler and attractive from the perspective of energy consumption (Qian et al. 2007). This method is also a promising technique since it implements nontoxic, non-flammable, cheap, and readily available fluid as the solvent for extraction (Molero et al. 1996). For instance, CO_2 require low temperature (31.1 °C) and low pressure (73.8 atm) to reach the supercritical condition. Supercritical fluid is defined as fluid formed at conditions above the critical properties for that particular solvent. During supercritical conditions, a fluid is neither liquid nor gas and it has unique properties in between liquid and gas. For instance, supercritical fluid possesses liquid-like densities, but has high diffusivity and compressibility similar to gas. Therefore, supercritical fluid has enhanced solid solubility compared to liquid or gas solvent. Slight changes in temperature or pressure can cause big alteration towards the fluids properties such as density, solubility, or diffusivity (Herrero et al. 2006). At supercritical conditions, the fluid has low viscosity and relatively high diffusivity in which it is able to diffuse easily within the extraction matters (Herrero et al. 2006). Thus, by modifying the extraction condition such as pressure, temperature, and CO_2 flow rate, the solubility strength of the fluid can be amended and higher extraction yield could be obtained.

Molero et al. (1996) extracted grape seed oil (GSO) using SC-CO_2 and found that the yield of GSO is higher compared to the extraction using liquid CO_2. Using the same operating condition, Molero et al. (1996) obtained same yield of GSO to those conventional extraction using hexane. Yet, the extraction using SC-CO_2 is more preferable and economical since it is solvent-free (Molero et al. 1996). In addition, Patel et al. (2006) claimed that the quality of the obtained oil using SC-CO_2 is better compared to the oil that has been obtained using normal thermal route. Till date, there are limited studies of SFE using SC-CO_2 that have been conducted on biomass to extract bio-oil. Mostly, the SFE is implemented in food and pharmaceutical industries. Therefore, this chapter provides an insight in extracting bio-oil from oil palm biomass by implementing SFE using SC-CO_2 under various extraction conditions.

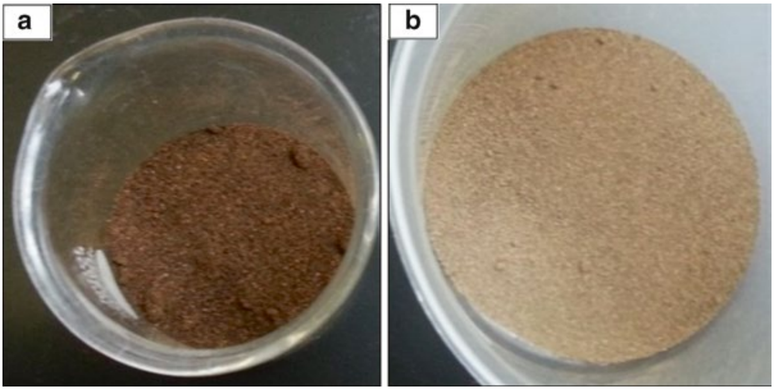

Fig. 3.7 Physical appearance of OPEFB (**a**) before extraction, and (**b**) The residue looked dry, lighter and turned into more fine particles after the extraction was conducted

3.3.1 Preparation of Raw Material

Figure 3.7 illustrates the changes in physical appearance of OPEFB before and after the extraction. The biomass was collected from nearby local oil palm plantation. It was cleaned by removing the sand and air dried for one day. The biomass was collected from nearby local oil palm plantation. It was cleaned by removing the sand and air dried for one day. The biomass was ground and sieved into the intended particle sizes, which in this case was 0.15 mm. To keep the sample fresh, it was kept in the refrigerator (6 °C) prior to extraction.

3.3.2 Extraction Process

Figure 3.8 illustrates the SFE SC-CO_2 extraction system that has been applied in this study. A 10 g of the sample was filled into the extractor (TharDesigns, 25 mL) and placed in the oven (EYELA WFO-400). Liquid CO_2 is supplied from the gas cylinder with purity of 99 % and the flow rate was adjusted using CO_2 delivery pump (Jasco). The gas passed through the chiller to liquefy the stream before entering the oven which was preheated at the desired temperature. A back pressure regulator was used to manually regulate the extraction pressure. The extraction took place for 120 min and the extracted bio-oil was collected in the sample bottle. The wet CO_2 gas that has been released from extractor was measured using wet gas meter before vented. Table 3.2 indicates the extraction conditions and the manipulated extraction parameters in this study.

The extracted bio-oil obtained during the extraction was in waxy state. It was weighted and diluted in 10 mL of DCM prior to analysis using GC-MS. Figure 3.9 demonstrates the changes in physical appearance of the extracted bio-oil obtained during the extraction and after being diluted in the solvent.

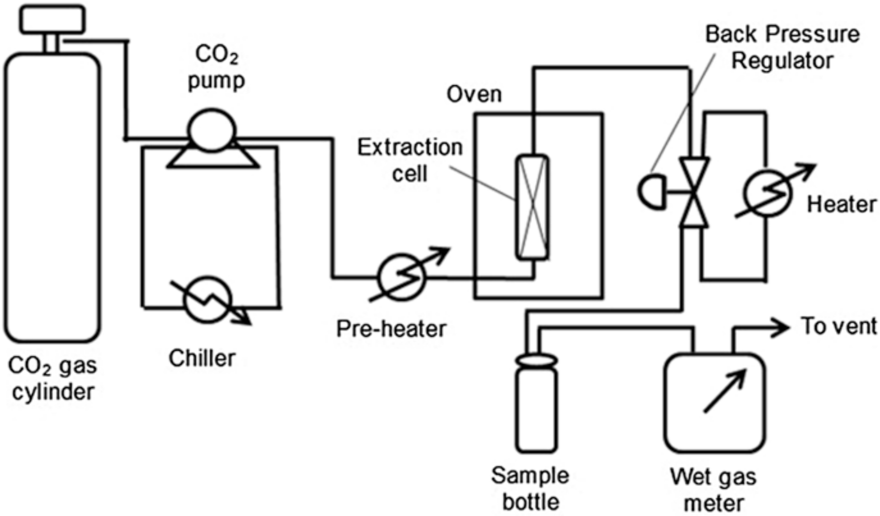

Fig. 3.8 Set-up of SFE system in GOTO Laboratory, Nagoya University, Japan

Table 3.2 Extraction conditions of the manipulated parameters

Varied parameters	Pressure (MPa)	Temperature (°C)	Flowrate (mL/min)
Temperature	40	60	5
		70	
		80	
CO_2 flow rate	40	70	3
			4
			6

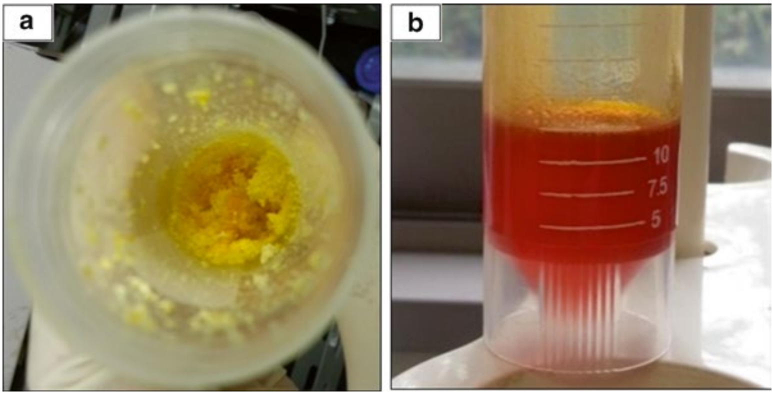

Fig. 3.9 Physical appearance of (**a**) waxy bio-oil (**b**) diluted bio-oil in DCM

Table 3.3 Composition of three main components in biomass

Component	Composition (%)
Hemicellulose	26.9
Alpha-cellulose	26.6
Lignin	18.6

3.3.3 Gas Chromatography Mass Spectrometer Analysis

Gas chromatography mass spectrometer (GCMS) (Agilent) is used to analyze the presence of compounds and their composition in the extracted bio-oil. Helium with flow rate of 3 mL/min was the carrier gas and split less column HP-5MS is used to analyze the components in the sample using NIST Library. The column temperature was kept constant at 150 °C for 3 min, then ramp to 320 °C for 10 min with heating rate of 5 °C/min.

3.3.4 Determination of Yield

Yield of bio-oil is expressed as the yield of crude extracts with respect to the biomass. Therefore, weight of feed bio mass and extracted bio-oil was recorded. The expression applied was quoted in Eq. 3.1.

$$\text{Yield}\ (\text{wt}\%) = \frac{m_{\text{extract}}}{m_{\text{biomass}}} \times 100. \tag{3.1}$$

m_{extract} is mass of the extract (g); and m_{biomass} is mass of the biomass (g)

3.3.5 Analysis of Chemical Composition

Table 3.3 describes the amount of main components in the biomass OPEFB. Cellulose, hemicellulose, and lignin are the major components that made up the biomass. Cellulose and hemicellulose are the compounds which are mainly involved and converted into bio-oil during the extraction compared to lignin. Therefore, high composition of these components reflects that OPEFB is a good source to obtain bio-oil.

3.4 Effect of Extraction Temperature

Near to critical state, fluid density is highly sensitive to temperature because a slight increment in temperature can lead to a large decrease in fluid density and solubility (Bimakr et al. 2009). It will accelerate mass transfer and improve extraction yield.

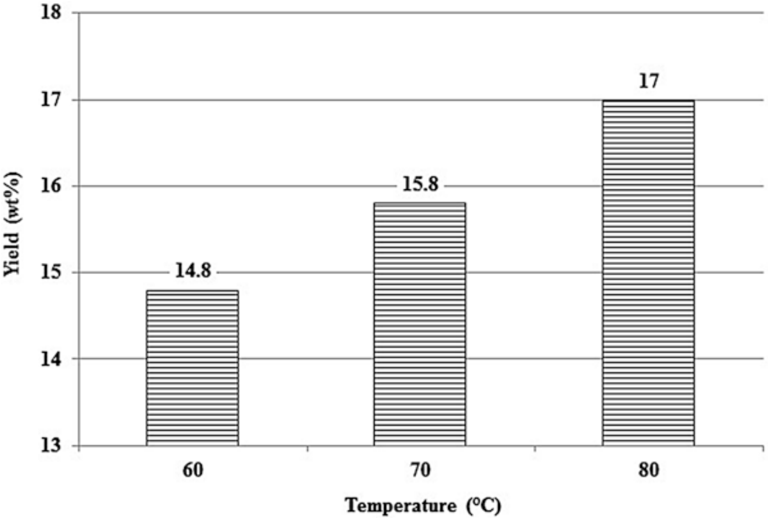

Fig. 3.10 Yield of bio-oil obtained under different extraction temperature

As indicated in Fig. 3.10, a yield at 17 wt% was maximized at temperature of 80 °C compared to 14.8 wt% at the lowest temperature of 60 °C. According to Machmudah et al. (2007), higher temperature contributed to the decomposition of cell walls, and as a result oil extracted increased. Leo et al. (2005) also claimed that high temperature enhanced the oil solubility in the CO_2 fluid due to lower solvent strength since the fluid density tends to decrease.

Effect of extraction temperature on composition of major compounds was demonstrated in Fig. 3.11. Extraction temperature was varied from 60 to 80 °C. Composition of glycerol trilaurate (C_{39}) was identified to be maximized at lowest extraction temperature of 60 °C. But, the concentration kept decreased with an increase in temperature. Inversely, composition of palmitic acid (C_{16}) increased with respect to temperature from 16.63 to 24.41 %. Concentration of stearic acid (C_{18}) decreased from 12.05 to 11.47 % when the temperature was increased but later increased at temperature 80 °C.

According to Zaidul et al. (2007), the extraction of triglyceride in the fatty acid constituents is highly dependent on solubility of the fatty acids in the SC-CO_2. It depends on the length of hydrocarbon chain, functional group, extraction pressure, and temperature (Zaidul et al. 2007). In this case glycerol trilaurate (C_{39}) composition decreased once the temperature increased from 60 to 80 °C. The same behavior was observed by Medina-Gonzalez et al. (2012) who studied the phase equilibrium of SC-CO_2 with respect to glycerol. The finding indicates that in CO_2-rich phase, glycerol has low solubility in CO_2 as the temperature increased (Medina-Gonzalez et al. 2012). Thus, the mole fraction of glycerol trilaurate (C_{39}) is decreased as illustrated in Fig. 3.11.

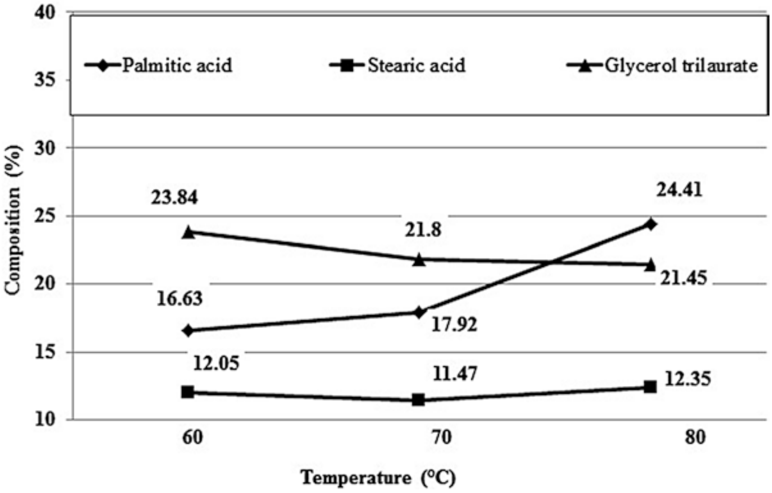

Fig. 3.11 Concentration of three major compounds in the extract at different reaction temperature

3.5 Effect of CO_2 Flow Rate

Fluid flow rate is also a factor that influences extraction efficiency since it determines solvent to solid ratio (Patel et al. 2006). It was observed that total liquid yield increased once flow rate of fluid was increased (Patel et al. 2006). When higher flow rate of CO_2 was supplied into the extraction cell, higher yield of bio oil was recovered due to better mass transfer. Figure 3.12 described that yield increased once flow rate was increased from 3 to 4 mL/min before it decreased at 6 mL/min. Rahman et al. (2012) mentioned that mass transfer can be enhanced once the flow rate is increased since the extracted oil will saturate to exit the solvent (SC-CO_2), hence maximize the extraction. However, Rahman et al. (2012) claimed that "any additional flow rate" cause imbalance of equilibrium condition causing the solvent to be unsaturated and reduce the extraction efficiency. This argument applies for the observed behavior in Fig. 3.12.

Effect of solvent amount on the concentration of major compound is illustrated in Fig. 3.13. Flow rate of CO_2 was varied which signify the amount of CO_2 fluid presence for the extraction. At all flow rates, glycerol trilaurate (C_{39}) concentration was the highest while stearic acid (C_{18}) was the lowest. Composition of glycerol trilaurate (C_{39}) and stearic acid (C_{18}) increased with respect to the fluid flow rate. However, concentration of palmitic acid (C_{16}) decreased from 16.5 to 13.35 % when the flow rate was increased to 4 ml/min and later increased to 14.56 % once flow rate was increased to 6 mL/min.

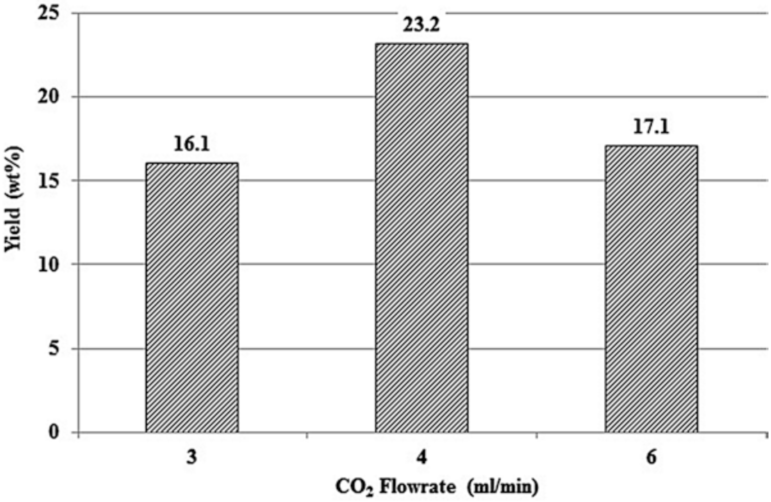

Fig. 3.12 Yield of bio-oil obtained under different CO_2 flow rate

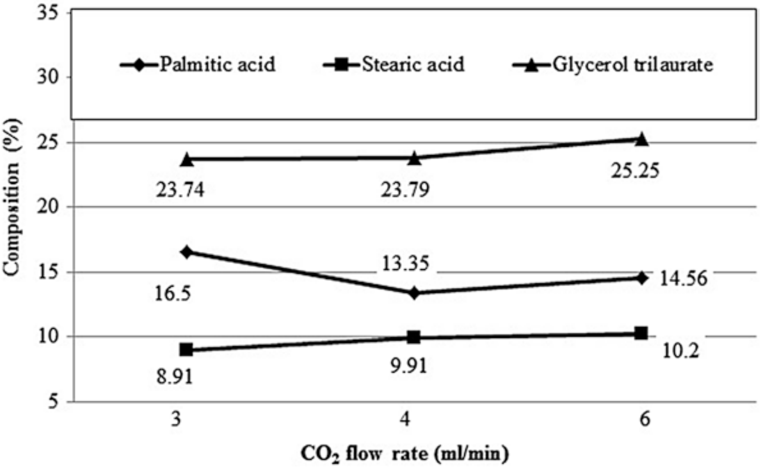

Fig. 3.13 Concentration of three major compounds in the extract at different CO_2 flow rate

3.6 Conclusion

Mass production of oil palm biomass illustrates the capability of this agricultural waste as the reliable and sustainable energy resource. The properties of oil palm biomass which is made up of lignocellulosic material enable the waste to be converted into various types of biofuel using many conversion techniques. In this case, empty fruit bunch demonstrated its capability to be converted into bio-oil via one of the thermochemical promising route, SFE SC-CO_2. While studying the effect of temperature, the highest yield obtained was 17 % at the highest extraction temperature which is 80 °C. Palmitic acid (C_{16}) and stearic acid ($C_{18:0}$) composition increased with respect to temperature increase. Further, the highest yield was obtained at flow rate of 4 mL/min, which is 23.2 %, and the composition of glycerol trilaurate (C_{39}) is at the maximum at these conditions compared to palmitic acid (C_{16}) and stearic acid ($C_{18:0}$).

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Chapter 4
Bioenergy Derived from Electrochemically Active Biofilms

Mohammad Mansoob Khan

Contents

Abstract Microorganisms (bacteria) naturally form biofilms on solid surfaces. Biofilms can be found in a variety of natural sites, such as sea water sediments, soils, and a range of wastewaters, such as municipal, dye, agricultural, and industrial wastewaters. The biofilms are normally dangerous to human health due to their inherited robustness. Electrochemically active biofilms (EABs) generated by electrochemically active microorganisms (EAMs) have potential applications in bioenergy production, green chemical synthesis, bioremediation, bio-corrosion mitigation, and biosensor development. EABs have attracted considerable attention in bioelectrochemical systems, such as microbial fuel cells (MFCs) and microbial electrolysis cells, where they act as living bio-anode or bio-cathode catalysts. EABs are an anode material in MFCs that generate an excess of electrons and protons by biologically oxidizing substrates, such as sodium acetate or organic waste, and the flow of these electrons produces significant amounts of electricity. Recently, it was found that EABs can be used as a biogenic-reducing tool to synthesize metal nanoparticles

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and metal–metal oxide nanocomposites. The EAB-mediated synthesis of metal nanoparticles and metal–metal oxide nanocomposites is expected to provide a new avenue for the greener synthesis of nanomaterials with high efficiency than other synthetic procedures. It was also found that EABs could be effectively used as a tool to provide electrons and protons by biologically decomposing acetate which is later used in the presence of a suitable catalyst for the bio-hydrogen production. These nanoparticles as well as nanocomposites syntheses and bio-hydrogen production takes place in water at 30 °C and does not involve any energy input which make these approaches highly efficient. These findings show that EAB is a fascinating biogenic tool for MFCs, nanomaterials synthesis, bioremediation, and bio-hydrogen production.

Keywords Electrochemically active microorganisms • Electrochemically active biofilms • Biogenic tool • Microbial fuel cells • Nanomaterials synthesis • Bio-hydrogen production

4.1 Introduction

In general, microorganisms naturally form biofilms on solid surfaces for their mutual benefits such as protection from environmental strains caused by contaminants, nutritional depletion, or imbalances. Biofilms can be found in a variety of natural sites, such as sea or river water sediments, soils, and a range of wastewaters, such as domestic, municipal, dye, agricultural, and industrial wastewaters (Borole et al. 2011; Babauta et al. 2012). The biofilms are normally hazardous to human and animal health due to their inherited sturdiness and infectious nature. On the other hand, recent studies suggested that electrochemically active biofilms (EABs) (Fig. 4.1) generated by electrically active microorganisms (EAMs) have properties and potential that can be utilized to catalyze or control the electrochemical reactions in a range of applications, such as bioenergy production, biogenic chemical synthesis, bioremediation, bio-corrosion mitigation, and bio-sensor development (Borole et al. 2011; Babauta et al. 2012; Erable et al. 2010; Rittmann et al. 2008; Halan et al. 2012; Kalathil et al. 2013a). EABs have attracted considerable attention in bioelectrochemical systems (BESs), such as microbial electrolysis cells (MECs) and microbial fuel cells (MFCs), where they act as living bio-anode or bio-cathode catalysts (Kalathil et al. 2013a). EABs are an anode material in MFCs that generate an excess of electrons and protons by biologically oxidizing substrates, such as sodium acetate or other organic wastes. The flow of these biologically generated electrons produces significant amounts of electricity, whereas the produced protons (H^+) moves to the cathodic chamber of MFC where it may be reduced by electrons to H_2 gas in the presence of a suitable catalyst such as gold or oxidized to H_2O (Dulon et al. 2007; Logan et al. 2005; Khan et al. 2014). The discoveries of EAMs forming biofilms which are able to transfer directly electrons on electrode surfaces have boosted the development of MFCs. The mechanisms of electron transfer have been demonstrated to be either direct, involving membrane-bound cytochromes for instance, or through

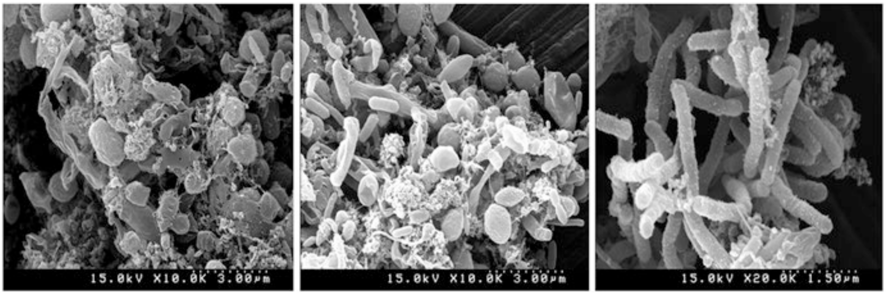

Fig. 4.1 Scanning electron microscopy images of mixed culture EABs showing different types of bacteria on biofilm

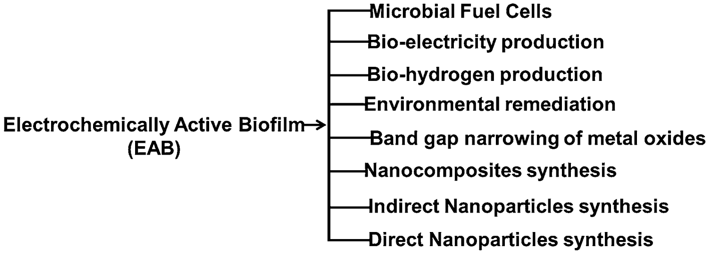

Fig. 4.2 Applications of mixed culture EABs for various possible applications

natural electron mediators that are produced by the microorganisms and remain entrapped in the biofilm (Bond et al. 2002). The involvement of conductive pili in electron transfer has also been demonstrated (Babauta et al. 2012; Erable et al. 2010; Rittmann et al. 2008; Halan et al. 2012). MFCs utilize microbial EABs as catalysts to convert the chemical energy contained in a large variety of organic compounds directly into electricity and various other products such as H_2O, H_2, etc. MFCs produce a lower power density than fuel cells but the increasing interest in sustainable energy sources is promoting intense research leading to fast improvements.

Recently, it was found that EABs can be directly used as a biogenic tool (Fig. 4.2) to synthesize metal nanoparticles and metal–metal oxide nanocomposites (Kalathil et al. 2011, 2012; Khan et al. 2012, 2013a, b; Ansari et al. 2013a). The EAB-mediated synthesis of metal nanoparticles and metal–metal oxide nanocomposites is expected to provide a new way for the greener synthesis of nanomaterials with comparatively high efficiency than the other synthetic procedures. It was also established that EABs could be effectively used as a tool to provide electrons and protons by biologically decomposing acetate which is later used in the presence of a suitable catalyst for the bio-hydrogen production (Khan et al. 2013c, 2014; Kalathil et al. 2013b). Further, it was also found that EABs could be exploited to narrow the band gap of metal oxides such as TiO_2, ZnO, SnO_2, and CeO_2 (Kalathil et al. 2013a, b, c; Ansari et al. 2013b, 2014). These EAB-mediated nanoparticles as well as nanocomposites syntheses, bio-hydrogen production, and metal oxide modification processes do not involve any external energy input (energy supply) which makes these methodologies highly efficient and useful. These findings show that EAB is a fascinating biogenic tool for MFCs, nanomaterials syntheses, bioremediation, and bio-hydrogen production.

4.2 Applications of EABs as a Bioenergy Source

The chemical energy stored in the bonds of organic compounds (such as acetate) is utilized using EAMs which oxidizes organic compounds into harmless by-products such as protons, electrons, and CO_2 (Kim et al. 2012; Logan and Rabaey 2012; Pant et al. 2012; Han et al. 2013; Rozendal et al. 2009). Recently, it was established by many researchers that these electrons and protons can be used for various purposes in MFCs such as electricity generation, CO reduction, etc. (Kim et al. 2012; Logan and Rabaey 2012; Pant et al. 2012). Very recently, it was also reported that nanomaterials such as metal nanoparticles and metal-metal oxide nanocomposites can be in-situ synthesized successfully using EABs (Kalathil et al. 2011, 2012; Khan et al. 2012, 2013a, b; Ansari et al. 2013a, 2014). Following are the few examples which show that how the energy stored in the organic compounds is biologically exploited for various green synthesis, environmental remediation, bioelectricity, and bio-hydrogen production. In general, when one mole of acetate is biologically decomposed by EABs, it gives two moles of HCO_3^-, nine moles of H^+, and eight moles of electrons as shown by following reaction (Logan and Rabaey 2012; Rozendal et al. 2009; Khan et al. 2014).

$$CH_3COO^- + 4H_2O + EABs \rightarrow 9H^+ + 8e^- + 2HCO_3^- \ldots\ldots \qquad (4.1)$$

4.2.1 Bioelectricity Production

EABs are used as living bioanode catalysts in MFCs to generate electricity (Kim et al. 2012; Logan and Rabaey 2012; Pant et al. 2012; Han et al. 2013). The EAB oxidizes organic substrates, such as acetate to electrons, protons, and CO_2 without combustion. The electrons produced are transferred through an external circuit, whereas the protons migrate to the cathode via a cation exchange membrane to cathode and react with oxygen to produce water (Fig. 4.3). The most striking feature of this technology is that a simultaneous wastewater treatments, nanomaterials synthesis, bio-hydrogen production, and bioelectricity generation can be achieved without the need of energy input (Han et al. 2013). Though the produced electricity is not too high, but no energy input, nanomaterials synthesis, bio-hydrogen production, and wastewater treatment, makes this approach efficient (Kalathil et al. 2013b; Han et al. 2013).

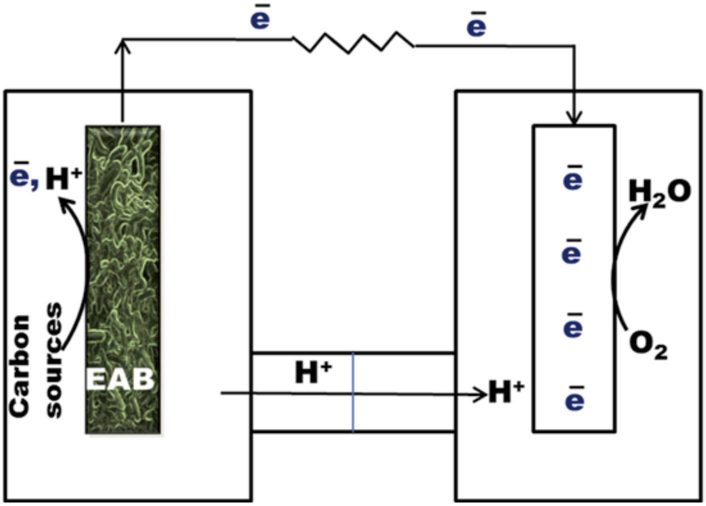

Fig. 4.3 Bioelectricity production in MFC using mixed culture EABs

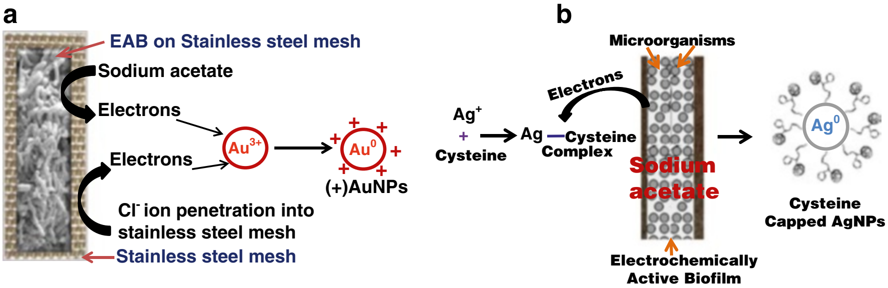

Fig. 4.4 Synthesis of (**a**) (+)AuNPs, and (**b**) Cys-AgNPs using EABs

4.2.2 Synthesis of Metal Nanoparticles

Metal nanoparticles such as gold nanoparticles (AuNPs) (Khan et al. 2013c; Kalathil et al. 2013b), silver nanoparticles (AgNPs) (Kalathil et al. 2011), and cysteine-capped silver nanoparticles (cys-AgNPs) (Khan et al. 2012) were reported to be synthesized by EABs as a reducing tool in the presence of sodium acetate as an electron donor (Kalathil et al. 2013b; Logan et al. 2005). Here, sodium acetate acts as carbon source and biologically oxidizes to electrons, protons, and CO_2. Respective precursors were used to synthesize the different metal nanoparticles in the presence of sodium acetate as a carbon source which provides plenty of electrons for the reduction of metal ions into zero-valent metal nanoparticles. Figure 4.4a shows the

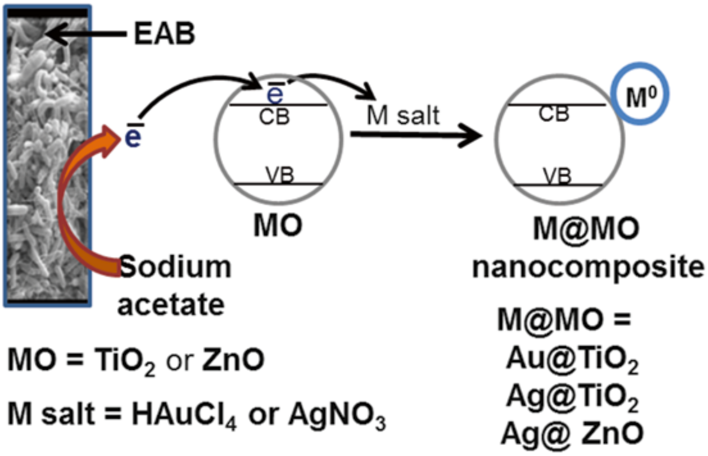

Fig. 4.5 Synthesis of $Au@TiO_2$, $Ag@TiO_2$, and Ag@ZnO nanocomposites using EABs

synthesis of AuNPs using EAB formed on stainless steel as a support. Similar approach was used to synthesize AgNPs (Kalathil et al. 2011). Presence of stainless steel as a support for EAB enhances the availability of electrons by Cl^- penetration into it (Khan et al. 2013c; Han et al. 2013). Figure 4.4b shows the synthesis of cys-AgNPs using EABs and sodium acetate as an electron source (Khan et al. 2012). The synthesized nanoparticles were used for different applications, for example, bio-hydrogen production (Khan et al. 2013d) and anti-microbial activity (Khan et al. 2012).

4.2.3 Synthesis of Metal-Metal Oxide Nanocomposites

Another very interesting use of EABs was to synthesize different types of nanocomposites. New reports show the use of EABs as a biogenic tool to synthesize metal–metal oxides nanocomposites such as $Au@TiO_2$, $Ag@TiO_2$, and Ag@ZnO nanocomposites in the presence of sodium acetate as a carbon source (Kalathil et al. 2012; Khan et al. 2013a; Ansari et al. 2013a). Figure 4.5 shows a common proposed mechanism for the synthesis of nanocomposites. Here too, the electrons produced by the EABs were used for the reduction of the metal ions at the surface of metal oxides. This leads to the formation and anchoring of metal nanoparticles at the surface of metal oxides. The reported methods are green as the entire synthesis takes place in water at 30 °C. The advantage of this protocol is that it does not involve any energy input and the products obtained are quite free from any impurities or by-products. The synthesized nanocomposites were used for various applications such as sensing (Khan et al. 2013b), dye degradation (Kalathil et al. 2012; Khan et al. 2013a; Ansari et al. 2013a), etc.

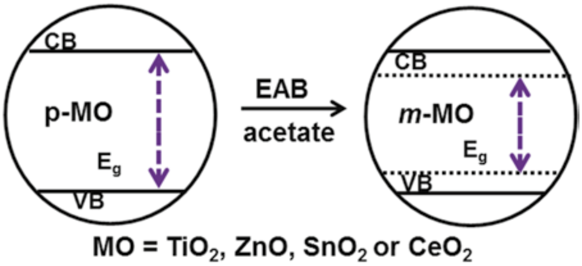

Fig. 4.6 Modifications of metal oxides (TiO_2, ZnO, SnO_2, and CeO_2) using EABs

4.2.4 Modifications of Metal Oxides

Recently another use of EABs was discovered which is highly motivated, i.e., band gap engineering of metal oxides such as TiO_2, ZnO, SnO_2, and CeO_2. The approach is quite simple, efficient, and produces the defected metal oxides having reduced band gap in comparison to pure metal oxides (Kalathil et al. 2013a; Ansari et al. 2013b, 2014). Figure 4.6 shows the proposed mechanism to narrow down the band gap of the different metal oxides using EAB as a band gap engineer. The EAB produced electrons and protons interacted with the metal oxides and produced some defects such as oxygen vacancies, low valent ion formation, etc. (Kalathil et al. 2013a; Ansari et al. 2013b, 2014). The defected metal oxides were used as visible light active photocatalyst materials for environmental remediation. The band gap-narrowed metal oxides were used for several exciting studies and applications such as visible light-induced photocurrent and dyes degradation of different classes induced by visible light (Kalathil et al. 2013a; Ansari et al. 2013b, 2014).

4.2.5 Bio-hydrogen Production

The use of EABs seems to be fictions; however, it is a fact and also reported for bio-hydrogen production in presence of gold nanoparticles as catalyst and sodium acetate as a carbon source which provides electrons as well as protons. Figure 4.7 shows the proposed mechanism for the bio-hydrogen production. The biologically produced electrons and protons combine at the surface of AuNPs following the Volmer-Heyrovsky mechanism (Kalathil et al. 2013c; Brust and Gordillo 2012). The observed bio-hydrogen production rate was ~105 ± 2 mL/L/day (Khan et al. 2013d). The bio-hydrogen production in MFC was also reported and found ~1.5 mL/h (Kalathil et al. 2013c).

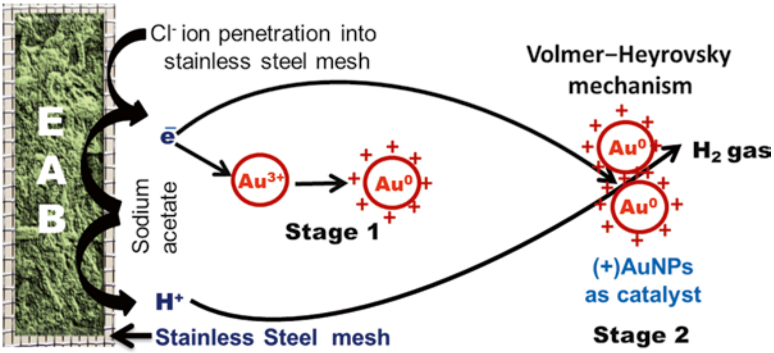

Fig. 4.7 Bio-hydrogen production using EABs in the presence of (+)AuNPs

4.2.6 Environmental Remediation

Recently, it was also reported that EABs could be directly used for the environmental remediation such as dye (methylene blue) degradation in the presence of suitable catalyst such as Au@TiO_2 (Kalathil et al. 2013d). Here too, the degradation process does not need any energy which makes it efficient.

In summary, EABs are biogenic tool that is used for various applications such as nanomaterials synthesis, band gap engineering, bio-hydrogen production, and environment remediation. The beauty of EABs is that its use does not need any energy input and the products obtained are free from impurities. The energy stored in the organic molecules are released with the help of EABs and used up for various applications. These approaches show that EABs acts as a fascinating biogenic tool which is easy to prepare and use.

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Chapter 5
In-Situ Transesterification Reaction for Biodiesel Production

Ahmad Hafiidz Mohammad Fauzi, Ramli Mat, and Anwar Johari

Contents

Abstract Biodiesel synthesis can be conducted using transesterification of triglycerides in the presence of catalyst and alcohol. The oil extraction and transesterification steps are carried out separately for the conventional biodiesel production, which can result in longer time requirement and using different operating units. An alternative to the conventional method is the in-situ transesterification process, where it combines both extraction and transesterification processes into a single-step process. Biomass feedstock is used directly in the in-situ method, which can reduce the time required to obtain biodiesel, as well as conduct both processes simultaneously.

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The single-step process can be integrated with other technology such as microwave irradiation to enhance biodiesel productivity. Furthermore, the in-situ transesterification process involving microalgae feedstock has started to gain attention from researchers, where microalgae biomass is utilized as a feedstock for the in-situ transesterification process without the lipid extraction step prior to the transesterification reaction. This chapter focused on the in-situ transesterification process for biodiesel production, particularly for both catalytic and non-catalytic processes, and also the application of the single-step process for biodiesel synthesis from microalgae.

Keywords Biodiesel • Transesterification • Catalyst • In-Situ • Microalgae

5.1 The Importance of Crude Oil and Its Derivatives

Crude oil is an important source of energy that has played an integral role in our society for a very long time. It is extremely important throughout the world, as the derivatives of crude oil are used in different applications in our daily life. For example, gasoline and diesel fuel are used as fuel in internal combustion engine, base oil as lubricant, petrochemical products (plastic, paint, adhesive), and many more. The straightforward refining process enables the production of a variety of products based on crude oil. The process occurs at different temperatures within the fractionation column, depending on the final products. Three major categories from crude oil-refining process are light, medium, and heavy distillates and residuum. Different sectors depend on the use of crude oil, where four of the main sectors are transportation, industrial, residential and commercial, and electric power (EIA 2012). According to the U.S. Energy Information Administration (U.S. EIA), transportation is the second largest energy consumer in the U.S. after industrial sector, and it was estimated that, in 2010, about 97 % of energy consumption in the transportation sector came from petroleum, which is obtained by processing crude oil (EIA 2012).

Although we are heavily dependent on crude oil, there are some concerns regarding the continuous use of crude oil and its derivatives as it has finite supply and is nonrenewable. With the continuous use of crude oil and its derivatives, Maggio and Cacciola (2012) forecasted that the oil production is expected to decline after they predicted the peak productions of oil will occur between year 2009 and 2021. Based on the data obtained from BP Statistical Review of World Energy 2013 (BP 2013), the production and consumption of oil steadily increased over the past 10 years, and since year 2007, the consumption of oil exceeded its production, and this situation is alarming due to the finite amount of crude oil available.

Other than that, combustion of fossil fuel releases substances that are harmful to human and also the environment, such as carbon dioxide, carbon monoxide, sulfur dioxide, and particulates. The biggest concern with the product from combustion of fossil fuel in the engine is carbon dioxide (CO_2), as it is the most significant greenhouse gas that contributes to global warming potential compared to others. Statistical data has shown that the CO_2 emissions increased steadily each year since 1965, and there was an increase of approximately 36 % of world's total CO_2 emissions from year 2000 to 2012, where the emission recorded in 2012 was 34,466 million tons of CO_2 emitted (BP 2013). In addition, among the four main sectors that depend on the use of crude oil and its products as the source of energy, transportation sector recorded the highest CO_2 emissions among those four sectors (1,802 million metric tons of CO_2) in the U.S. for year 2011, which accounts for 79 % of the total CO_2 emission (EIA 2012). The products include aviation gasoline, distillate fuel oil, jet fuel, motor gasoline, and diesel.

5.2 Biofuel as an Alternative to Fossil Fuel

In order to alleviate the problems regarding finite amount of crude oil reserve and harmful consequences due to emissions from combustion of fossil fuel, countries around the world have turned their attention to its alternative, biofuel. Biofuel is a type of fuel that is produced from biomass source as a substitute for crude oil. There are two common biofuels that have received considerable attention from users, which are bioethanol and biodiesel. The emergence of biofuel as a substitute to crude oil seems to be important in an effort to reduce the release of CO_2 into the atmosphere, as the impact of global warming can be reduced. Other than that, biofuel has higher oxygen content than petroleum, which leads to higher percentage of complete combustion, and at the same time, the amount of hydrocarbon, carbon monoxide, and particulate emissions is reduced (Tye et al. 2011).

Biofuels production increased from year to year. As reported by BP (2013), the world's total biofuels production increased almost sevenfold since 1992, where around 60,220 thousand tons of oil equivalent biofuels were produced in 2012, with almost 50 % of the total biofuels produced in North American countries (U.S. and Canada). This trend highlights the significant role of biofuels in reducing the dependency on crude oil, and also in ensuring that sustainable biofuel production has positive impacts on CO_2 emission. With the availability of these biofuels, the dependency on crude oil can be decreased, especially for the transportation sector. Using bioethanol as a fuel additive can reduce the emission of carbon monoxide and other substances that caused smog, while biodiesel can be utilized as an alternative for fossil diesel in diesel engines (Tye et al. 2011).

The main process involved in the production of bioethanol is the conversion of sugars into alcohol (i.e., ethanol) via fermentation process. During the production, hydrolysis of carbohydrates in biomass source produces sugars, and further conversion will produce bioethanol. It is suitable to be used as fuel additive that can increase the octane level for improving engine performances, and the by-product from bioethanol, dried distillers grain with soluble DDGS, can be used as livestock feed. Another type of biofuel that can be used as an alternative to crude oil derivatives is biodiesel. Different from bioethanol, biodiesel is mainly produced from feedstocks that contain triglycerides. Biodiesel can be obtained via transesterification process, where triglycerides are converted into fatty acid alkyl esters (FAAE) in the presence of catalyst and alcohol, such as methanol. Biodiesel can replace fossil diesel for any diesel engine application. The high viscosity of vegetable oils and animal fats is reduced via transesterification or esterification reactions, and the resultant product can be used directly or blended with fossil diesel.

5.2.1 Biodiesel Production

Two methods that are commonly applied for biodiesel synthesis are transesterification and esterification processes. In the transesterification process, biodiesel is produced from transesterification of triglycerides in the presence of alcohol and catalyst, and the by-product from the process is glycerol. According to the stoichiometric ratio of the transesterification reaction, 3 mol of alcohol are required for 1 mol of triglyceride for the reaction to proceed, and this produces 3 mol of fatty acid alkyl esters and 1 mol of glycerol. Usually, large amount of alcohol is required to shift the reaction towards the product formation and increase the biodiesel yield, as transesterification is an equilibrium reaction. Besides, the yield can also be obtained faster by conducting the process at elevated temperature, and also by employing suitable catalysts, depending on the types of the process.

In contrast to transesterification reaction, esterification involves production of biodiesel from free fatty acid (FFA), where 1 mol of FFA is converted to 1 mol of FAAE in the presence of alcohol and catalyst. Moreover, water is a by-product for this reaction, instead of glycerol. Esterification reaction is important for feedstock that contains high amount of FFA, as this can interfere with the process, especially when alkaline catalysts are used for biodiesel synthesis. Both esterification and transesterification processes can be performed subsequently, where esterification process is employed in the first step to minimize the FFA content in the feedstock, and then followed by transesterification process for the conversion of feedstock to biodiesel. However, this two-step biodiesel synthesis involves the use of two different catalysts; acid catalyst for esterification reaction, and alkaline catalyst for transesterification, which can increase the production cost.

Catalysts are utilized for biodiesel synthesis to increase the reaction rate for the formation of biodiesel. Besides, the use of catalyst also allows the reaction to be conducted at lower reaction temperature and faster reaction compared to the reaction conducted without catalyst. Figure 5.1 shows different types of catalysts that are utilized in biodiesel synthesis. Generally, they can be divided into three main categories, which are homogeneous, heterogeneous, and enzyme catalysts. At the moment, most biodiesel production at the industrial scale is conducted using homogeneous catalyst, especially alkaline catalyst, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). For feedstock with high FFA content, homogeneous acid catalyst is preferred as acidic catalyst can withstand the presence of FFA, which is converted to FAAE via esterification process. Soap formation can be observed if the feedstock with high FFA content is employed in biodiesel synthesis using alkaline

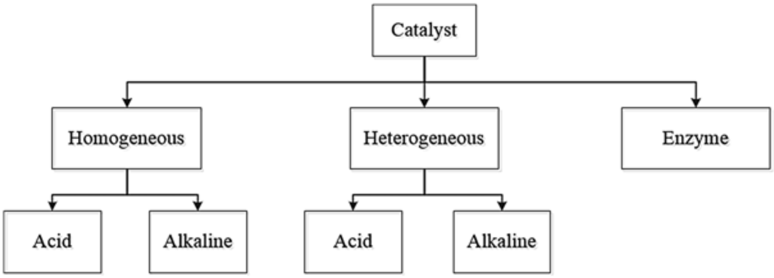

Fig. 5.1 Types of catalysts used in biodiesel production

catalyst. This will reduce biodiesel yield and further complicates the downstream processing of biodiesel synthesis.

Although homogeneous catalysts are preferred to catalyze biodiesel synthesis, one of the main disadvantages is that the separation of the catalysts from the reactants at the end of the reaction can be difficult. As the catalysts are in the same phase with the reactants, they are usually removed from the reactants after separation of biodiesel from glycerol, and further washing of biodiesel is required to remove any traces of catalysts completely from biodiesel and improve its purity. In recent years, the applications of ionic liquids as catalysts for biodiesel production have been reported extensively (Elsheikh et al. 2011; Man et al. 2013). Ionic liquids (ILs) are made from a combination of different types of cations and anions, and their negligible vapor pressure, high thermal stability, and good solubility and miscibility with reactants allow them to be recovered and recycled after the transesterification reaction is finished, which is one of the benefits of using ILs (Mohammad Fauzi and Amin 2012). They also have excellent catalytic activity in catalyzing the transesterification reaction, where most of them are Brønsted acidic ionic liquids (Ghiaci et al. 2011; Fang et al. 2011).

Heterogeneous catalyst is another type of catalyst that is used for biodiesel production (Mat et al. 2012). Although many research have employed heterogeneous catalysts to obtain biodiesel at the laboratory and pilot scale, there are limited applications of this type of catalyst at the industrial scale. The utilization of heterogeneous catalysts enables transesterification reaction to be conducted in continuous process as the catalysts can be placed in fixed bed reactor, and they can be replaced or regenerated once their catalytic activity has deteriorated. However, the operating conditions for heterogeneous catalysts can be quite severe, where longer reaction time and elevated temperature are required due to the different phase between catalysts and reactants. Enzyme is another interesting option as catalyst in biodiesel production, as high purity biodiesel can be obtained, and there is no formation of soap when feedstock of high FFA is used, where enzyme can be used to simultaneously conduct esterification of FFA and transesterification of triglycerides in a single step (Taher et al. 2011). However, high cost and enzyme's deactivation hinder its utilization for large-scale biodiesel production.

5.3 In-Situ Transesterification

Conventional biodiesel production involves a two-step process, where oil is extracted from biomass feedstocks prior to conducting transesterification reaction. This method is not really efficient, as different equipments are used for both processes, and longer time is required as the processes cannot be conducted at the same time. In addition, after the oil extraction step, the leftover biomass needs to be separated before proceeding with the transesterification process. There is also the possibility of using different solvents for these two processes, which can increase the operating cost for biodiesel production. Hexane is usually chosen for the extraction of oil from biomass due to its good solubility with the triglycerides. In contrast, methanol, which is commonly used as the solvent in the transesterification process, has poor miscibility with oil or lipid, and resulted in low extraction efficiency (Mat et al. 2011; Lee and Lim 2012).

A process known as in-situ transesterification combines both extraction and transesterification processes, where they proceed simultaneously in a single step. It is also known as reactive extraction process. The difference between conventional and in-situ transesterification is shown in Fig. 5.2. For the conventional process, the oil extraction and transesterification processes are conducted in two separate steps. After the oil is obtained, only then the transesterification step can be carried out. This process can also be quite lengthy, as biomass left after the oil extraction phase needs to be separated from the oil, and the solvent used must also be removed to

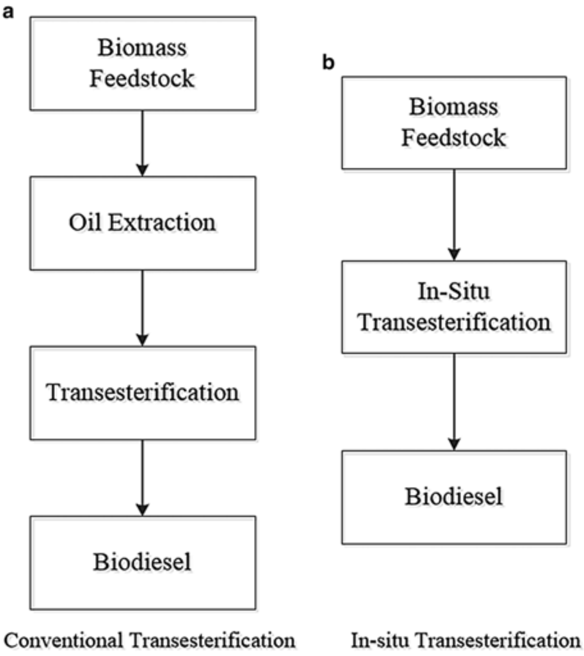

Fig. 5.2 Comparison between (**a**) conventional and (**b**) in-situ transesterification

prevent any interference with the transesterification process. In the in-situ transesterification, the biomass feedstock is used straightaway as the raw material, where the oil extraction and the conversion to biodiesel are combined in a single step, and can even also be conducted in a single reactor. The in-situ process reduces the amount of solvent required as methanol can be used simultaneously for extracting the oil from biomass, and also as the solvent for transesterification reaction.

5.3.1 Catalytic Process

The presence of catalyst in in-situ transesterification process for biodiesel production is important, as it speeds up the reaction to obtain biodiesel. Homogeneous catalysts are preferred to heterogeneous catalysts, as the latter are less efficient in terms of mass transfer process between feedstock in the form of seed with the solid catalyst. Table 5.1 summarizes previous in-situ transesterification processes that utilized homogeneous catalyst for biodiesel synthesis. All catalysts utilized in respective processes are alkaline homogeneous catalyst, either using potassium hydroxide or sodium hydroxide. Different types of feedstocks have also been used (i.e., rapeseed, jatropha, palm oil).

Zakaria and Harvey (2012) conducted direct production of biodiesel from rapeseed using in-situ transesterification process and catalyzed by NaOH. Aside from focusing on the effect of operating parameters, they also studied the effect of water towards the reaction by comparing the ester yield of wet (6.7 wt% moisture) and dry (0 wt% moisture) seeds. Ester yield increased for higher methanol to oil ratio up to nearly 900:1, but decreased afterwards and resulted in harder separation between ester and glycerol phase. At constant molar ratio of methanol to oil, the final equilibrium ester yield was achieved for seeds with smaller size (300–500 μm) faster than those with larger size (1,000–1,400 μm), where they mentioned that the extraction rate was enhanced by reducing the size of seeds used. On the other hand, higher reaction temperature (60 °C) allowed the final yield to reach equilibrium faster than those processes conducted at lower temperature (30 and 40 °C). Finally, for the effect of water content in the feedstock, there was not much difference for the ester yield for both wet and dry feedstocks, which lead to the conclusion that the process economics can be improved by excluding the moisture content removal step for seed with less than 6.7 wt% moisture content.

Biodiesel production from rapeseed by in-situ transesterification process was conducted by Abo El-Enin et al. (2013), which also include the techno-economic cost analysis related to the process. KOH was selected to catalyze the reaction. From the study, higher biodiesel yield was achieved with increasing KOH concentration and reaction time, but decreased for value of higher than 0.02 N and 100 min, respectively. Meanwhile, there was minimal change in methyl ester yield when molar ratio of alcohol to oil increased from 1,000:1 to 1,500:1. For the cost evaluation study, the analysis was performed for the production of biodiesel for 1.0 ton. By assuming the plant capacity of biodiesel production (50,000 tones/year) and the

Table 5.1 In-situ transesterification for biodiesel production from various feedstocks

Feedstock	Catalyst	Alcohol	Alcohol: seed ratio	Time (h)	Temp (°C)	Mixing speed (rpm)	Optimum Yield (%)	References
Rapeseed	KOH	Methanol	720:1	1.0	65	Not mentioned	90	Abo El-Enin et al. (2013)
Jatropha	KOH	Methanol	6:1	5.0	50	800	87	Amalia Kartika et al. (2013)
Oil palm fiber	KOH	Methanol	225:1	9.6	60	300	97	Jairurob et al. (2013)
Jatropha	NaOH	Methanol	400:1	1.0	60	400	95	Kasim and Harvey (2011)
Rapeseed	NaOH	Methanol	475:1	1.0	60	200	89	Zakaria and Harvey (2012)

cost of rapeseed ($250/ton), the gross profit was found to be almost twice as much compared to the conventional method, with the percentage simple rate of return (%SRR) for the in-situ transesterification process (79.5 %) was way higher than the conventional method (29.4 %). They proved that in-situ transesterification process was more promising and gave higher gross profit than the conventional method, provided that the methanol recovery step was carried out properly as it is an integral part for in-situ biodiesel production.

The productions of biodiesel from in-situ transesterification using jatropha as the feedstock have also been studied (Kasim and Harvey 2011; Amalia Kartika et al. 2013). The influence of parameters involved for in-situ transesterification from jatropha has been studied by Kasim and Harvey (2011). A trend of decreasing yield and methyl ester content was observed when higher size of jatropha was used, where the highest yield (86.1 %) was obtained for feed with particle size of less than 0.5 mm. Increased mixing speed of the reaction mixture leads to higher responses, while no significant responses were observed when the mixing speed was increased from 300 to 400 rpm. On the other hand, no significant change in the yield and methyl ester content was observed when reaction temperature was increased from 30 to 60 °C, as well as extending the reaction time from 10 to 60 min. The responses were highest when NaOH concentration of 0.15 N was applied. Higher or lower catalyst concentration produced lower yield and methyl ester content. They observed the formation of soap for NaOH concentration of 0.2 N, which then lowered the amount of yield obtained. Lastly, the highest yield was detected when methanol to oil molar ratio was 600:1, but the authors mentioned that higher molar ratio can lead to problems in the downstream separation processes.

Another study that involved biodiesel synthesis from jatropha seeds was conducted by Amalia Kartika et al. (2013). In-situ transesterification was carried out using jatropha seeds with moisture content of less than 1 %, and then ground for a mesh size of 35. They included the use of co-solvent to improve the miscibility of the mixture, as well as accelerate the reaction by using n-hexane. It was observed that biodiesel yield increased with higher amount of KOH catalyst and ratio of methanol to seed used. In addition, using methanol to seed of ratio less than 6:1 resulted in lower biodiesel quality produced, which correspond to high acid value and viscosity and low FAME purity. Based on the experiments conducted, the highest crude biodiesel yield (87 ± 1 wt%) was obtained after 5 h reaction time by using methanol to seed ratio of 6:1, 0.075 mol/L KOH in methanol, stirring speed of 800 rpm, and temperature of 50 °C. The authors highlighted that the effect of temperature on biodiesel yield was more significant than stirring speed and reaction time, based on the ANOVA analysis of the experimental data at $p = 0.05$. In addition, the biodiesel produced using the in-situ transesterification process met the specifications of Indonesian Biodiesel Standard, particularly for its density at 40 °C, viscosity at 40 °C, and flash point, but the cetane number did not meet the required specification.

In addition to rapeseed and jatropha, a group of researchers performed in-situ transesterification for biodiesel synthesis using palm fiber (Jairurob et al. 2013). Based on the analysis of fatty acid profiles, the main components in the oil extracted from the fiber were palmitic acid and oleic acid. The fiber, also known as after-stripping sterilized palm fruit (A-sSPF), was then subjected to in-situ transesterification process in the presence of KOH as the catalyst. Biodiesel yield was higher than 90 % for methanol to oil molar ratio of 200:1 and KOH loading of 3 % w/v were employed. Then, the optimization of reaction parameters was performed using Taguchi method. The optimal yield (97.25 % w/w) can be obtained for methanol to oil ratio of 225:1, catalyst loading of 3.85 % w/v of KOH, reaction temperature of 60 °C, and conducted for 9 h and 36 min. The authors also compared biodiesel production using two-step process (i.e., oil extraction and transesterification/esterification process) with in-situ transesterification process. Biodiesel yield using the former method produced 174.6 biodiesel/kg of fresh fruit bunch (FFB), while the latter produced 271.9 g biodiesel/kg FFB. The difference in the amount of biodiesel yield was due to the amount of oil lost in the single-step process, as it simplified biodiesel synthesis from palm fiber.

5.3.2 Non-catalytic Process

In order to improve the feasibility of biodiesel production, the in-situ transesterification process can be conducted in the absence of catalyst. This means that the production cost can be reduced as no catalyst is involved in the process. Plus, no additional chemical is required to stop the transesterification reaction. For example, the addition of acetic acid glacial was needed to suppress the reaction and neutralize the alkaline catalyst for in-situ transesterification process (Zakaria and Harvey 2012). This step can be eliminated when the reaction is conducted without using any catalyst. Furthermore, the absence of catalyst simplifies the purification of biodiesel, where usually biodiesel is washed several times to remove any traces of catalyst from biodiesel, especially when homogeneous catalyst is employed.

Aside from the non-catalytic system, only a single solvent is used in the process, where methanol is often used as the solvent. The process is carried out at elevated temperature and pressure, where methanol is heated and pressurized until it reaches the supercritical state. In this form, the miscibility of supercritical methanol with oils and fats is enhanced, which enables the in-situ transesterification process to be conducted without any catalyst. Tan et al. (2011) performed the in-situ transesterification of waste palm cooking oil (WPCO) using the supercritical method. After the predetermined reaction time, biodiesel was separated with glycerol in a decanter, with no additional step of catalyst removal required. This makes the separation step easier, as the presence of catalyst adds extra steps to the process, including stopping the transesterification reaction, as well as removing catalyst from biodiesel. Furthermore, about 80 % biodiesel yield can be obtained by conducting the reaction for only 20 min. The resultant biodiesel was also found to have flash point and kinematic viscosity that agreed to the standards specified by ASTM test methods.

Lim and Lee (2013b) studied the process parameters in a supercritical in-situ transesterification process from *Jatropha curcas* L. seeds for biodiesel production. After the seeds were ground and dried accordingly, the supercritical reaction was conducted by varying different parameters for the optimization study. There was no significant difference in the extraction efficiency for different space loadings, which was related to the interphase mass transfer resistance. The use of methanol alone as the solvent in the reaction was sufficient, as the addition of co-solvent (i.e. *n*-hexane) decreased the FAME yield, and the authors suggested that the dilution of oil/methanol interphase may have occur when *n*-hexane was used. Higher reaction temperature resulted in higher FAME yield, same is true for reaction time, but the latter was more effective at lower temperature. Elevated temperature allowed the conversion of oil to methyl ester at faster reaction rate. Lastly, the effect of mixing intensity was significant to the supercritical process when the reaction was not conducted at the optimum condition. FAME yield of 99.67 % was obtained when the supercritical in-situ transesterification was performed at optimum condition.

The same authors extended their study to observe the effect of different co-solvents in the supercritical in-situ transesterification for biodiesel synthesis (Lim and Lee 2013a). Supercritical process is usually energy-intensive, as the process is conducted at high operating temperature and pressure. One of the methods that can be used to alleviate this condition is by the addition of co-solvent. Co-solvents with easier separation from products and their inertness in the supercritical process are suitable to be applied in the process. Several co-solvents have been considered, including pentane, heptane, toluene, tetrahydrofuran (THF), carbon dioxide (CO_2), and nitrogen (N_2). They found that the higher amount of pentane applied resulted in the decrease of both extraction efficiency and FAME yield, as it may have dilute the concentration of methanol, hence reducing its ability to extract polar compounds. Heptane, on the other hand, enhanced the extraction efficiency as it has higher solubility towards the nonpolar molecules. Aromatic hydrocarbons (i.e., toluene, THF) improved the extraction efficiency, but the co-solvents content higher than 3.0 mL/g diluted the concentration of methanol. The inertness of N_2 did not really improve the extraction efficiency and FAME yield of the process. Finally, the application of CO_2 as co-solvent allows the optimum FAME yield to be obtained at lower temperature and also lower the methanol to solid ratio.

5.3.3 Advanced Process for In-Situ Transesterification

At the moment, the only feasible method to produce biodiesel is using transesterification reaction, where triglycerides are converted to fatty acid alkyl esters in the presence of alcohol and catalyst. While homogeneous catalysts allow the reaction to proceed at moderate operating conditions, the homogeneity of the catalyst with the reactants can become an issue, especially if acidic catalysts are used as acidic wastewater is generated during purification of biodiesel. On the other hand, heterogeneous catalysts offer the recyclability of catalysts, but the reaction requires higher temperature and longer reaction time. In order to overcome these difficulties, novel processes and process intensification technologies are applied to enhance biodiesel productivity. Among the technologies available for the process intensification are membrane reactor, ultrasonic and microwave-assisted processes, and reactive distillation (Fauzi and Amin 2013).

The use of microwave irradiation is one of the processes of intensification studied to increase the productivity of biodiesel production. It is considered to be more effective than the conventional heating in transesterification or esterification reactions, where electromagnetic radiation at microwave length is transmitted and influenced the molecular motions, but does not alter the molecular structure of substance (Kumar et al. 2011). This resulted in shorter reaction times and energy-efficient operation. Da Rós et al. (2012) demonstrated the application of microwave-assisted biodiesel production from beef tallow using enzyme as the catalyst. Usually, the time required to achieve high biodiesel yield in transesterification process catalyzed by enzyme would be long as the reaction is slow. However, with the utilization of microwave technology, the authors showed that in the presence of microwave irradiation, the highest transesterification yield can be achieved within 8 h of reaction time, compared to 48 h required for the reaction that used conventional heating. They highlighted that the enhanced emulsification speed that influenced the mass transfer between reactants was achieved for the microwave-assisted process.

Microwave technology is also suitable to be integrated with in-situ transesterification process. In the study conducted by Patil et al. (2011), dry algal biomass was used directly as the feedstock for biodiesel production in the microwave-assisted in-situ transesterification process. The irradiation was supplied by using an 800 W microwave, while methanol was used as the alcohol as they mentioned that methanol is a strong microwave absorption material, which can improve the rate of transesterification reaction. The highest FAME yield recorded was 80.1 %, which can be obtained in just 6 min of reaction. This shows that the presence of microwave irradiation reduced the reaction time for biodiesel production significantly.

The same group extended their study in the microwave-assisted in-situ transesterification with slight modifications to the previous study, where wet algal biomass was used, and the process was combined with supercritical ethanol technology (Patil et al. 2013). They focused on using wet sample instead of dry sample as drying of microalgae is energy-intensive and can be costly. From the results, it can be observed that the highest biodiesel yield obtained barely exceeded 30 %. The yield increased with higher wet algae to ethanol ratio, but decreased for value higher than 1:9 wt/vol, while longer reaction time resulted in higher biodiesel yield, with reaction time longer than 25 min did not show any obvious change in the yield. They determined that the optimum yield can be achieved by using wet algae to ethanol ratio of 1:9 wt/vol, reaction time of 25 min, and reaction temperature of 260 °C.

5.4 In-Situ Microalgae Transesterification

Different types of feedstocks have been considered with the aim for sustainable biodiesel production. Vegetable oils are preferred as the feedstock for biodiesel synthesis, as they contain less free fatty acids. Current feedstocks for commercial biodiesel production used vegetable oils such as soybean and oil palm, which can result in shortages of food production. In order to avoid problems related to food

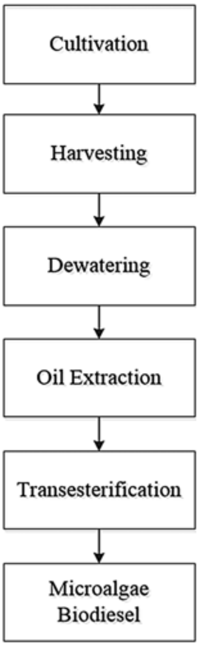

Fig. 5.3 Steps involved in microalgae biodiesel production

shortages, microalgae have started to emerge as a favorite alternative to conventional feedstocks among researchers for biodiesel synthesis. Known as the third-generation biodiesel feedstock, microalgae have the benefits of higher biomass productivity and oil yield compared to other oil-bearing feedstocks, with the yield as high as 25 times than traditional biodiesel crops, such as oil palm (Ahmad et al. 2011).

There are several steps involved before microalgae oil can be converted to biodiesel. These steps are summarized in Fig. 5.3. Cultivation phase is where the microalgae increased their body mass for several days, and water and CO_2 are the key elements for the cultivation of microalgae. Next, the dewatering step follows after they have been harvested, where water is separated from microalgae biomass. This is to prevent problems during the extraction and transesterification processes due to the presence of water. After that, lipids are extracted from microalgae biomass, where the obtained lipids will then be converted to biodiesel, while the remaining microalgae biomass will be utilized for other uses. In-situ transesterification is suitable to be used for producing biodiesel from microalgae, where the lipid extraction and transesterification steps can be combined into a single step. Several researchers have conducted the single-step biodiesel synthesis using in-situ transesterification process, which are summarized in Table 5.2. Most of them used methanol as the alcohol in the process, with homogeneous catalysts (i.e., KOH, H_2SO_4) preferred to catalyze the reaction.

In-situ transesterification of *Chlorella pyrenoidosa* microalgae was performed by D'Oca and coworkers (2011). They compared the efficiency of conventional extraction-transesterification method with the in-situ process. Initially, they studied

Table 5.2 Biodiesel production from in-situ transesterification process from different microalgae species

Species	Catalyst	Alcohol	Algae amount (g)	Alcohol: biomass ratio	Time (h)	Temp (°C)	Yield (%)	References
Chlorella pyrenoidosa	H_2SO_4	Methanol	100.9	2:1	4	60	7.8	D'Oca et al. (2011)
Commercial microalgae	H_2SO_4	Methanol	2.5	4:1	2	65	98.0	Haas and Wagner (2011)
Nannochloropsis sp.	Mg-Zr	Methanol	1	36:1	4	65	28.0	Li et al. (2011)
Nannochloropsis sp.	KOH	Methanol	2	9:1	0.1	64	80.1	Patil et al. (2011)
Spirulina	KOH	Methanol	0.5	2:1	1	Room	76.0	Xu and Mi (2011)

the lipid extraction process using magnetic stirring and ultrasonication methods, where they found that longer time allowed more lipids to be extracted, with higher lipid recorded for magnetic stirring method at 120 min. Also, the highest lipid extracted occurred when a mixture of chloroform and methanol was used. For biodiesel production, the conventional extraction-transesterification method produced higher FAME yield (10.6 %) compared to the in-situ process (8.4 %), although the latter used higher amount of catalyst loading (20 % H_2SO_4). The low FAME yield recorded may be due to the low amount of lipid in microalgae, with insufficient reaction time as the transesterification process using acid catalyst requires extended reaction time to achieve high yield, whereas the reaction was only conducted for 4 h.

Xu and Mi (2011) used *Spirulina* as the microalgae feedstock for biodiesel production involving in-situ transesterification technology. KOH was utilized as the catalyst, with the effects of different co-solvents in the conversion examined. Some of the important criteria of co-solvents highlighted by the authors are immiscible in water, miscible with triglyceride and methanol, maintained inertness in the in-situ reaction, and low toxicity. Out of five solvents that met these criteria, the optimum biodiesel yield was observed when the reaction was conducted in the toluene-methanol mixture with 2:1 ratio of volume per volume. They mentioned that the best solvent system may vary for different microalgae species as the constituents in microalgae depend on the microalgal species. Plus, the ratio of the binary mixture must be correct, as methanol is a polar compound, while toluene is a nonpolar compound. Incorrect ratio will lead to more extraction for one type of compound, either polar or nonpolar.

The utilization of heterogeneous catalyst in one-step biodiesel production from *Nannochloropsis* sp. was studied by Li et al. (2011). Magnesium-zirconia (Mg-Zr) solid base catalyst was synthesized prior to the in-situ reaction. Higher methyl ester yield was obtained for higher amount of Mr-Zr used, where the catalyst amount of 10 % gave the highest yield at methanol-dichloromethane volume of 45 mL, and decreased for catalyst loading for 15 % catalyst. Meanwhile, it was observed that the one-step transesterification managed to produce higher methyl ester yield compared to the two-step conventional method, where the authors highlighted that the one-step method simplified the conversion process, as well as reduced the numbers of operating units and the overall process costs. Plus, the heterogeneous catalyst enabled easier separation of catalyst from microalgae residue, although the reported methyl ester yield was low compared when using homogeneous catalyst.

5.5 Conclusion and Future Perspective

In the wake of continuous use of crude oil, biofuel emerges as a suitable alternative that can ease our dependency on crude oil and its derivatives, especially in the transportation sector. Biodiesel, which can be produced from either transesterification of triglycerides or esterification of free fatty acids, requires the lipid extraction and conversion to biodiesel steps to be conducted separately in the conventional biodiesel production. To improve the feasibility of biodiesel synthesis, in-situ transesterification method offers the simplification of the conventional process, where the lipid extraction and conversion to biodiesel is conducted simultaneously in a single operating unit. The one-step method reduces the time required to obtain biodiesel, as well as reduces the amount of solvents used by utilizing the same solvent for both extraction and transesterification processes.

Homogeneous catalysts are more suitable to be employed in the in-situ transesterification process as heterogeneous catalysts interfered the mass transfer process between reactants involved in the process. The inclusion of co-solvent can help to enhance the one-step process to obtain biodiesel. In addition, in-situ transesterification can be enhanced to improve biodiesel productivity either by conducting the process in the absence of catalysts (i.e. supercritical methanol), or by integrating the process with other novel process (i.e. microwave irradiation). The single-step process also starts to gain attention for biodiesel synthesis from microalgae. In the process, microalgae biomass is used directly as the feedstock, where simultaneous lipid extraction and transesterification of lipid to biodiesel occur at the same time.

Although the in-situ transesterification method seems as beneficial in terms of conducting two different processes simultaneously, there are some areas that require improvements to ensure that the process is feasible to be conducted, especially at the industrial scale. The first area is related to the use of novel processes to enhance the in-situ transesterification reaction. Different types of novel processes are available, and studies that focused on integrating the in-situ method with novel processes should be carried out to improve biodiesel productivity. Another area is regarding the use of co-solvents in the in-situ transesterification. There are many co-solvents that can enhance the reaction; therefore, determining types of solvents suitable for the in-situ process is important as well for the feasibility of biodiesel synthesis in larger scale.

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Chapter 6
Abaca Fiber: A Renewable Bio-resource for Industrial Uses and Other Applications

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Contents

Abstract Abaca fiber is considered as one of the strongest among natural fibers which is three times stronger than sisal. This is one of the finest among natural fibers and believed to be resistant to salt water decomposition than any other vegetable fibers. It originated in the Philippines and is one of the dollar earners of the country for centuries. The fiber cells of mature abaca is longer and has thicker cell wall than younger abaca pseudostems which would suggest that the cell growth is more on the increased in length and thickened cell walls rather than the expansion of the cell diameter by itself. Aside from the novel compounds, the dominance of some essential elements in the abaca fiber would possibly lead to soil fertility decline due to crop uptake. Moisture content of the dried fiber should be lower than 14 % to avoid deterioration and microbial damage caused by molds and fungi.

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Tensile strength and E-modulus are important parameter of abaca fiber specifically for aerospace and automotive applications. Pulp and paper are the principal interest best suited for bank notes, currency papers, cigarette filters, toiletries, lens cleansing, tea bags, and other related products. Composites were also an interesting uses of abaca fiber for aerospace and automotive industries. Geotextiles are other uses of natural fibers (e.g., abaca) for environmental protection specifically for soil conservation and control of soil erosion. New application of natural fiber is on the rise such as the preparation of cellulose nanocrystals as components of the composites. However, threats and emerging issues are one of the concerns in the sustainability of the major abaca growing areas around the globe. Nutrient depletion, which often leads to soil degradation, is one of the major threats of the industry. As a consequence, under these conditions, abaca plants are vulnerable to various environmental stresses such as the occurrence of the threatening disease such as the abaca bunchy top virus disease.

Keywords Abaca (*Musa textilis* Nee) • Natural fiber • Specialty paper • Composites • Geotextiles

In the global market, abaca fiber is commonly known as Manila hemp which is also considered as one of the strongest among vegetable fibers. It is much stronger than sisal and more resistant to salt water decomposition than any other natural fibers. It is a biodegradable material that possesses higher tensile strength and lower elongation in both wet and dry states compared to the synthetics ones. This is a unique property of abaca fiber which has superior quality compared to that of the rest of natural fibers derived from various economically important fiber crops.

This particular crop is widely grown in the Philippines primarily for its fibers which are utilized for various industrial uses. The major key players and processors of the abaca fiber include the pulp, cordage, and fibercraft industries. It is considered as one of the pillars among export commodities of the country that continues to be one of the important sources for employment and foreign exchange earnings. This is an economically important crop of the country because of its wide range of uses particularly in the manufacture of tea bags, meat casing, currency notes, cigarette filter paper, cable insulation, and a host of other industrial products. These are some of the wide array of applications for this particular highly valued agro-based natural fiber.

6.1 Physico-chemical Characteristics of Abaca Fiber

6.1.1 Physical Dimensions of Abaca Fiber

The ultimate fiber cells of abaca are 3–15 mm long and 3–30 μm in diameter, with lumen width of about 3 μm (Kohler 2006). In cross section, they are oval or rounded polygon with five or six sides. Longitudinally, they are tapering gradually to a

Table 6.1 Average cell length, diameter, width, and wall thickness of five abaca varieties (Moreno et al. 2006)

Variety	Cell length (mm)	Cell diameter (mm)	Lumen width (mm)	Wall thickness (mm)
Inosa	3.29	0.0231	0.0201	0.0015
Laylay	3.35	0.0232	0.0196	0.0018
Linawaan	2.81	0.0340	0.0310	0.0016
Lagwis	2.75	0.0335	0.0300	0.0017
Minenoga	2.82	0.0320	0.0295	0.0016

pointed or rounded end (Bawagan et al. 1972; Batra 1985; Sun 1998). Fiber cells have large lumen and sometimes, relatively thin walls. The hollow structure of the fiber cells may have contributed to the lower density of the fiber bundle.

Almost all natural fibers have similar cell length with abaca fiber. Both hemp and abaca have similar cell widths of 0.02–0.05 mm (Rowell 1995). The length of abaca fiber bundle resembles that of jute fiber; however its diameter is bigger. Among the common abaca varieties grown massively in the Central Philippines, var. Laylay has the longest cell length of 3.35 mm followed by Inosa at 3.29 mm while Lagwis the shortest with only 2.75 mm (Table 6.1). Linawaan has the largest diameter of 0.034 mm followed by Lagwis. In terms of cell wall thickness, Laylay showed the thickest wall at 1.8 μm while Inosa is the thinnest of only 1.5 μm (Moreno et al. 2006).

Fiber cells of mature stalks are more uniform and longer than from younger stalks. It has also thicker walls of about 2.3 μm. The cells from younger stalks have bigger lumen to wall ratio than the cells from mature stalks. Generally, the fiber cell of mature stalk is longer and has thicker cell wall than cells of younger stalk. This observation may mean that the cell growth is more on the increasing length and the thickening of the cell walls but not on the expansion of the diameter of the cell itself.

6.1.2 Moisture Content

The presence of hydroxyl groups or weak hydrogen bonds in natural fibers like abaca becomes a drawback in its application for resin matrices since it absorbs and releases moisture rapidly (Biswas et al. 2001). This leads to poor wettability with resin and weak interfacial bonding. Consequently, composites have poor environmental performance due to delamination under humid conditions. Through appropriate pretreatment of the fiber, its moisture absorption is reduced and the wettability with the resin is improved (Rowell et al. 2000).

Different plant-based natural fibers vary in their equilibrium moisture content with respect to the levels of relative humidity. The moisture content of fiber from the newly harvested abaca is about 45 % and reduced to about 8 % after 2–3 h of sun drying under summer weather condition (Sinon 1997). In the Philippines where the temperature range between 23 and 30 °C and RH between 60 and 75 %, abaca fiber can be stored safely at storage conditions of 8–12 % moisture content.

However, above 14 % of moisture content, abaca fiber starts to deteriorate due to microbial infestation (e.g., molds and fungi).

Likewise, abaca fiber showed an interesting characteristic in both the moisture uptake of dry fiber and the corresponding water release by the moist fiber. In the first 20 min, the rate of moisture uptake of dried abaca fiber was fast and slowed down after 30–60 min. The highest moisture content (i.e., 4.5 %) is reached when the RH is between 32 and 37 % with a temperature range of 24–26 °C. Likewise, fiber subjected to 92 % RH initially gained 23 % MC. Furthermore, natural fibers released at a minimum of 11.7 % MC in 60 min having a RH and temperature range between 45 and 47 % and 20–22 °C, respectively.

6.1.3 Tensile Strength, Elongation at Break and Elastic Modulus of Abaca Fiber

The quality of natural fiber for reinforcement is usually evaluated in terms of its tensile strength. This is the maximum stress of the stress–strain curve, where stress is defined as force per sectional area and strain (or elongation) is defined as percent of extension (mm) divided by the length (mm). Since the cross section of natural fibers is irregular and difficult to measure, strength is expressed in relation to its specific weight, as specific strength denoted in cN/tex, where cN (centi-Newton) is the unit of force at breaking point and *tex* is the linear density equal to the mass of the fiber in grams per 1,000 m length.

Another important parameter in assessing fiber quality is the modulus. This is the stress needed to affect a certain strain of the material, i.e., the slope of the material's stress–strain curve, which is a measure of the material's stiffness classified as absolute or specific modulus. The absolute modulus of the fiber is the slope of its stress versus strain curve, taken at low elongation in the proportional zone, while specific modulus is its elastic modulus divided by its mass density. This measurement is a very important feature for natural fibers in cases where maximum strength for minimum weight is required such as in aerospace and automotive applications.

Kohler and Kessler (2000) reported that abaca, hemp, kenaf, and sisal have specific tensile strength in comparison to glass fiber. They found out that hemp and scutched flax were the only natural fibers that have comparable specific modulus with glass. They also reported that scutched flax has significantly greater elastic modulus than unretted and STEX flax. It can also be noted that materials having higher tenacity and elastic modulus are suitable reinforcement for plastics with high rigidity and impact strength, while materials having high tenacity and lower elastic modulus are potential reinforcements for plastics exposed to high bending stresses.

Likewise, Munot (2002) reported that substitution of abaca fiber to glass fiber for W168/W169 in direct long fiber thermoplastic compounding for under panel in A-class passenger car has an estimated savings of about 8 %. He found out that the density of natural fibers is almost half of that of glass fiber. However, the tensile strength of glass fiber is more than thrice that of natural fibers. In terms of E-modulus and specific E-modulus, flax and abaca surpass glass fiber.

6.1.4 Chemical Composition

Natural fibers are composed of cellulose (60–67 %), hemicellulose (12–20 %), lignin (3–12 %), wax (0.3–1.5 %), and water-soluble materials (1–10 %) (Escolano et al. 1976; Escolano 1977). Cellulose is a natural polymer consisting of D-glucose monomer units. These are largely crystalline, organized into microfibrils and is very stable in normal environments.

Cellulose is a linear chain of different glucose units and is considered a structural component of the cell walls of many plants. The walls where the cellulosic substances can be found may also contain polyphenols such as lignins and to some extent structural proteins. The prevalence of polysaccharides in this particular cellular organelle is advantageous for plants as they are generated directly from the products of photosynthesis.

The positioning of the three hydroxyl groups in each glucose monomer, strong hydrogen bonds are formed between this group and the adjacent chains. The H-bonding of many cellulose molecules results in the formation of crystalline microfibrils as well as in an amorphous form (Carpita 2012) that can interact to form fibers. Cellulose fibers contain about 500,000 cellulose molecules. The high tensile strength of cellulose is attributed to the strong H-bonding that is formed in cellulose molecules (Biagiotti et al. 2004). Hemicellulose is made up of highly branched sugars such as five-carbon, six-carbon, and uronic acid. When it is hydrolyzed by diluted acid or base it releases products high in xylose which is a five-carbon sugar. The swelling of fiber bundle when exposed to high moisture is due to the absorption of hemicellulose with water.

On the other hand, lignin is a highly branched phenolic polymer with a complex structure made up of phenylpropanoid alcohols that may be associated with celluloses and proteins. These compounds are found in the middle lamella of the fiber bundle. Likewise, they are also present in the walls of the fiber cells. Together with hemicellulose, they are the cementing materials of the fiber cells that make up the fiber bundle with high tensile strength.

Bismark et al. (2004) reported the approximate chemical composition of abaca and other natural fibers. They found out that abaca has cellulose contents of only 63.2 % while hemp has the highest of 67 %. However, abaca has the highest hemicellulose of about 20 % while sisal has the lowest of only 12 %. Flax has the lowest lignin of only 4 % while abaca and jute are the highest with 12 %. Del Rio and Gutierrez (2006) determined the chemical characteristics of abaca fiber for the manufacturing of pulp for the specialty paper production.

Among the parameters evaluated, it was noted that Klason extractable lignin (11.8 %) was found to be the dominant component and the least was that of the water-soluble extracts (0.3 %). Accordingly, the neutral monosaccharides identified, glucose (87 %) to be the highest simple sugar and the least was noted in the rhamnose and galactose sugars (0.2 %, respectively). The rest of the neutral simple sugars were found to be intermediary such as arabinose (1.6 %), xylose (7.5 %), and mannose (3.5 %). Likewise, novel compounds were identified and isolated in abaca fiber such as free sterols, fatty acids, steroid ketones, triglycerides, and series of

Table 6.2 Macro- and micro-nutrient contents of abaca fiber at harvest (Armecin 2008)

Nutrient element	Mineral composition
N (%)	0.038 ± 0.0014
P (%)	0.010 ± 0.0021
K (%)	0.416 ± 0.1645
Ca (%)	0.114 ± 0.0121
Mg (%)	0.051 ± 0.0052
Fe (ppm)	180.00 ± 24.8902
Mn (ppm)	97.40 ± 12.0208
Zn (ppm)	9.76 ± 4.5113

Values are mean ± SE ($n = 6$)

p-hydrocinnamyl compounds (Del Rio and Gutierrez (2006); and phenylphenalenon (Del Rio et al. 2006). The presence of these compounds suggests for a specific functioning in the plant system and which can also be used as a parameter to assess the quality of the fiber.

Aside from these novel compounds identified, essential elements specifically the macro- and micro-nutrients are important components in the functioning and fiber production in the pseudostem tissue of abaca plant. The high concentration of K in this particular tissue is associated with its high concentration in the harvested fiber (Table 6.2). It is possible that the influx of K ions in abaca tissue concentrated in the pseudostem contributed to the high K concentration in the fiber (Armecin 2008; Del Rio and Gutierrez 2006). Likewise, the fiber was also found to be high in Fe. It is believed that these nutrients would cause potential risk to nutrient depletion due to crop removal.

6.2 Integrated Industrial Uses of Abaca

6.2.1 Abaca for Pulp and Paper

The principal interest for abaca fiber (i.e., non-wood fiber) is that it provides fibers for excellent quality for making specialty paper or it constitutes the sole affordable source of fibrous raw materials. In addition, a non-wood plant such as abaca is an alternative to the increasingly scant forest wood as a source of pulp (Jimenez et al. 2007). For pulp and paper, and composite, cellulose is the most important part of the fiber. This is obtained by removing other chemical components in the fiber bundle. Fats in the fiber surface are removed with benzene. Water-soluble compounds from dewaxed fibers can be removed by boiling it with water. Likewise, water-soluble pectic acid from pulp containing calcium, magnesium, and iron salts can be removed by boiling in 0.1 N alkali. Similarly, dissolved pectin in boiling ammonium oxalate or citrate and can be precipitated with calcium ions (Batra 1985).

The pulp of natural fibers is best suited for making specialty papers. Thinness combined with high strength and durability is every essential for the production of cigarette, bank notes, technical filters, and other related products. This high-end products constitute a large portion of total utilization for many natural fibers. Piotrowski and Carus (2010) reported that a very large portion of cigarette paper is made from flax and hemp. Tea bags are almost exclusively made of abaca owing to the fibers exceptional water resistance.

6.2.2 Natural Fibers for Composites

Composites are hybrid materials made of a polymer resin reinforced by fibers. The physical and chemical identities can be retained for both fibers and matrices. However, they produce a combination of properties that cannot be achieved with either of the constituents acting alone. In general, fibers are the principal load-carrying members, while the surrounding matrix keeps them in the desired location and orientation. Likewise, these materials would act as a load transfer medium between them and protects them from environmental damages due to elevated temperatures and humidity (Mallick 2007).

Concerns about the natural environment, protection of natural resources, and the opportunity to reuse old packaging materials are on the rise. These materials then, all contribute to the growing interest in environmentally friendly substitutes obtained from renewable sources. Natural fibers are fibrous materials derived from plants and animals, produced as a result of photosynthesis (Simon 1998; Zahedifar 1996). Composites made from natural fiber and polymer such as abaca (Symington 2001; Teramoto 2004; Tobias 1990) are potential replacement (Bruce 2000; Byrd 2001) of glass fiber materials. This is renewable (Bartl et al. 2004; Dweib 2004; Gowda et al. 1999) in nature and biodegradable (Simon 1998; Nishino 2003; Ochi 2006; Oksman et al 2003; Winter 2003) after its use.

Abaca fiber composite was developed as substitute to fiber glass in the car industry (Cho et al. 1997; Fries 2000). Rieter Automotive System (Switzerland) in partnership with Daimler Chrysler AG (Germany) and Manila Cordage Co. (Philippines) has produced a composite based on abaca (*Musa textilis* Nee) fiber reinforcement of a PP matrix. This is used in under floor components and as covering of spare tire wheel (Lelivelt 2003; Daimler Chrysler 2005). Lately, they have also increased the use of renewable materials in some vehicles by up to 98 % over previous models by using natural materials such as flax and abaca fibers. The newest Mercedes S-class vehicle has 27 components made from natural-fiber composites which weigh 43 kg (73 % more than previously). Daimler Chrysler's innovative application of abaca fiber in exterior under floor paneling on the Mercedes A-class, manufactured from abaca plant fibers, which are extremely elastic and have impressive tensile strength, has recently been recognized (Daimler Chrysler 2005). The versatility of natural fibers composite in combination with different production techniques would open up new possibility for wide applications especially in the developing countries where natural fibers are indigenous and abundant (Alves et al. 2000; Rijswijk et al. 2001). In the USA the demand for natural fiber in the automobile industry is expected to rise annually by 30 % and that in the construction sector by as much as 60 %.

Likewise, substitution of glass fibers in automotive composites, the specific tensile strength, elongation at break and specific elastic modulus are very important properties of natural fibers. Their lower density compared to glass fibers allows it to achieve similar strength of the end product but with lighter weight. This leads to the utilization of a lower power engine and reduction of CO_2 emission. However, developers believed that the production and processing of natural fiber is CO_2 neutral (Riedel et al. 2000). Although the tensile strength of abaca is lower than glass fiber, its specific modulus is greater than glass and when compared on modulus per cost basis, abaca is better. Apart from much lower cost and the renewable nature of abaca, much lower energy requirement for its production makes it an attractive reinforcing fiber in composites.

6.2.3 Abaca Fiber for Geotextiles

Geotextiles are woven materials either from synthetics or natural fibers which are used to cover sloping soil surface primarily to prevent erosion (Lee et al. 1994). The use of woven abaca fiber minimizes water loss in steep slopes and along hill sides as a consequence for too much precipitation. This is also an effective covering to control sedimentation by capturing soil particles removed from other locations. Sometimes it can be used for drainage control that helps reduce the velocity of water moving downstream that caused flooding and damage to soil and vegetation. Important considerations to soil engineering play an important role in designing various geotextile materials.

In some instances, geotextiles from natural fibers are not suitable as reinforcement in road construction and permanent support to vegetation in channels with high flow velocities. It is because of their generally lower strength and limited life in moist and biologically active environments (Kaniraj and Rao 1994). However, this is a good material in moderate slopes and always disturbed sites where water flow is of low to medium velocities. This condition will give the soil long-term protection for establishing healthy vegetation. Thus, soil protection or erosion control products from natural fibers can vastly accelerate and protect the growth of surface vegetation.

The generally expensive costs of abaca fiber compared to coir, makes the latter more preferable raw material for the production of natural-fiber geotextiles. However, in terms of strength and stability of the end product, abaca is far better than coir.

6.3 New Application of Abaca Fiber

Natural fiber was the main reinforcement material available for fiber-reinforced composites before man-made fiber was developed. However, in recent years the main driving force in the use of abaca and other fiber plant sources for composites was mainly technical (Oksman et al. 2003). The use of natural fibers as potential reinforcement for both organic and inorganic matrices is on the rise. The growing interest in the use of natural-fiber-reinforced composites was brought about by environmental concerns and increasing production cost. There is an extensive research in some areas concerning natural fiber composite materials. This focuses on the preparation of cellulose nanocrystals for applications including composites (Winter 2003). It is currently the subject of intensive study of various research groups around the world. High expectations from the industry will lead to a new era of high-performance bio-based composite materials. Intensive research activity is another area of interest that would pave the way for the production of polymers from renewable resources. With these developments, commercial production of polymers from renewable resources like polylactic acid (PLA) is considered as a leading enterprise (Oksman et al. 2003).

6.4 Conclusions and Future Challenges

The abaca industry is presently facing several concerns especially in crop production, and in the processing and marketing of the fiber. These concerns are mainly affected by different factors such as low fertility of the soil (Armecin et al. 2005), soil degradation, improper management, and disease caused by bunchy top virus (Bajet and Magnaye 2002).

As reported by FIDA (2008), the national average in abaca fiber production of the country is about 800 kg per hectare. This is way behind its potential production of about 2–3 tons per year. Most of the abaca farms in low producing areas produce only about 500 kg/year. This low production is caused by factors such as low fertility of the soil which is the result of several other factors. One of these is erosion of the top soil. Since abaca is usually planted in hilly or mountainous areas, most of the top soils are carried along with moving rain water from the top of the mountain downhill. Other factor in soil fertility is on the transfer of dry matter during harvesting. Instead of returning the waste material back to soil as fertilizer, these are carried out from the farms to the stripping centers. In some cases, abaca farms have low maintenance since cleaning activities are only done during harvesting time which happens thrice or four times a year. Thus, downward trend in abaca production is mostly observed especially in very old plantation areas of more than 30 years. Nutrient management studies and soil health assessment are still on progress seeking for an appropriate management strategy in rehabilitating and improving degraded abaca growing areas.

The low abaca production of the country is greatly affected by bunchy top virus disease (Raymundo 2001; FIDA 2008). This virus has significantly reduced abaca plantation in Davao during the 50s, in Bicol areas during the 70s, and presently damaging about 50 % of the plantations in Central Philippine islands, the highest abaca producing province in the country. This virus has no cure at the moment. However, government effort is focused only on proper farm management and eradication of infected plants to prevent the spread of the disease. Research efforts are also focused on the development of new varieties resistant to the virus either through traditional breeding activities or through biotechnology. So far, no resistant variety has been developed yet.

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Chapter 7
Microalgal Biomass as a Source of Renewable Energy

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Abstract With the economy destruction and rapid declination of fossil fuels provision, there is an urgent need of low carbon economy generation. Traditional sources of energy have concerns regarding their security and longevity. Searching for fossil fuel energy alternatives is now given more and more attention. Energy produced using micro-algal biomass provides the solution to current dilemma, which not only is renewable source of energy but is environment friendly. Microalgae on account of their high oil composition and rapid biomass generation have great potential for biofuel production and hence have emerged as the most promising raw material for generation of bioenergy. Progress in research methodology for catalytic reactions has gone quite far that has made the efficient conversion of biomass into biofuels possible. Procedures including hydrolysis, followed by trans-esterification, hydrogenation, and isomerization have undergone a great deal of improvement in the last decade from which microalgal lipids have to go through to obtain high-grade hydrocarbons. There are a variety of methods to address microalgal processing suggesting that microalgae are very potent candidates for bioenergy production.

Keywords Biodiesel • Biogas • Bioethanol • Microalgae • Torrefaction

7.1 Introduction

We are living in a world where energy requirements increase everyday. Initially these requirements were met by using fossil hydrocarbons. But fossil fuels are a major source of pollution so there has been a decline in their usage as motor oils due to the progressive introduction of fuel alternatives. Other than that, fossil fuels are also a non-renewable energy source. There is a limited amount of fossil fuels; as we set up more oil fields the older ones get depleted. This also destabilizes the prices of fossil fuels as its demand increases.

Vegetal biomass is now considered as the most important alternative to fossil hydrocarbons. This is because vegetal biomass is produced by consuming solar, geothermal, and wind energy source. Vegetal biomass can be converted into feedstock that can be used as an alternative for oil in industries. Moreover, setting up of large-scale biomass production units can allow us to balance the CO_2 emission with CO_2 absorption. Vegetal biomass causes less environmental pollution than other fuel sources, e.g., coal. Combustion of vegetal biomass yields about 0.2 % SO_2 and 3–5 % ash as compared to coal yielding 2–3 % SO_2 and 10–15 % ash (Sorokina et al. 2012). The reason behind this is fossil fuels contain sulfur, nitrogen, and mineral matter in much higher quantities as compared to the biomass. The most appropriate method of using biomass is by converting it into biofuel. There are various techniques to convert biomass into biofuel; however, the most appropriate biomass-producing crop has not yet been determined. Therefore, it is essential to find an optimum biomass-producing source, which is readily available and highly productive.

There are three generations of biofuels. The first generation uses conventional crops such as soybean, sunflower, and sugarcane as raw material. First-generation biofuels are abundantly produced in the world. The second-generation biofuel production utilizes inedible raw materials such as wood processing and agricultural waste. The second generation is clearly more viable than the first generation as it is abundantly provided and does not utilize edible material. The third-generation biofuel production is associated with the microalgal biomass processing. Microalgal biomass is superior to other bioresources as an energetic raw material. Unlike the terrestrial plants, its growth is more productive and less costly. Some microalgae can yield about 98 m^3 ha^{-1} of high-grade biofuel. Economic calculations show that the cost of microalgal biomass production per year, for an annual output of 100 t, is $3,000. Microalgae are the most quick-growing and highest energy plants. They can provide a basis for industrial scale biofuel production, and therefore, also the sustainable development of future energy economy (Sorokina et al. 2012).

7.2 Overview of Microalgal Biomass Production Techniques

Microalgae nowadays are of significant interest for large-scale production of biofuel because they synthesize useful quantities of triacylglycerides and polysaccharides. These serve as raw material for the production of bioethanol and biodiesel, which can be used as transport fuels.

7.2.1 Cultivation of Microalgae

7.2.1.1 Raceway Pond System

A raceway pond comprises of an oval channel in a closed loop. It is about 0.25–0.4 m in depth and is open to the air. The water containing the necessary nutrients and CO_2 is pumped in a cycle. Due to reduced average light supply in the depth of the pond, raceway pond systems never reach suitable productivity rates. Moreover, the energy cost of pumping water is high.

7.2.1.2 Photobioreactors

Photobioreactors (PBRs) consist of a system of transparent tubes in which the culture medium is enclosed and pumped for circulation from a central reservoir. PBRs are better for controlling algae culture environment, but they are more expensive than raceway ponds.

7.2.2 Biomass Harvesting

For large-scale production of biofuel from microalgae, a highly efficient system for harvesting of biomass is required. The techniques that are currently applied in harvesting biomass from microalgae include centrifugation, flocculation, gravity sedimentation, electrophoresis techniques, screening and filtration, and flotation (Uduman et al. 2010).

7.2.2.1 Centrifugation

By the process of centrifugation, a large proportion of microalgae can be removed from culture medium. Chen et al. (2011) mentioned that centrifugation of pond effluent at about 500–1,000 × g shows almost 80–90 % of microalgae removal from culture medium in 2–5 min. Centrifugation is a more preferred method of harvesting the microalgae from culture medium (Grima et al. 2003); however, it can damage the cell structure of microalgal cells (Knuckey et al. 2006).

7.2.2.2 Flocculation

In this process, dispersed particles aggregate to form large particles. These large particles, because of their greater weight, settle down from where they can be easily recovered.

7.2.2.3 Gravity Sedimentation

This technique uses gravitational force for sedimentation of algal cells. Algal cells settle according to their density, radius, and sedimentation velocity. Low-density microalgae are separated unsuccessfully by settling (Edzwald 1993) hence decreasing the efficiency of harvesting.

7.2.2.4 Electrophoresis Technique

Another approach to separate microalgae without any chemicals is the electrolytic method. It involves setting up of an electric field which causes charged microalgae to gradually move out of the solution. Hydrogen generated during the electrolysis of water sticks to the microalgae, which are then carried to the surface (Mollah et al. 2004). The benefits of using this method include:

- Environmental compatibility
- Versatility
- Energy efficiency
- Safety
- Selectivity
- Cost-effectiveness

7.2.2.5 Screening and Filtration

The process involves the introduction of the suspension through a screen of a particular pore size.

7.2.2.6 Flotation

It is a process of separating microalgae using gravitational forces. Air bubbles attach themselves to solid microalgae particles which are then carried to the surface of the liquids.

7.2.3 Cell Disruption

There are two methods for the microalgal cell disruption; chemical disruption and mechanical disruption. Though the mechanical method of disruption requires large amount of energy, still it is preferred over the chemical method because it avoids chemical contamination of cells and does not affect the overall functionality of the cellular content (Chisti and Moo Young 1986; Mata et al. 2010). The microalgal cells can be mechanically disrupted through the processes:

- Homogenization
- Ultrasound
- Milling
- Autoclaving

GEA Process Engineering (2011) states that homogenization can be highly efficient, with a percentage efficiency of about 77–96 %. This means 77–96 % of microalgal cells will be ruptured. But Greenwell et al. (2010) mentioned that for homogenization of 10 L of microalgal suspension having microalgal cell concentrations ranging between 100 and 200 g L^{-1}, we would require a high amount of energy of about 1.5–2.0 kWh.

Another mechanical disruption method is sonication. It involves applying ultrasound ranging between 20 and 50 kHz to the sample. The frequency is generated electronically and the energy is transferred to sample mechanically via a metal probe. The high frequency generates an area of low pressure. The microalgal cells move towards the area of low pressure. This area of low pressure has the highest impact of ultrasound frequency which ultimately breaks open the cell.

7.2.4 Compound Extraction

The extraction of lipids from the microalgal can be done on cryodessicated material efficiently (Fajardo et al. 2007). Ninety-six percent ethanol is used for the extraction of lipids from lyophilized biomass. A system having two phases is formed by the addition of hexane and water to the extracted crude oil. The purified lipids are then transferred to the hexane phase. Majority of the impurities get left behind in the aqueous phase.

Carbohydrates present in microalgal cells are of much complex nature and consist of neutral sugars and amino sugars. Carbohydrates found in the microalgal biomass can be quantified by using phenol–sulfuric acid. The sugars are first hydrolyzed to furans, which are then quantified by spectrophotometry. The carbohydrates can be extracted by chromatography and acid hydrolysis. Other than that, cell walls of microalgae can also be hydrolyzed for the production of reducing sugars by using cellulase (Fu et al. 2010).

7.2.5 Fractionation and Purification

Microalgal biomass includes lignocellulosic components. Lignocellulosic components are a resource of relatively low value but they can be used for the production of fuels and help us meet the present fuel and energy requirements. Research and development of biorefining technology is ongoing. One of the approaches is the pretreatment of raw microalgal biomass, resulting in its fractionation into separate biopolymers, which are mainly lignin, hemicellulose, and cellulose. The cellulose content obtained through this approach can be hydrolyzed easily for obtaining simple sugars.

7.3 Microalgal Strains for Bioenergy

The world's energy consumption rate increases day by day due to an ever-increasing population and the overall desire for a better living standard. This consumption rate of energy usage combined with the knowledge of the threat that carbon dioxide poses on the climate has led many researchers, scientists, and environmental engineers to study the potential of biofuels as an alternative to overcome the problems caused by pollution. Among the potential biofuel sources, microalgae are considered as the most efficient. Microalgae are the most adaptable and sustainable energy source.

Bioenergy production from microalgae is believed to be one of the most efficient alternatives for the development of CO_2-neutral fuels for several reasons:

1. Microalgae have the most suitable growth rates for biomass production.
2. They have a higher efficiency of photon conversion which results in a higher biomass yield per unit of surface.
3. They can synthesize and accumulate large quantity of neutral lipids.
4. They can (under specific growth conditions) release hydrogen.
5. They can provide additional benefits of wastewater bioremediation.

One friendly way of producing energy is the production of photobiological H_2 using *Chlamydomonas reinhardtii* (a microalgal strain). Other microalgal strains that can be used include *Chlorella vulgaris*, *Phaeodactylum tricornutum,* and *Nannochloropsis* species.

7.4 Conversion of Fatty Acids into Bioenergy

The conversion of fatty acids obtained from microalgal biomass into biodiesel for the production of energy is done by transesterification process. Transesterification is a chemical reaction through which fatty acids are bonded to alcohol, resulting in the production of methyl esters of fatty acids commonly known as fatty acid methyl esters (FAME) and glycerol. FAME basically is biodiesel. This process reduces the viscosity of fatty acids and makes them combustible (Chisti 2007).

For the transesterification process, one mole of alcohol is used to transesterify one mole of esters. Likewise, for the transesterification of one mole of triglyceride, 3 mol of alcohol is used (Fukuda et al. 2001). This process is a reversible reaction, therefore, for a high yield, 6 mol of methanol are used for each mole of triglyceride. This large excess ensures the reaction is driven in the direction of FAME (Fukuda et al. 2001).

The transesterefication process can be catalyzed by acids, alkalis, lipase enzymes, and microwave heating.

7.4.1 Acid-Catalyzed Transesterification

The process is driven to completion by the large excess of methanol. In the presence of a large excess of methanol, the free fatty acids are rapidly transesterified into methyl esters at a temperature of about 80 °C. The molar ratios and temperature are the most significant factors affecting the yield of FAME (Zheng et al. 2006).

7.4.2 Alkali-Catalyzed Transesterification

It is about 4,000 times faster than the acid-catalyzed transesterification (Fukuda et al. 2001). It involves the use of sodium and potassium hydroxides as commercial catalysts. An even better catalyst such as sodium methoxide is also used, but sodium hydroxide and potassium hydroxide are often chosen for their cost. Water presence can cause base hydrolysis so the reaction is kept dry. The optimum conditions for the alkali-catalyzed transesterification include atmospheric pressure and a temperature of around 60 °C. In these conditions, the reaction is completed in approximately 90 min (Chisti 2007).

7.4.3 Lipid-Catalyzed Transesterification

Nowadays, the lipase-catalyzed transesterification for FAME production is of great interest. The use of lipase enzymes does offer many important advantages, but is not yet feasible because of the high cost of the catalyst (Fukuda et al. 2001).

7.4.4 Microwave Heating

Microwave heating can also be used for speeding up the transesterification process. This process uses additional catalysts such as scandium triflate and bismuth triflate. Upon providing a temperature of 150 °C by microwaves, the reaction is completed in about 20 min (Sochaa and Sello 2010; Levine et al. 2012).

7.5 Converting Carbohydrates into Bioenergy

Algae mostly do not contain simple carbohydrates or easily hydrolysable polysaccharides. Most commonly found carbohydrates in algae are mannanes, cellulose, ulvan, fucans, xylanes, alginic acid, agarose, porphyran, furcelleran and funoran, mannitol, and laminarin. Starch and cellulose are only present in minor quantities. The yield of ethanol production from biomass is dependent upon the presence of fermentable sugars. Algae have only a low level of fermentable sugars, most of the microalgal biomass is lignocellulose which, as mentioned earlier, is a low value resource but it can replace petroleum by providing fuel and energy.

The lignocellulosic components, which are present in microalgal biomass, can provide fuel and energy. One biorefining technique is the pretreatment of raw microalgal biomass. This enables us to obtain biopolymers such as lignin, hemicellulose, and cellulose. The cellulose content obtained through this approach can be hydrolyzed easily for obtaining simple sugars.

Carbohydrates present in the microalgal biomass are converted into bioethanol for bioenergy production by the biochemical conversion of carbohydrates into ethanol. This can be done in two different ways:

7.5.1 Anaerobic Digestion

It is the introduction of microorganisms in an oxygen-free environment for the breakdown of organic material, which in this case is carbohydrate. Anaerobic digestion is a multistage process and is mostly used for methane gas production and carbon-rich biogas production. In the first stage, microorganisms breakdown complex carbohydrates into simpler ones. In the second step, the simpler carbohydrates are anaerobically metabolized into alcohols, mainly ethanol and CO_2. If the reaction progresses further, ethanol is metabolized into methane gas and CO_2.

7.5.2 Fermentation

At its most basic level, fermentation means the use of yeasts to convert carbohydrates into alcohol, notably ethanol, also called bioethanol. Ethanol production from cellulose by fermentation is more complex than conversion of carbohydrates and starch components of microalgal biomass. Lignocellulosic biomass must first be broken down into simpler sugars before being fermented into ethanol. The components of lignocellulose (cellulose, hemicellulose, and lignin) have strong chemical bonds and are difficult to separate. Mechanical pretreatment and enzymatic treatments are necessary for the breakdown of lignocellulose (Zhao and Shengdi 2013). After the breakdown, the resulting carbohydrates are fermented into bioethanol.

7.6 Processing Techniques Involved in Bioenergy Production/Biomass Conversion Technologies

Bioenergy is the energy made available from biological resources and is renewable in nature. One way to get this bioenergy is from biomass obtained from microalgae. The key to the production of bioenergy from microalgal biomass depends upon identifying the best strain and the separation of biomass from the oil. There are several techniques used for the conversion of biomass obtained from microalgae into bioenergy. Some of these techniques or processes are:

7.6.1 Gasification

Gasification is one of the best-proven methods for the production of bioenergy from microalgal biomass. Gasification comes under the category of thermochemical conversion, which involves breaking the organic components of biomass thermally (Tsukahara and Sawayama 2005) and is an exothermic reaction. In this method (Gasification), partial oxidation of biomass is carried out at high temperature of approximately 800–1,000 °C, yielding a combustible gas mixture (Clark and Deswarte 2008). During the process, a combustible mixture of gases containing CO, CO_2, H_2, NH_2, and CH_4 is produced by the reaction of water and oxygen with the microalgal biomass (Demirbas 2001). This mixture of gases is called Syngas or Producer gas. Syngas can be cleaned and used in gas engines as a fuel and turbines and can also be burnt directly (McKendry 2002a) or it may be upgraded to liquid fuel or chemical feedstock by biological fermentation (Datar et al. 2004). Two of the microalgae that have been mentioned in the literature to produce bioenergy are *Spirulina* (Arthrospira) and *Chlorella vulgaris*. The work on *Spirulina* was carried out by Hirano et al. in 1998 in which they partially oxidized the micro algal specie at 800–1,000 °C and that on *C. vulgaris* by Minowa and Sawayama in 1999 in which they gasified algae with nitrogen cycling in a novel system to obtain fuel rich in methyl (Brennana and Owendea 2010).

7.6.2 Pyrolysis

Pyrolysis is one of the other simple conversion methods to produce bioenergy from microalgal biomass. It basically means the thermal cracking or decomposition of biomass. It is carried out at lower temperature of 400–500 °C as compared to gasification and is endothermic in nature. It yields a heterogeneous mixture of solid, liquid, and gaseous intermediates and occurs without oxygen unlike the process of gasification. The liquid content also called bio-oil or pyrolysis oil resembles a very viscous tar and can be upgraded to fuels (and can be used as a motor fuel but only after removing oxygen from it) or chemicals because of its high oxygen content and alkalinity and fuel can be obtained by solid part (char) or it can be used for soil amendment (Field et al. 2013). Pyrolysis is further divided into fast and slow pyrolysis. Fast pyrolysis produces bio-oil or pyrolysis oil and takes a few seconds to minutes, while the slow pyrolysis takes minutes to days for completion and is aimed at producing solid part also called as char (Babu 2008). However, there is a problem with pyrolysis that creates an urge to upgrade pyrolysis oil to lower oxygen content and remove alkalis because it is unstable with acidic nature and dissolved solids (Chiaramonti et al. 2007). In 2004 Miao and Wu used fast pyrolysis to produce bio-oil from heterotrophic microalgae *Chlorella protothecoides*. They found that the bio-oil produced had a low amount of oxygen, low viscosity, high heating value and lower density as compared to biofuel obtained from autotrophic species and wood.

7.6.3 Direct Combustion

Direct combustion is one of the other very important thermochemical conversion techniques used for producing bioenergy from microalgae. According to Gaul (2012), it is one of the most dominant processes used for the production of bioenergy worldwide. Direct combustion is usually carried out in a furnace or a boiler in which biomass is directly burnt in the presence of air (O_2) to produce hot gases which are formed because of the conversion of stored chemical energy in the biomass and these hot gases can then be used to produce bioenergy. It involves the heat production accompanied with the production of CO_2 and H_2O from the oxidation of biomass rich in carbon and hydrogen. But this process like others also has some issues, which makes it a bit unsuitable. Firstly the direct combustion of biomass needs some pretreatment of biomass like drying, chopping, and grinding which increases the production cost as well as more energy is utilized (Goyal et al. 2008). Secondly if the combustion is not carried out properly means that in case of imperfect combustion, there is a production of intermediates and some environmental pollutants like CH_4, CO, and particular matter (Tanger et al. 2013). Thirdly the fuel production associated with direct combustion has fuel impurities. It contains sulphur and nitrogen, which causes the emission of sulphur and nitrogen oxides SOx and NOx, respectively, (Robbins et al. 2012).

7.6.4 Transesterification

Transesterification is a process in which “R” group of an ester gets exchanged with the “R” group of an alcohol in an acid/base-catalyzed reaction. It can be used for the production of bioenergy from microalgal biomass. The lipid content in particular the triglyceride content of algal biomass reacts with alcohol in the presence of a catalyst resulting in the formation of biodiesel. The reaction is characterized by the replacement of “R” group of triglyceride with the OH of alcohol particularly methanol resulting in the production of methyl esters (biodiesel). In an experiment carried out by Hossain et al. (2008) and his colleagues, the production of biodiesel from two species that are *Oedogonium* sp. and *Spirogyra* sp. was compared. They showed that the percentage of algal dry weight was higher in *Oedogonium* sp. as compared to the *Spirogyra* sp. before oil extraction but after oil extraction it was higher in *Spirogyra*sp. On the other hand, the extracted oil and biodiesel production both were minimum in *Spirogyra* sp. and maximum in *Oedogonium* sp. Johnson and Wen (2009) worked on algal specie *Schizochytrium limacinum*. The purpose of their experiment was to observe the potential of biodiesel production from this algae using two different methods; the first one involving oil extraction followed by transesterification (two-step process) and the second one involving the direct transesterification of algal biomass (one-step process). Their results indicated that the one-step process of direct transesterification of algal biomass resulted in high yield of crude-biodiesel as compared to the two-step process depicting that the algae *Schizochytrium limacinum* is a good feedstock for the production of biodiesel via direct transesterification.

7.6.5 Hydro Cracking

Hydro cracking is a catalyst-associated reaction that is mostly used for the separation of petroleum products. It is assisted by an elevated partial pressure of hydrogen gas, which purifies the hydrocarbon stream from sulphur and nitrogen hetero atoms. But products of microalgal hydro cracking are different from those of petroleum products, so for hydro cracking of microalgae a different set of catalysts is needed that is able to withstand elevated temperatures and pressures as well as high water and phosphate contents (Sorokina et al. 2012).

7.6.6 Biochemical Conversion Technologies

Biochemical conversion is the biological process to convert biomass into bioenergy using methods such as anaerobic digestion, alcoholic fermentation, and photo biological hydrogen production.

7.6.6.1 Anaerobic Digestion

It is the conversion of algal biomass into biogas. The biogas consists primarily of methane and CO_2 with the traces of gases such as H_2S. This sort of reaction occurs in digesters where organic biomass is broken down to produce biogas in a series of three successive steps including hydrolysis, fermentation, and methanogenesis. During hydrolysis the complex organic mass is broken down into soluble sugars which is then fermented into alcohols, acetic acid, and volatile fatty acid along with the gas containing hydrogen and carbon dioxide which is then converted into methane by methanogens in the last step of methanogenesis (Cantrell et al. 2008). This method not only produces high amount of energy, but also leaves a waste rich in nutrient that can be used again as a new medium for algal growth (Olguín et al. 2000). But there is one problem with this process too that is the microalgae that have a high protein content result in low C/N ratio thus affecting the performance of digester. In 2007, Yen and Brune presented a solution to this problem by adding waste paper with a high carbon content to algal biomass resulting in a high C/N ration and consequently doubled the amount of produced methane as compared to pure algal biomass.

7.6.6.2 Alcoholic Fermentation

It is the simple conversion of sugars in the biomass of algae into ethanol. The sugars of the biomass are mixed with yeast and water in large tanks called fermenters. The yeast converts the sugars in the biomass to ethanol (McKendry 2002b). The product obtained then passes through a distillation process that removes the water and other impurities and gives concentrated alcohol, which is then condensed and can be used as fuel for cars. The solid by-product of the reaction can be utilized for gasification or cattle feed. Ueno et al. in 1998 investigated the production of ethanol by microalgae *Chlorococcum littorale* using dark fermentation under anaerobic conditions. They found that 450 μmol g^{-1}-dry wt. was the highest productivity of ethanol at 30 °C.

7.6.6.3 Photo Biological Hydrogen Production

H_2 is one of the important molecules and is an efficient energy carrier and microalgae can photoproduce it because they possess all the metabolic, genetic, and enzymatic characteristics to produce it. There are fundamentally two approaches to produce hydrogen gas from microalgal, one of them is a two-step process while the second is simultaneous production of hydrogen. In the two-step process, the microalgae are first grown photosynthetically under normal conditions and in the second stage they are grown anaerobically by depriving them with sulphur and hence starting consistent production of hydrogen gas (Melis and Happe 2001). In the second approach called the simultaneous production of H_2, the electrons produced from the photosynthetic reduction of water are acted upon by hydrogenase to produce H_2. Although the yield of hydrogen gas is greater in case of simultaneous production process, this productivity is limited by the inhibition of hydrogenase by oxygen produced from photosynthesis.

7.7 Torrefaction

No doubt algal biomass is a good source for the production of renewable energy, but there are certain properties of biomass that are unsuitable. These include high moisture content, low calorific value, high oxygen, and its fibrous nature, which make the process control more complex. To improve the biomass properties and avoid the above-mentioned problems, scientists developed the process of torrefaction.

Torrefaction is a thermal conversion process operating at a low temperature of 200–300 °C. It is also called as mild pyrolysis, roasting, and high temperature drying and is carried out in the absence of oxygen (Stelta et al. 2011). Torrefaction is like pretreatment of biomass. It reduces the oxygen content of the biomass, increases the calorific value of biomass, and also destroys its fibrous nature. One of the other benefits of torrefaction is that after torrefaction the hydrophobic nature of the biomass is enhanced which makes the storage of torrefied biomass easier than non-torrefied one. The torrefaction process is divided into five main stages, which are: (1) Initial heating, (2) Pre-drying, (3) Post-drying, (4) Torrefaction, and (5) Solids cooling (Stelta et al. 2011).

- *Initial heating*: In this stage the biomass is heated. The temperature is increased in the start and moisture starts to evaporate at the end of this stage.
- *Pre-drying*: The water is evaporated from the biomass at 100 °C.
- *Post-drying*: Biomass is heated to 200 °C. All the water is released and some loss of mass occurs.
- *Torrefaction*: During this stage the actual process of torrefaction occurs.
- *Solids cooling*: In this stage the torrefied material is cooled below 200 °C.

7.8 Emerging Pathways for Microalgal Biofuel Production

With the increasing rapid reduction in the amount of fossil fuels and the increasing demand of the biofuel, new pathways are emerging to produce biofuel with better quality and quantity. In this regard, three of the emerging pathways for the production of biofuel from algal biomass are being explained. All these processes have the same goal to produce better biofuel, but they differ in their lipid extraction method and end products. These processes have the advantage of increasing the biodiesel yield, net energy ratio, and better environmental performance.

7.8.1 Hydrothermal Liquefaction

Hydrothermal liquefaction also called thermochemical liquefaction is a process that involves the production of liquid fuel directly from the wet algal biomass (Patil et al. 2008). It is a high pressured and low temperature reaction which usually occurs at 5,000–20,000 Kpa (Kilo pascal) and 300–350 °C in the presence of catalyst to yield bio-oil (Goyal et al. 2008). Thermo-chemical conversion can have advantage over direct combustion because it does not involve pretreatment especially drying of the biomass, which saves a lot of energy, but, on the other hand, the reactor system for thermo-chemical conversion is expensive. Minowa and his colleagues carried out experiment on *Dunaliella tertiolecta*. They found that the algal cells of *Dunaliella tertiolecta* with a moisture content of 78.4 wt% yielded about 37 % oil on organic basis when they were thermally liquefied at 300 °C and 10,000 Kpa.

7.8.2 Oil Secretion

The method of oil secretion basically aims to cultivate microalgae such that they will secrete the oil. The media is taken out of the photobioreactor and oil is recovered using conventional oil and water separator. The biomass is harvested in the same way as for other processes. The biomass is then anaerobically fermented in the digester producing liquid and biogas. The biogas is burnt and the liquid digestate is then recycled so that the nutrients can be reused (Delruea et al. 2013).

7.8.3 Alkane Secretion

The model for the alkane secretion process is very similar to that of oil secretion. In this process, phase separation is carried to separate the secreted alkanes from the cultivation media. This retrieval of alkanes is performed in an oil water separator. The difference between the density of alkanes and the media allows this separation. According to one hypothesis, these secreted alkanes can be used directly in motors. This sort of approach saves the energy, which may be utilized for upgrading and refining of the products (Delruea et al. 2013).

7.9 Biorefinery Concept for Biofuels and High Value Products

"Bio refinery" depends on the idea of petroleum refineries, which produces number of fuels and end products from crude petroleum. Biorefinery merges various processes and apparatuses to generate power, biofuels, and high value biomass chemicals. It strives towards processing of sustainable biomass into an array of commercialized energy and products (Demirbas 2009).

Following are the steps involved in biomass production through microalgae and microalgal-based biorefinery: microalgae cultivation, harvesting of biomass, disruption of cell, compound extraction, fractionation, and purification. The main gist of this theory is to dissuade and recover the desirable compounds from the same biomass batch, in order to produce intact commercialized products. One of the major bottlenecks of the biorefinery concept is the fractionation step, as it is hard to separate various compounds without causing any damage to other fractions (Vanthoor-Koopmans et al. 2013).

The main compounds having grave importance produced from microalgae are lipids, carbohydrates, and proteins. Microalgae lipids are of interest because they have essential fatty acids, e.g. ecasopentoic acid (EPA) and docasahexanoic acid (DHA), which are not present in food crops and other various fatty acids (omega-3, γ-linolenic acid, etc.). For biodiesel production, lipids can be used as feedstock.

Certain catalyst and alcohol are required for the conversion of lipids into biodiesel (fatty acids methyl esters FAME). However, neutral lipids (triacylglycerides TAGs) are only suitable for this purpose.

Nowadays optimization of conditions for microalgal production abundant in lipids is the main focus. Carbohydrates are also preferred as feedstock for various biological biomass conversion technologies, especially for fermentation technology of sugars for bioethanol production. When microalgal cells are cultivated under stress conditions, both lipids and carbohydrates make up to 60–65 % dry weight associated with abiotic factors like salinity, temperature, nutrient starvation/limitation, and light intensity.

Proteins produced through microalgae are also of vital importance as their nutritional quality is comparable to other food proteins because of their good amino acids proportion and profile. It seems that main biomass composite are total proteins that lower significantly during stress conditions where lipids and carbohydrates are built up. Methods that are involved in conventional purification of proteins include precipitation of aluminum sulphate, precipitate formation, salting out, chromatography, and electrophoresis, which are assumed to be cost and time-consuming and affect the protein activity. Extraction of microalgal high value and bioactive compounds can be done through a number of methods used in general for plant bioactive compound extraction (Becker 2007).

In biorefinery concepts under mild conditions, the co-extraction and separation of proteins and lipids through ionic liquid method seems very promising. Biorefinery done through microalgae is at initial stages and research is needed on this topic (Lin et al. 2013). When the desired compound or compounds are extracted, the remaining leftover biomass can be utilized by any of the conversion technologies for biomass energy like anaerobic fermentation, digestion, liquefaction, etc. for the production of biofuels. For example, *Nanochloropsi*s sp. can be utilized for pigment and lipid extraction and unexploited biomass can be used for the production of bio-hydrogen through dark fermentation. Biomethane can be produced using residues of biomass of feedstock microalgae after lipids extraction (Serive et al. 2012).

7.10 Problems Associated With Bioenergy Generation from Microalgal Strains

Nowadays, biomass production through microalgal strains is still not a realistic option for intake as synonymous to the current terrestrial crops for energy production. On the basis of many LCA studies, the efficiency ratio of conversion of energy obtained through microalgae is consequentially lesser than oil extracted from palm, jatropha, and rapeseed indicating untenable production of microalgal biofuel. In the overall microalgal process chain, several energy hotspots are identified including harvesting/dewatering of microalgal biomass, photobioreactor operation, and production of inorganic nitrogen source. It is advised that microalgal culture for biofuel generation should be treated with wastewater to downgrade the heavy dependence on the nutrients extracted from inorganic nutrients. Protein extraction and separation are difficult as they have poor stability and are denatured under acid, alkali, or high temperature. On the other hand, in biorefinery it is vital to build up a technique that enables extraction of an array of metabolites considering the hardness of extraction, their inaccessibility, and/or wide range of polarities.

Lipid extraction through microalgae in the downstream process represents a difficult task. Method of Physical Extraction utilized in the oil extraction from oil-bearing crops is not up to the mark in the extraction of lipids through microalgae as the lipids are integrated within the cell wall layer. In disruption methods of cell, precautions should be taken to check the energy level as it deviates very easily towards the negative balance. It should be added that the choice of cell disruption methods, extraction conditions, and largely chemical solvents are based upon strains of microalgae. For optimum extraction of lipids, there is no singular method for all types of strains of microalgae. To improve the microalgae production of biodiesel, several breakthrough technologies, i.e. in situ transesterefication, surface extraction/transestererification, hydrothermal recovery, and transestererification coupled with ultrasonic and microwaves, are still to be ascertained. Many strategies utilized to strengthen this biofuel production require extensive research. To gain significant breakthrough we need progress in this area as to produce greener, sustainable, and stable biofuel.

7.11 Economic Feasibility of Microalgae to Biofuel

A wide range of bioactive compounds of high value to be utilized as natural resources, pigments, pharmaceutical compounds, polysaccharides fatty acids, and health foods can be obtained through microalgae. Through a high value coproduct strategy, economic usability or possibility of biofuel production through microalgae can be significantly improved. It involves production of microalgae passing through certain stages in a farming facility of microalgae (CO_2 mitigation), from harvested algal biomass extracting bioreactive products processing through thermal energy (gasification, pyrolysis, or liquefaction), different applications reforming biofuels and from resulting liquid, vapor, or solid phases extracting high value chemicals. By applying high value coproduct strategy integrated with biorefinery, we can upgrade significantly the collective cost-effectiveness of production of biofuel through microalgae (Sorokina et al. 2012). Other than some microalgal compounds, which are already produced at commercial level, most of the high value compounds, which are produced by microalgae, are not built up in the market for high value products produced through microalgae (Brentner et al. 2011).

Commercially used carotenoids are estimated on the current global market in 2010 at $1.2 billion, with a probability to grow to $1.4 billion in 2018 with 2.3 % compound annual growth rate. β-carotene market value is estimated in 2010 at $261 million and is expected to grow to $334 million by 2018 with 3.1 % compound annual growth rate while the commercial value of lutein was about $233 million in 2010 and is estimated to peak by 2018 to $309 million with 3.6 % compound annual growth rate. Use of bioplastics was 0.64 Mt globally in 2010 and 0.85 Mt in 2011 and is expected that their use will rise up to 3.7 Mt by 2016 with 34.3 % high compound annual growth rate. In 2011, global demand of glycerol was 1,995.5 Kt and is estimated to rise to 3,060.4 Kt by 2018, while the worldwide supplement and vitamin market is about $68 billion.

Besides the constraint of utilization of water, nutrient and occupation of land, concept of cultivating biomass through microalgae for high value chemicals generation linked with the production of biofuel to accumulate world's needs for means of transportation is massive pressure (Markou 2012). One consequence is the overuse of high value microalgal products in the global market. It is estimated that the production of bioethanol and biodiesel will double between 2007 and 2017 touching 125 and 24 billion liters, respectively. By taking assumptions that the activity of biomass produced through microalgae to the production of biofuel might be 30 % and that the yield of biodiesel is 0.30 L kg^{-1} while that of bioethanol is 0.25 L kg^{-1} both of which are dry microalgal biomass, an initial assumption of the biomass produced through microalgae in the global annual scale is 175 million tons of dry biomass per annum covering a surface of about 2–9 Mha (estimating a yield of microalgal dry weight biomass 20–100 tha^{-1} yearly).

7.12 Biodiesel, Biogas, Bioethanol Production from Microalgae

7.12.1 Biodiesel

Fatty Acid Alkyl Esters, which is a constituent of biodiesel, is another source of diesel fuel extracted from the reaction of vegetable oils or lipids and alcohols with or without the help of a catalyst. Transesterification is the process through which oil is converted into fatty acids (biodiesel) (Chisti 2007). Biodiesel acts as a biodegradable alternative fuel, which is nontoxic and derived from renewable sources. Biodiesel is produced in many countries from soybeans, palm oil, corn oil, and canola oil. The animal fat and waste cooking oil are other sources of biodiesel production in the commercial market. But modern research and experimentation have proven that through microalgal cultivation, biodiesel production is truly superior to all other forms and has the potential to make fossil fuel utilization completely extinct. Algae are cosmopolitan and have dry mass weight of in between 20 and 80 % oil weight. They have much rapid growth rate than terrestrial crops. It is estimated that oil production yield from algae ranges from 20,000 to 80,000 L per acre per year. It is 7–31 times better than the next best crop, palm oil. Due to their easy compliancy and acclimation to the conditions of growth, the use of algae as energy crop has possibilities. Because of the research done in this field, it is proved that the oil produced through algae can be an important source of biodiesel. Many different species are better suited for the production of different types of biofuels. Algae has emerged as having the highest potential for biodiesel production. Processes for the production of biodiesel through microalgae include a bioreactor for producing large amount of microalgal cells, next is the separation of cell from the growing medium and then extraction of lipids (Chisti 2007). Those algae, which produce greater lipid content would be ideal for biodiesel production. By medium alterations, lipid content can be enhanced. Lower nitrogen source in the medium causes greater deposition of lipid in the cell. At lower cell density, nitrogen would have worked up earlier, when the starting concentration in the medium was low. Through this, cell can accumulate lipid in their cell when there is a good injection of light, resulting in excess metabolic flux produced through photosynthesis on a unit biomass basis. In addition to the concentration of nutrient, condition of culture also plays a vital role, i.e., light, temperature, pH and CO_2 concentration (Huang and Chen 2010).

After cultivation of microalgae, harvesting of biomass is the next. It can be produced through sedimentation microscreen centrifugation, flocculation, or filtration of membrane. It is required to be dried by releasing water. To get oil, dried biomass is extracted through vacuum. Then the oil is passed on to the biodiesel production unit (Ahmad et al. 2011).

7.12.2 Biogas

Biogas includes both methane and hydrogen gas and it can be extracted by the exploitation of microalgae through many processes and steps. Exploitation of solar energy photosynthetic spectrum can be utilized to produce chemical energy through microalgae complemented by bacteria to prepare methane. In the process, mass production of algae is done through light and carbon. The algal biomass serves as a source of sustenance for anaerobic digester feeding by using anaerobic bacteria for producing methane. For algal biomass production, the source of carbon can be wastewater for eukaryotic algae and through atmosphere or from exhaust gases combustion of both prokaryotic and eukaryotic algae (John and Anisha 2011). Many micro- as well as macroscopic algae can be used for the production of biogas. It is proven by the data of technical feasibility on anaerobic digestion of biomass from algae. For example, biomass can be utilized from macroalgae, green alga *Ulva lactuca*, red marine alga *Gracilaria*, and giant brown kelp *Macrocystis pyrifera*. Some of the microscopic alga, which can be successfully utilized for methane production are mixed culture of *Chlorella* spp. *and Scenedesmus* spp., mixture of *Euglena* spp., *Chlorella* spp., *Oscillatoria* spp., *Scenedesmus* spp., and *Synechocystis* spp., *Scenedesmus* spp. culture only and together with either *Euglena* spp., *Spriulina* spp., *MIcractinium* spp., *Melosira* spp. *or Oscillatoria* spp., the mixture of *Hyddictyon reticulatum and Cladophora glomerata*.

Hydrogen gas is considered to be a fuel ideal for the world in which air pollution has been accumulated to arrest global warming in an economically sustainable manner. Thus, H_2 gas is evolving itself as a fuel of the future to the carrier of energy nowadays. However, none of the production processes currently available can economically produce renewable H_2 gas, i.e., photovoltaics-electrolysis and biomass gasification can yet generate hydrogen fuel for less than US$20/G.I., which is a realistic target for renewable H_2 gas maximal cost (Harun et al. 2009). There is an increased interest for renewable H_2 gas through microalgae. Many countries of Europe, United States, and Japan have done extensive research on microalgal cultivation for H_2 gas production. The concept of process for the production of biohydrogen is based on the formation of protons from direct transfer of electrons from water by coupling the water splitting photosynthesis reaction of reduction of ferrodoxin to a H_2 evolving hydrogenase; a process now known as "direct bio photolysis." "Indirect biophotolysis" is another process, which utilizes adapted green algae anaerobically. It involves oxygen evolving through spatial separation and reactions producing H_2 coupled through CO_2 intermediate fixation into carbohydrates. A variation is to utilize microalgae to make organic substrates through fermentation that are changed into H_2 by photosynthetic bacteria. Both of these processes are of great importance in applied phycology and energy production through microalgal biomass.

7.12.3 *Bioethanol*

The increasing industrial and social awareness of the impact of fossil fuels and their rising cost have established a necessity for more stable options of fuel. Production of renewable bioethanol from biomass consistent of starch and sugar materials is considered to be one of many possibilities and it is nowadays being produced significantly (Pienkos and Darzins 2009). Outburst of population coupled with increasing influx of motorization has pointed us the demand of large amount of fuel. In this age of environmental as well as economical concern, algae having the potential of accumulation of increased cellulose/starch storage can act as an effective alternative to crops that provide food for the production of bioethanol. For a sustainable future, it can act as a green fuel. Some of the species of algae can make ethanol during a process called dark anaerobic fermentation and thus can act as a source for the production of ethanol. As of late, microalgae that are oleaginous can produce large cellulose/starch biomass waste that can be used for the production of oil, which can be then run through hydrolysis to make syrup rich in sugar to serve for ethanol production as substrate (Radakovits et al. 2010).

Use of ethanol as an additive of fuel or as source of fuel directly has been increased significantly due to the regulations imposed by the government and in several cases as incentives implemented because of economic and environmental concerns and also to lower the dependency on fossil fuels. As a result, many countries have developed their own internal market for the utilization of bioethanol. Almost all of bioethanol is generated from grain or sugarcane currently but other alternative technologies should also be looked into, which can be efficient as well as economical. Many microalgal strains were taken from seawater and examined and experimented for bioethanol production. Some has greater growth rate, i.e., 20–30 dry biomass/m^2/day and greater starch content of more than 20 % dry base. *Chlorella vulgaris* has 37 % starch content, which is very high and hence starch is taken from its cell, saccharified and fermented with yeasts. Ethanol conversion rate is 65 % as compared to the theoretical value. The starch extracted from algae is considered to be an excellent source for the production of ethanol by applying conventional process. Intracellular fermentation of starch under dark anaerobic conditions is examined as an alternative source of production of ethanol. Increased ethanol is obtained from *Chlamydomonas reinhardtii* and Sak 1 extracted from seawater. This process shows mass concentration of ethanol 1 % (w/w). The properties of production of ethanol are observed at the intracellular level with *Chlamydomonas*. The results obtained show that intracellular production of ethanol is easier, simpler, and its energy is lower than the conventional fermentation process of ethanol. If the productivity rate of microalgae can be enhanced, this setup should be effective for the fixation of CO_2 and production of energy (Li et al. 2008). Macroalgae can also serve as a source of renewable biomass used for the production of ethanol. Very little has been done on this issue currently and extensive research is necessary in this area in the future for the progressive utilization of biomass acquired through algae and their wastes products to generate bioethanol fuel which is environment friendly.

7.13 Future Prospects

Sustainable biofuels are required to substitute the petroleum-based transport fuels, which cause climate change and global warning and are also being depleted. Two possible renewable sustainable fuels that can be utilized and have captivated the most attention are biodiesel and bioethanol. Biodiesel and bioethanol extracted from microalgae are the only option for renewable biofuel with the potential to displace fossil fuel without causing any adverse effects to the environment and economy. Production of biofuel through microalgae is superior than biofuel production from oil crops. For example, studies in the U.S. suggests that biodiesel can replace all fuel used for the consumption of transport. It will require 0.53 m^3 of biodiesel yearly at the modern consumption rate. We cannot utilize waste cooking oil, oil crops, and animal fat to realistically state our demands. Biodiesel production through microalgae between 1 and 3 % of the total US area that is used to grow crops would be sufficient in the production of algal biomass that fulfills 50 % of the needs of transport fuels (Courchesne et al. 2009).

Other than biofuel, microalgae can be used to produce large amount and range of bio-products, i.e., medicine, food, cosmetic industry, and have novel applications. Through microalgal approach, we can efficiently heighten the biofuel overall cost-effectiveness. Different developments in technology including advancements in biomass harvesting of microalga, layout of photobioreactors, drying and other several downstream processes are vital fields which can also lead to the increased cost-effectiveness and thus implementation in the commercial market of biofuel by using microalgal strategy (Brennan and Owende 2010).

7.14 Conclusion

Due to the rapid and excessive use of energy in today's world, its demand is increasing day by day. At this time algal biomass could serve as a promising source of renewable energy. Using the above-mentioned processes, we can obtain a large amount of energy from algal biomass. The above discussion gives an insight of how algal biomass can be processed through several processes to finally convert it into energy. Using these processes, we can obtain biogas, bioethanol, biodiesel, and other products. The use of microalgal biomass may also resolve the pollution issues caused by the use of fossil fuel. In short, energy obtained from microalgal biomass can serve as an alternative for the fossil fuel.

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Chapter 8
Lignocellulosic Biomass: As Future Alternative for Bioethanol Production

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Contents

Abstract Biofuels provide a potential and promising green alternative to avoid the global political instability and environmental crises that arise from dependence on petroleum. It has an important role to mitigate global warming and to conserve fossil fuels. Currently, starchy crops such as corn are utilized as a source of raw material for the production of bioethanol but it cannot meet global fuel requirements. Besides, due to their food value these conventional crops are not able to cater the demand of biofuel production. Therefore, lignocellulosic biomass seems to be an attractive alternative for inexorable supplies of biofuels, cutting down the credence on fossil fuel resources. Lignocellulosic biomass feedstock is abundant, recyclable, cheap, and

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is evenly distributed in nature. However, lignocellulosic bioethanol production is not commercialized at a large scale due to certain economic and technical barriers which make ethanol production exorbitant. Therefore, research should be focussed to develop commercially profitable processes (green technology) for bioethanol production. Moreover, current approach is focussed on enzyme-based conversion of lignocellulosic biomass to bioethanol. The assurance of highly dynamic conversion coupled to a "Green" technology is now universally appealing. Therefore, the main aim of this chapter is to critically analyze the current situation and future needs for technological developments in the area of producing liquid biofuels from lignocellulosic biomass. It primarily covers distinct lignocellulosic biomass conversion technologies, challenges, and future research targets.

Keywords Lignocellulosic biomass • Agriculture residue • Bioethanol • Conversion technologies

8.1 Introduction

Currently, the economy of the nation is solely dependent upon the nonrenewable energy resources such as coal, petroleum, natural gas, etc. that are being used for the generation of electricity, fuel, and other goods (Uihlein and Schbek 2009). In the new era of industrialization, the demand for the petroleum resources has gained a steep rise in energy sector and today these fossil energy resources contribute about 80 % of the primary energy consumption in the world, of which about 58 % alone is consumed by the automobile sector (Agrawal 2007; Escobar et al. 2009). Because of such huge consumption of these fossil fuels especially in urban areas the pollution level increases at a very high pace. Therefore, the concentration of GHG-emissions in the earth's atmosphere has immensely enhanced (Ballesteros et al. 2006). Besides, other factors that are responsible for high energy consumption include population explosion, industrial prosperity that ultimately lead to deleterious effects to the ecosystem such as global warming, biodiversity loss, etc. (Gullison et al. 2007). Further, it is predicted that the total global oil production will begin to decline within near future due to the limited resources of fossil fuels (Campbell and Laherrere 1998). Besides, due the ill effects associated with these conventional energy resources, scientists all over the globe switched on towards green energy resources that are renewable, sustainable, cost-effective, and eco-friendly (Prasad et al. 2007; Singh et al. 2010). Among the various green energy resources biofuels (bioethanol, biodiesel) gained a world-wide importance due to eco-friendly nature. To boost the lignocellulosic bioethanol industry, various developed countries directed state policies towards the improvement and economic utilization of biomass feedstock for meeting their future energy crises in order to meet GHG reduction targets as specified in the Kyoto Protocol as well as to decline reliance and dependence on the supply of nonrenewable energy resources. Biomass being abundantly available in nature is commonly used in a combined heat and power programme (CHP) to generate heat and electricity. However, at present it is also being used to generate liquid fuels such as bioethanol for automobiles (Demirbas 2005). Currently, it has gained a worldwide interest both at international and national levels. The world market for bioethanol has entered a phase of rapid and transitional growth. With the result, many nations are shifting their research focus towards sustainable and green sources for bioethanol production because of depleting conventional energy reserves.

Although bioethanol has tremendous potential in transport sector to replace gasoline but at present it is not cost-effective when compared to nonrenewable energy resources. However, during the last few decades bioethanol production shows an increasing trend with 31 billion liters during 2001 to 39 billion liters in 2006 and is expected to reach about 100 billion liters in 2015 (Taherzadeh and Karimi 2007a). Currently, Brazil and the USA are the leading countries using sugarcane and corn respectively as raw material for bioethanol production contributing about 62 % of the world bioethanol production (Kim and Dale 2004). However, the bioethanol production from these food crops possess certain limitations as it cause food crisis especially in developing countries. Besides, the cost that is involved in biofuel production is also an important factor to commercialize this technology. In order to overcome these challenges, lignocellulosic biomass that is considered as a green gold is a promising alternative to avoid the existing competition of food verses fuel caused by grain-based bioethanol production (Bjerre et al. 1996). Lignocellulosic biomass typically contains 50–80 % (dry basis) carbohydrates that are generally composed of pentose and hexose sugars. Moreover, lignocellulosic biomass has a potential to produce about 442 billion liters of bioethanol. Kim and Dale (2004) reported that these green energy sources have the potential to produce about 491 billion liters of bioethanol/annum which is about 16 times greater than the actual global bioethanol production. It has been revealed that an average individual in the United States produces about 1.8 kg of municipal solid waste (MSW)/day which mainly contains about 75 % cellulosic biomass (wastepaper, wood wastes and cardboard). Therefore, a city with one million people generates about 1,800 tonnes of MS Winto to, or about 1,300 tonnes/day of organic material. About 330 L of bioethanol is produced/ton of biomass waste. Thus, the total biomass waste generated/day from a city with one million individual produces approximately about 430,000 L of ethanol/day that is sufficient fuel to cater the needs of more than 58,000 people in the US; 360,000 people in France, or nearly 2.6 million people in China at current rates/capita fuel use. This green gold is renewable, cost effective, abundant and evenly distributed throughout the nature. Lignocellulosic biomass includes grasses, agricultural waste, forest residues, etc. Comprehensive research has been carried out on bioethanol production from lignocellulosic biomass during the last two decades (Cadoche and Lopez 1989; Binod et al. 2010). Hence bioethanol generation could be the sustainable and green route to the effective utilization of biomass feedstock. This chapter presents a brief overview of the applicable technologies for bioethanol production using lignocellulosic biomass as a substrate source.

8.2 Background

Henry Ford in 1925 considered grain alcohol or ethanol as future fuel. He further quoted a well-known statement, “The fuel of the future is going to come from apples, weeds, sawdust almost anything. There is fuel in every bit of vegetable matter that can be fermented. It remains for someone to find out how this fuel can be produced commercially better fuel at a cheaper price than we know now.” Today Henry Ford’s futuristic vision significance can be easily understood. Biofuels the important component of “Green Technology” is a promising alternative to replace fossil fuels. Biofuels is a promising alternative that reduces dependence on petroleum resources and has gained a widespread attention throughout the world especially in developing nations (Pickett et al. 2008). In early 1860s little attention was paid towards bioethanol production due to low prices of fossil energy resources but during 1908 Henry Ford developed a Ford Model T that has the ability to operate on ethanol, gasoline, or blends of both (Bernton et al. 1982). However, bioethanol gained importance during 1970s when abruptly the price of petroleum resources arose besides one of the constituent (methyl tertiary butyl ether (MTBE) used in gasoline was declared as a toxic pollutant (Kovarik and Kettering 1982). The government of United States (US) focus on novel R&D programs directed toward the development of more ecofriendly, sustainable and promising alternative fuels generated from cheap renewable sources. Initially, during 1980 and 1990, there was great effort from the government sector to boost industrial efforts toward production of bioethanol from biomass feedstock by providing subsidies to farmers, tax-exemptions, and support bioethanol research programs. In recent years biofuel production exhibits an increasing trend from about 4.4 billion litres during 1980 to 50.1 billion litres in 2005 (Murray 2005), with further dramatic increases in future. Now-a-days US become the leading producer of bioethanol with about 13.5 billion gallon capacity. Currently, about 200 operational corn-based ethanol plants are operating in 29 states (RFA 2010) most of them are placed in the “corn belt” in the US Midwest (Gnansounou 2010). Despite of the global economic burden during 2010, bioethanol production continues to expand rapidly and contributes significantly to the economic development of rural communities in the US (RFA 2010). Biofuels seems to be a potential alternative to expel the use of fossil fuels as an automotive fuel and lower toxic emissions. In particular, cellulosic bioethanol is believed to possess tremendous potential in this regard, even though there are currently no commercial scale plants in the United States (Raneses et al. 1998). Although lot of R&D work has been done on lignocellulosic bioethanol production, until 1995 not even a single plant capable of converting lignocellulosic biomass to bioethanol via biological route on the commercial scale has been put into operation (Szczodrak and Fiedurek 1996). However, during World War II, when wartime conditions altered the economic growth, few cellulosic-bioethanol plants were constructed and regulated in distinct countries (Russia, Korea, China, Germany, Switzerland, and the USA) to provide an alternative energy resource. However, many of these plants were closed at the end of the war due to competition with synthetically produced petroleum products (Badger 2002). The first demonstration plant based on lignocellulosic feedstock was developed in Canada during 2004 (Tampier et al. 2004). Further, novel green technologies have been developed to enhance the bioethanol production (Natural Resources Canada's Management Team 2005). Recently, in US cost-effective technologies utilizing lignocellulosic feedstock for the production of bioethanol have started to emerge (Badger 2002). In Canada, commercial scale cellulosic-bioethanol plant using proprietary enzymatic hydrolysis technology was developed by Iogen Corporation limited. During 1997, they partnered with Petro-Canada to generate cellulose–bioethanol inaugurated with one million gallon/year ethanol demonstration facility using corn stover and switchgrass as bio-feedstocks. Another bioethanol plant was developed in Sweden during 2005 using sawdust as a raw material. However, the plant is still in infancy stage, but the optimism is high. In near future, Sweden could become competent of bioethanol from forest residues especially wood and wood residues, which would be a much more green way of supplying bioethanol to the Swedish market (Advanced course in LCA 2005).

8.3 Biofuel: Solution to Sustainable Energy

Biofuels generally include liquid, gas, and solid fuels predominantly generated from bio-renewables or combustible renewable feedstock. Currently wide range of fuels (ethanol, butanol, biodiesel, and bio-hydrogen) can be produced from these green energy sources (Demirbas 2008). Contemporary much attention has been dedicated to the transformation of biomass feedstock into bioethanol, considered the cheapest and cleanest liquid fuel alternative to petroleum resources. Due to ill effects of the global warming, scientists all over the world had paid much attention towards the latest cost-effective technologies responsible for bioethanol production. Biofuel sector has gained a momentum across the world because of following reasons: (1) Sustainable and renewable. (2) Eco-friendly in nature thus mitigates GHG-emissions. (3) Abundant and evenly distributed in nature. (4) Provide an economic boost to rural communities (5) Alleviate dependence on foreign oil, promising alternative to petroleum reserves (Farrell et al. 2006). Moreover, in the current scenario the production from huge oil reserves is declining at a faster pace of 4–5 % annually, finally the world production of oil is expected to peak in near future. Hence, as an alternative to nonrenewable energy resources, biofuels have been characterized as an inexorable preeminent supplier of green energy sources that have the capability to enhance the security of supply, lower the GHG emissions, and contribute to the steady income for farmers.

8.4 Lignocellulosic Feedstock

Lignocellulosic biomass constitutes the world's largest renewable and sustainable resource for bioethanol production. Monserrate et al. (2001) reported that an estimated 7.5×10^{10} tons of cellulose is annually synthesized through photosynthetic processes. In the world there are distinct biomass resources which are generally categorized into four categories viz. wood residues (sawdust and other organic matter) constitutes the largest green energy source for bioenergy production. The other biomass reserves include municipal solid waste (MSW), agriculture waste, and potential energy crops. Among them, energy crops seem to be the largest, attractive, and future resource of biomass because of short harvesting period and less energy inputs (Monique et al. 2003). The agro-wastes (rice straw and wheat straw) are mainly produced by Asian countries and each year a major portion of agricultural residues is disposed of as waste. Karimi et al. (2006) estimated that about 600–900 million tons/year rice straw is generated globally. In some regions only a small fraction of these agro-wastes are exploited as animal feed while rest is destroyed by burning which ultimately affects the environment (Wati et al. 2007). In United States, majority of the corn straw approximately about 90 % is left in the fields (Glassner et al. 1999). In recent years, many European countries posed a ban on open field burning of these agro-wastes. In Brazil, the sugarcane by-products (bagasse) are utilized in combined heat and power program or cogeneration technology to generate heat and electricity (Banerjee et al. 2010). Now-a-days these agro-wastes are diverted towards bioethanol production by using latest technologies. It is estimated that rice straw has the potential to produce about 205 billion liters of bioethanol/annum. Besides, these potential biofeedstock possess significant advantages over the first generation biofeedstock for bioethanol production as they are not consumed as food. Lignocellulosic feedstock typically constitutes about 50–80 % carbohydrates which are polymers of C_5 and C_6 sugars. Currently, these carbohydrates are either chemically or biologically converted to yield bioethanol production. Perlack et al. (2005) estimated that United States alone produces about 1.4 billion tons of biomass (dry)/annum of which forests alone contribute about 30 %. Due to energy crises the world energy demand will extend to increase by 45 % during 2008–2030, an average rate of increase in 1.6 %/year. Conventional biomass conversion technologies are inefficient to meet the energy demand therefore, world is focusing on more innovative and noval green technologies for biofuel production using wide range of green energy resources.

8.5 Technologies Involved in Cellulosic Ethanol Production

Bioethanol production from lignocellulosic feedstock involves three main processes, viz. pretreatment, hydrolysis, and fermentation.

8.5.1 Pretreatment

Pretreatment process is generally used to alter chemical composition, size, and structure of biomass so that it becomes amenable to hydrolysis or biological treatment with increased yield of monomeric sugars (Moiser et al. 2005). It is considered as an essential step in the production of bioethanol. The lignocellulose biomass is composed of different polysaccharides (cellulose and lignin bound by hemicellulose chains). The aim of the pretreatment process is to make these polysaccharides amenable to enzymatic hydrolysis by decreasing the degree of crystallinity of the cellulose (Sanchez and Cardona 2008). Currently, numerous pretreatment technologies have been extensively studied to process biomass feedstock for bioethanol production. But, none of them can be declared as an efficient technology because each pretreatment technology has its own merits and demerits. The criteria for an efficient pretreatment technology should be: (1) to avoid size reduction and preserving hemicellulose fractions (2) to prevent loss or degradation of sugars formed (3) Avoid generation of inhibitors during degradation of biomass feedstock (4) to reduce energy inputs and (5) to reduce cost (Zheng et al. 2009). Besides, several other criteria are also taken into consideration such as, recovery of value-added coproducts (lignin) for bio-power production. In addition, pretreatment results must be weighed against their impact on the ease of operation and cost of the downstream processes and the trade-off between several costs (capital costs/operating costs and biomass costs (Palmqvist and Hahn-Hagerdal 2000). Currently, this technology is very expensive with cost as high as 30 cents/gal ethanol produced (Moiser et al. 2005). Recently techno-economic analysis has been made in order to assess the cost and performance of various pretreatment technologies (Eggeman and Elander 2005). Scientists all over the world are focusing to cut down the costs of pretreatment processes through extensive R&D programs. This step is currently a major challenge in the biofuel sector due to the crystalline nature of cellulose as it is recalcitrant to enzymatic hydrolysis. Therefore, various thermochemical techniques have been developed to promote its digestibility (Wyman et al. 2005). Kim and Holtzapple (2006) reported that there exists a direct correlation between lignin removal and cellulose digestibility. The various pretreatment technologies for biomass processing involve physical, chemical, and biological approaches. Sometimes for effective pretreatment of biomass a combination of either technique is being applied (Hsu 1996).

8.5.1.1 Physical Pretreatment Technique

Physical pretreatment does not involve the chemical agents to process the biomass but it involves liquid hot water pretreatment (LHW), steam explosion, mechanical comminution, and high energy radiation. The former two techniques are more common than the latter. Steam explosion is one of the effective approaches that decreases the degree of crystallinity of lignocellulosic biomass and makes it amenable to cellulase attack. During this method the biomass is heated utilizing high pressure steam (20–50 bar, 210–290 °C) for few minutes followed by sudden and rapid decompression to atmospheric pressure. Most steam treatment yields high semi-cellulose solubility and low lignin solubility. Without any catalyst, xylose sugars recovers between 45 and 65 %. This option seems viable if modified to increase the yield and reduce the cost. Another approach of pretreatment processes involves liquid hot water (LHW) in which compressed hot liquid water at pressure above saturation point is used to hydrolyze the matrix of hemicellulose. Pentose sugar (xylose) recovery is quit high (88–98 %) and no acid or chemical catalyst is required.

Although it is an interesting approach, but is still in infancy stage. In one experimental analysis, LHW was used to treat wheat straw and the results revealed that the optimum hemicellulose-derived sugar recovery was approximately about 53 % and enzymatic hydrolysis yield of 96 % (Perez et al. 2007). Besides, biomass size reduction is not needed as the particles are broken apart during pretreatment process that is why LHW appears promising and attractive pretreatment process for commercial scales (Weil et al. 1997). Moreover, some acids like acetic acid and other organic acids are also released from hemicellulose due to the cleavage of o-acetyl and uronic acid substitutions helps to catalyze the hydrolysis of polysaccharides (hemicellulose) into soluble sugars (oligosaccharides) first and then monomeric forms. However, under acidic conditions the monomeric sugars are frequently degraded into aldehydes (furfural, 5-HMA) which act as hindrances/ inhibitors to fermenting microorganism. Besides, due to the high dielectric constant of hot water it has the ability to degrade major portion of hemicellulose and few content of lignin, depending upon the temperature thus LHW plays a significant role just like an acid to degrade hemicellulosic biomass into soluble sugars and acids (Antal and Water 1996).

8.5.1.2 Chemical Pretreatment

This pretreatment approach involves the use of various chemicals such as ammonia/ dilutes acid, organic solvents, sulfur dioxide, carbondioxide and other chemicals. The most common chemicals studied are as follows: Acid catalyzed hydrolysis uses dilute sulfuric/hydrochloric or nitric acids. It has been reported that the appropriate concentration of dilute sulfuric acid ranges between 0.5 and 1.5 % and temperature above 160 °C has been found the most favored for industrial applications. Under these conditions high sugar yields from hemicellulose, at least 75–90 % yields of xylose (Sun and Cheng 2002). The acid should be recycled to reduce solid waste. It is regarded as an important pretreatment technique to produce high amount of sugars from hemicellulose. Hemicellulose is more amenable to dilute acid hydrolysis compared to cellulose (Cardona et al. 2009). However, one of the limitations of this technique is the production of various inhibitors (furfural, 5-hydroxymethylfurfural and acetic acid) which retards the growth of microorganisms. Therefore, some hydrolysates are being used for fermentation in order to detoxify such chemical inhibitors. Alkaline pretreatment uses bases like sodium or calcium hydroxide. During this process main portion of lignin polymer is removed and thus enhances the hydrolysis reaction. Although reactor costs are lower than those acid technologies but at the same time it involves expensive and toxic chemicals that have negative impact on the environment. Alkali pretreatment degrades cell wall by disrupting lignin, hemicellulose, and silica by either hydrolyzing uronic acid or acetic esters besides swelling cellulose. This swelling of cellulose in turn reduces its crystallinity. This pretreatment process involves lower temperature and pressure compared to other techniques (Moiser et al. 2005). Sun et al. (1995) carried out an experimental analysis to study the effectiveness of various alkaline solutions (1.5 % NaOH for 144 h; at 20 °C) using wheat straw as a substrate source and he found that it releases about 60 and 80 % lignin and hemicellulose respectively. Further it has also been reported that sodium hydroxide enhances hardwood digestibility from 14 to 55 % by decreasing lignin content from 24–55 to 20 % (Kumar and Wyman 2009).

8.5.1.3 Biological Pretreatment

Biological pretreatment involves the use of microorganism that possesses the ability to hydrolyze lignocellulosic biomass. Bacteria and fungi are the important sources of these extracellular enzymes (cellulases/hemicellulases/xylanases) that could be utilized for the hydrolysis of pretreated lignocellulosic biomass (Singh et al. 2008). Among the various cellulolytic microorganisms *Trichoderma* species which is considered as an industrial horse for biomass hydrolytic enzymes has been well studied (Xu et al. 1998). Sandgren et al. (2001) reported that *Trichoderma* has the ability to produce at least two cellobiohydrolases, five endoglucanases, and three endoxylanases but it possess less β-glucosidase activity that plays a pivotal role in polymer conversion (cellobiose to glucose) (Kovács et al. 2009). Another microorganism *Aspergillus* is very efficient in producing β-glucosidase (Taherzadeh and Karimi 2007b). Experimental analysis carried out by different researchers in which Trichoderma cellulase was supplemented with extra β-glucosidase and the results showed positive effects in degrading lignocellulosic biomass (Krishna et al. 2001). The efficiency of biological degradation of biomass depends upon the number of parameters like temperature, pH, substrate concentration, surfactant addition, and enzyme specificity and efficiency (Olsson and Hahn-Hägerdal 1996; Börjesson et al. 2007). Currently, the major bottleneck associated with lignocellulosic biofuel technology is the cost of enzymes (Banerjee et al. 2010). Therefore, research should be focussed to develop potent microbial strains that possess the ability to produce enzymes with high specificity and activity (Eggman and Elander 2005). Besides, some adjuvants like surfactants should also be used as they prevent the enzyme from unproductive binding with lignin polymer and thus lowers the enzyme loading (Eriksson et al. 2002). The enzymatic cocktails are usually blends of various hydrolytic enzymes (cellulases/xylanases/hemicellulases) that act synergistically on biomass. This method is economical, green, and cost-effective due to less mechanical support (Talebnia et al. 2010). It does not involve any chemical but low hydrolysis rates and low yields impede its implementation (Balat et al. 2008). Besides, it also involves some inhibitory molecules that impede its efficiency (Chandra et al. 2007). Shi et al. (2008) also reported that some microorganisms possess the ability to solubilize all the three types of biopolymers. Therefore, at the commercial scale, the biological pretreatment pathway faces many hindrances. Current research must be focussed to explore novel sources of enzymes with high potency. Moreover, genetic engineering plays a pivotal role to develop super strains that are highly capable of hydrolyzing cellulose and xylan along with simultaneous fermentation of glucose and xylose to ethanol (Lin and Tanaka 2006).

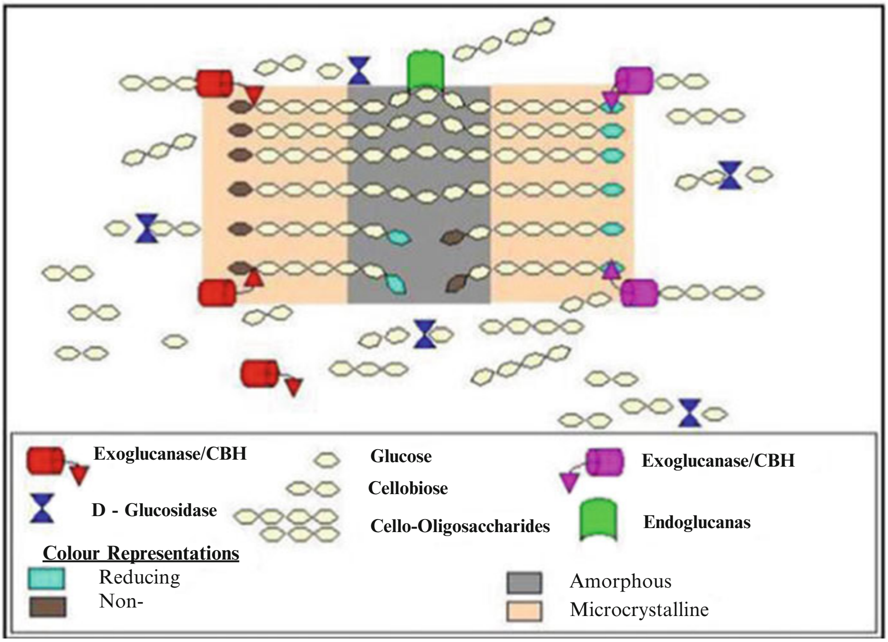

Fig. 8.1 Mechanism of *cellulase* action (Lynd et al. 2002)

8.5.2 Hydrolysis

Hydrolysis process is considered as an essential step to the effectiveness of a pretreatment operation (Gamage et al. 2010). During this phenomenon, the released polysaccharides like cellulose and hemicellulose are hydrolyzed into free monomeric sugars that are easily accessible for fermentation into bioethanol production (Chandel et al. 2007). Ferreira et al. (2009) reported that enzymatic hydrolysis is a dynamic approach compared to acid or alkaline hydrolysis as it is eco-friendly, cost-effective, and is energy efficient (Taherzadeh and Karimi 2007a). Besides, it also does not involve the formation of inhibitory or toxic by-products. Enzymatic hydrolysis is carried out by a complex of cellulase and hemicellulase enzymes that are extremely substrate specific (Banerjee et al. 2010). These enzymes are responsible for degrading the lignocellulosic biomass into simple sugars (Fig. 8.1). It has been reported that the optimum conditions for cellulase activity involves temperature of 40–50 °C and pH 4–5 (Neves et al. 2007). Similarly the optimum parameters for xylanase activity have also been reported to be 50 °C and pH 4–5 (Park et al. 2002). These hydrolytic enzymes are produced by various microorganisms including bacteria and fungi however; *Trichoderma* species is one of the most potent fungi to produce industrial grade cellulolytic enzymes. It produces a complete set of cellulase enzymes (endoglucanase, exoglucanase, and β-glucosidase) that cause cleavage of β-1, 4-glycosidic linkage (Eggeman and Elander 2005). These enzymes act synergistically to hydrolyze the biomass. Enzymatic hydrolysis was carried out using corn stalk as substrate source at 30 °C and pH 5 Belkacemi and Hamoudi (2003). The results revealed that the saccharification was 90 % and sugar was released after 10 h. Similar study was carried out by combination of *T. reesei* ZU-02 cellulase and cellobiase from *A. niger* ZU-07 improved the hydrolysis yield to 81.2 % with cellobiase activity enhanced to 10 CBU/g substrate (Chen et al. 2008). Moreover, there are certain adjuvants that enhance the hydrolysis process. In an experimental analysis, Börjesson et al. (2007) reported that addition of polyethylene glycol enhances the enzymatic transformation of soft lignocellulose from 42 to 78 % at 16 h at an optimum temperature of 50 °C. On addition of Tween 80 (5 g/L) boost hydrolysis yield by 7.5 %. Xu et al. (1998) reported that *T. reesei* degrade 68.21 % of alkali pretreated rice straw whereas upon enzymatic hydrolysis 73.96 % conversion was obtained from alkali assisted photocatalysis of rice straw. Wheat straw when pretreated with alkaline peroxide showed 96.75 % yield after enzymatic hydrolysis whereas atmospheric autocatalytic organosolv pretreated wet wheat straw produce above 75 % yield (Saha and Cotta 2006). Further, it has also been demonstrated that some metals such as, Ca (II) and Mg (II) substantially enhanced enzymatic hydrolysis via lignin-metal complexation (Liu et al. 2010). Hydrolysis of biomass can also be enhanced by using some additives (surfactants and bovine serum albumin) in order to block lignin interaction with cellulases (Eriksson et al. 2002). Similarly, Sewalt et al. (1997) have described that the detrimental effect of lignin on cellulases can be conquered by ammonization and distinct nitrogen compounds. Moreover, for efficient hydrolysis simultaneous approach of enzymatic treatment accomplished with the engineered co-fermentation microbial process known as simultaneous saccharification and fermentation (SSF) was developed (Cao et al. 1996). This phenomenon has gained importance during the late 1970s for its capability to diminish toxic by-product and subsequently enhance bioethanol production (Bisaria and Ghose 1981). Another approach for biomass hydrolysis involves separate hydrolysis and fermentation (SHF) processes but it possess certain limitations such as it involves the blockage of the hydrolytic enzymes (cellulases) by saccharide products like glucose and cellobiose. Unlike SHF, the SSF process carried out hydrolysis and fermentation simultaneously and thus keeps the sugar level too low to cause any noticeable cellulase inhibition (Kumar et al. 2009).

8.5.3 Fermentation

Biomass processing (pretreatment and hydrolysis) is an essential step to optimize the fermentation process (Gamage et al. 2010). These pretreatment techniques results in the formation of saccharified biomass that is now readily available for fermentation process by using several potent microorganisms. However, the major bottleneck in lignocellulosic biofuel technology involves the lack of potent

Table 8.1 Comparison between the two main fermentation techniques

Fermentation process	Features and advantages	Limitations	References
Simultaneous saccharification and fermentation	Low costs Higher ethanol yields due to removal of end product inhibition of saccharification step	Difference in optimum temperature conditions of enzyme for hydrolysis and fermentation.	Balat et al. (2008)
Separate hydrolysis and fermentation	Reduces the number of reactors required Each step can be processed at its optimal operating conditions Separate steps minimize interaction between the steps	End product inhibition minimizes the yield of ethanol. Chance of contamination due to long period process	Sanchez and Cardona (2008)

microorganisms that possess the ability to ferment both pentose as well as hexose sugars (Talebnia et al. 2010). To commercialize the lignocellulosic biofuel technology, an ideal microorganism must fulfill the following criteria. These include: (1) wide substrate utilization (2) high ethanol yield (3) capable to bear high titre of ethanol and temperature (4) ability to withstand inhibitors or toxic by-products present in hydrolysate and have cellulolytic activity. Currently, C_6 sugars (hexoses) are readily fermented into bioethanol but bioconversion of C_5 (pentoses) sugars into bioethanol is a recent approach. Fermentation of pentoses along with hexoses is not common among microorganisms (Toivolla et al. 1984). The well-known microorganism *S. cereviseae*possesses the ability to ferment only hexose sugar into bioethanol. Recently, novel microorganisms such as *Pichiastipitis*, *Candida shehatae*, and *Pachysolantannophilus* have been screened and characterized that possess the ability to ferment both C_5 as well as C_6 sugars into bioethanol. Thermophilic microorganisms are the ideal candidates for bioethanol production at the industrial level because they possess the ability to tolerate high temperature and toxic by-products formed during fermentation process. Currently, the main techniques that are usually involved in the fermentation of biomass hydrolysates are separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF). SSF is considered as a superior, cost-effective, and efficient technique for the production of bioethanol than SHF because it prevents the formation of inhibitory by-products and does not involve the use of separate reactors. However, any fluctuation in optimum temperature conditions of enzymes for hydrolysis and fermentation diminishes its efficiency (Neves et al. 2007). Buaban et al. (2010) reported that ethanol yield coefficient is higher under SSF than SHF because of more conversion of pentose sugar (xylose) into xylitol. Comparative study among these two techniques (SHF and SSF) is presented in Table 8.1. Apart from SSF or SHF, there are other alternative techniques which include consolidated bioprocessing (CBP) and simultaneous saccharification and co-fermentation (SSCF) (Cardona et al. 2009). The CBP technique is carried out inside a single reactor and the various steps involved in this process (cellulase enzyme production, biomass hydrolysis, and ethanol fermentation) are carried out simultaneously (Bjerre et al. 1996). This phenomenon is also termed as direct microbial conversion (DMC) and involves either mono- or co-culture of microorganisms to degrade cellulose polysaccharide into bioethanol. Moreover, CBF technique is cheap, easily available, and does not involve any costly inputs (Hamelinck et al. 2005). The various microorganisms used for the conversion of biomass into bioethanol during CBF technique include *Clostridium thermocellum, Neurospora crassa*, *Fusarium oxysporum* and *Paecilomyces* species. One of the important limitations related to this technique is that its efficiency is very low because of poor ethanol yield coefficient and long fermentation periods (3–12 days) (Szczodrak and Fiedurek 1996). In an experimental analysis, Sree et al. (1999) employ the use of some thermotolerant microorganisms (*S. cereviseae* strain-VS3) under solid state fermentation for the bioethanol production using potato and sweet sorghum as a substrate source. Recent approaches are focusing on development recombination yeast which can metabolize all forms of sugars to improve ethanol production and reduce operation costs. In this concern, two approaches are addressed. The first approach involves modifying the genetic makeup of particular microorganisms and their metabolic pathways (ethanologens additional pentose metabolic pathways). Secondly, with the help of genetic engineering, microorganisms should be engineered in such a way so that they are able to ferment both pentose as well as hexose sugars (Dien et al. 2003). Currently, a number of genetically modified microorganisms such as *P. stipitis BCC15191* (Buaban et al. 2010), *P. stipitis NRRLY-7124* (Nigam 2001), recombinant such as *E. coli KO11* (Takahashi et al. 2000), *C. shehatae NCL-3501* (Abbi et al. 1996), *S. cerevisiae ATCC 26603* (Moniruzzaman 1995) have been developed. Although various technologies have been developed to enhance bioethanol production from lignocellulosic biomass but there are still some hindrances that are needed to be addressed. These involve: (1) maintaining a stable performance of genetically engineered yeast in commercial scale fermentation operation (Ho et al. 1999) (2) developing more potent pretreatment technique for lignocellulosic biomass, (3) integrating optimal components into economic ethanol production system (Dien et al. 2003). Fermentation process involves either batch, fed batch, or continuous process depending upon various parameters like enzyme kinetics, kind of lignocellulosic hydrolysate, and economic inputs. Use of immobilized cell fermenter is found successful for ethanol production from hexoses (Godia et al. 1987). Talebnia et al. (2010) has been proposed certain anaerobic hemophilic bacteria (*Clostridium* sp. and *Thermoanaerobacter* sp.) to analyze the prosperity of fermentation at higher temperatures. Other genetically engineered thermotolerant microorganisms included are *K. marxianus*, *Candida lusitanieae*, and *Z. mobilis* (Bjerre et al. 1996) (Fig. 8.2).

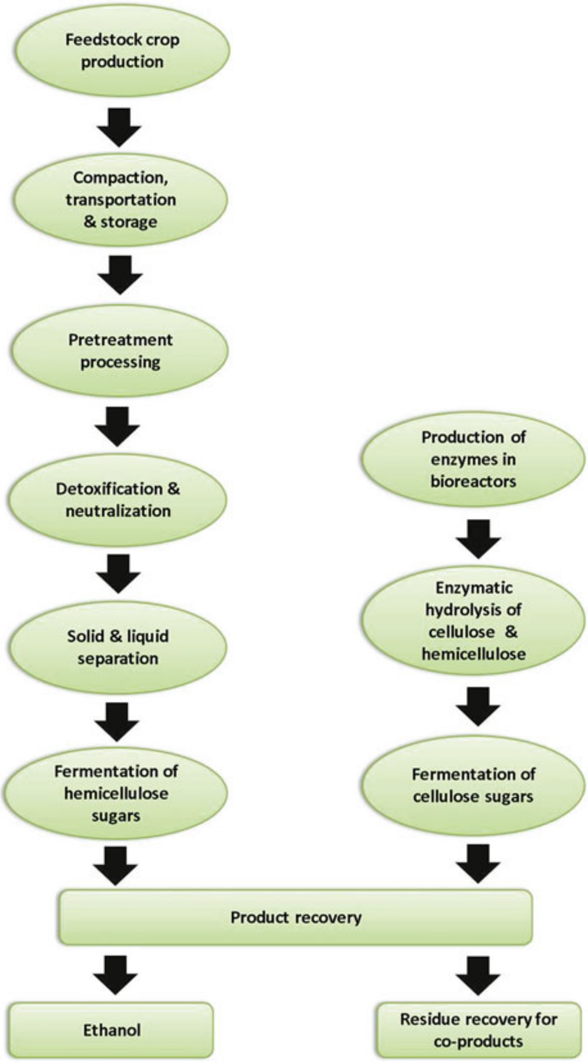

Fig. 8.2 Flowchart of cellulosic ethanol production from lignocellulosic biomass

8.6 Conclusion and Future Perspective

Lignocellulosic biomass is considered as an important green energy resources for economically attractive bioethanol production. These biomass feedstocks does not possess any food value besides, they don't require inputs like land, water, and other energy requirements. The second generation biofuels (lignocellulosic biofuel) possess a great advantage over the first generation biofuels (starchy crops) being cheap, renewable, and abundantly available source of sugar for fermentation into bioethanol production. Biofuels not only reduce the dependence on petroleum resources but also contribute to sustainable development by decreasing GHG-emissions. Currently, bioethanol production from lignocellulosic biomass is not cost-effective because of some barriers that are needed to be addressed. These include biomass feedstock, conversion technology, hydrolysis process, and fermentation. With respect to biomass feedstock major hindrances are supply, cost, handling, and harvesting. The major obstacles regarding conversion technology involve processing of biomass, convenient and cost-effective pretreatment process to detach hemicellulose and cellulose from their complex with lignin. Another objection is to develop an adequate and economical hydrolysis process for depolymerization of cellulose and hemicellulose to generate higher levels of simple sugars (Glucose). Enzymatic hydrolysis is considered as a potent phenomenon for saccharification of complex polymer. Currently, research has been focussed on cellulase engineering in order to cut down the cost of bioethanol production. Lastly, the challenges associated with fermentation process are pentose (xylose) and hexose (glucose) sugar co-fermentation besides the use of potent and efficiently engineered microbial strains. Future work should also be focussed to inhibit the generation of inhibitors (furfural, acetic acid) during biomass processing that acts as main barriers to decline the efficiency of hydrolysis and fermentation of biomass. In order to combat the challenges associated with lignocellulosic biofuel technology, novel approaches like genetic engineering, cellulase engineering should be employed so that production of bioethanol from lignocellulosic biomass may be successfully developed, optimized, and commercialized in the near future.

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Chapter 9
Utilization of Sawmill By-Product for Making Cellulose and Its Valuable Derivatives

M. Jonayed Choudhury and G.M. Arifuzzaman Khan

Contents

Abstract Nowadays, biomass is a valuable raw material not only for energy but also achieving the goal of sustainable development by converting into various life saving, decorative, structural and nonfood consumer products such as pharmaceuticals, paints, adhesives, textile products, polymer composites, cosmetics, papers, and various commodity specially cellulose derivatives. The main constituent of most biomass is cellulose. Sawdust is a good representative of abundant residual forest biomass and consists of 40–50 % of cellulose, 25–35 % of hemicelluloses, and 20–30 % lignin, approximately. It is frequently used for direct combustion in our subcontinent resulting in energy loss and environmental pollution. As it contains higher percentage of cellulose, it can be value-added by producing plenty of precious cellulose derivatives, for instance, carboxymethylcellulose (CMC) which is

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extensively used as emulsion stabilization, binder, thickener of paints, film-former in textiles, etc. A number of researches have been published on the preparation of cellulose derivatives from wood and sawdust. This chapter will accumulate some basic synthesis reactions and scope of applications of valuable cellulose derivatives.

9.1 Cellulose

In the modern world, the consumption of disposable materials has increased, and hence, the load on the environment has increased dramatically. Consequently, the demand for bio-based materials with renewable, low-cost, and sustainable properties has increased. Cellulose-based materials can potentially provide products to meet this demand. In addition, the chemical modification of cellulose-based materials could be developed to meet the requirements set for environmental legislation, by, for example, applying ionic liquid technology. Cellulose as a raw material has several useful attributes; it is abundant, bio-based, and renewable just to mention a few. Furthermore, cellulose has proved to be a versatile material due to its unique chemical structure, which provides a superior platform for several new biomaterials.

The chemical and physical properties of cellulose can only be properly understood by acquiring knowledge of the chemical nature of the cellulose molecule in addition to its structure and morphology in the solid state (Krässig 1996). A profound understanding of the structural properties of native cellulose is a requirement to understand the effects of different substituents on the chemical and physical properties of cellulose and its derivatives (Krässig 1996). At the molecular level the following concepts are considered: chemical constitution, molecular mass, molecular mass distribution, the presence of reactive sites, and potential intramolecular interactions. At the supramolecular level the following concepts are of importance: aggregation of the molecular chains to form elementary crystals and fibrils, the degree of order within and around the fibrils and fibrillar arrangement with respect to the fiber axis. The morphological level covers structural entities formed by cellulose molecules. As the structures get larger, they may become very complex.

Payen (1842) determined the elemental composition of cellulose contains 44–45 % carbon, 6–6.5 % hydrogen, and the rest consisting of oxygen. Based on these data, the empirical formula was deduced to be $C_6H_{10}O_5$. However, the actual macromolecular structure of cellulose was still unclear. Haworth proposed a chain-like macromolecular structure in the late 1920s, whereas Staudinger delivered the final proof of the highly polymer nature of the cellulose molecule (Haworth 1928, 1932; Staudinger 1960). Cellulose is linear chain homopolymer build up by the combination of anhydro D-glucopyranose units (AGU). These units are jointed each other by β-(1 → 4) glycosidic bonds with C-1 and C-4 position of two adjacent glucose moieties (Fig. 9.1). In the solid state, AGU units are rotated by 180° with respect to each other due to the constraints of β-linkage. Each AGU unit contains three hydroxyl (–OH) groups at 2, 3, and 6 carbon atom. Terminal groups at the either end

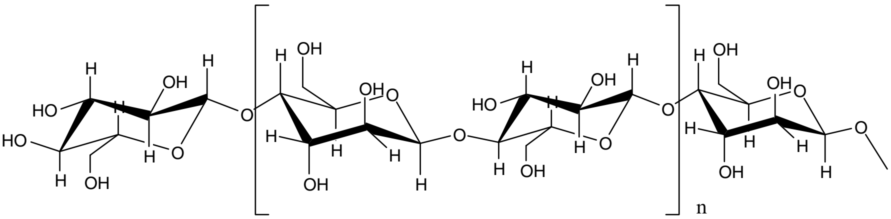


Fig. 9.1 Molecular structure of cellulose representing the cellobiose unit as a repeating unit showing reducing (*right*) and non-reducing (*left*) end-groups (Haworth 1932; Staudinger 1960)

of the cellulose molecule are not same in nature. The –OH group of C-1 at one terminal of the molecule contains an aldehyde group which possesses reducing activity. Aldehyde groups form a pyranose ring through an intramolecular hemiacetal form. In contrast, the –OH group of C-4 at another terminal of the cellulose chain is an alcohol-borne (–OH) constituent and thus is called the non-reducing end. It has been known from the infrared spectroscopy (IR), X-ray diffraction, and nuclear magnetic resonance (NMR) studies that the AGU ring possesses in the form of pyranose ring and this adopts the C1-chair formation which constitutes the lowest energy conformation for D-glucopyranose (Brown and Ley 1965; Chu and Jeffrey 1968; Berman and Kim 1968; Mitchell 1970; Koch and Peterlin 1970; Ham and Williams 1970; Ellefsen and Tonnesen 1971; Rao et al. 1957).

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups (Staudinger 1960). In addition, the β-glycosidic linkages of cellulose are susceptible to hydrolytic attack (Staudinger 1960). The hydroxyl groups of cellulose not only play the role of the characteristics reactions of primary and secondary alcohols, but also responsible for solubility of cellulose in different solvent (Staudinger 1960). Cellulose is insoluble in common organic solvents as well as in water. This may be due to that the hydroxyl groups are formed in the extensive hydrogen bonding network in both, intra- and intermolecular hydrogen bonding as shown in Fig. 9.2 (Krässig 1996). In order to dissolve cellulose, the prevailing hydrogen bonding network must be broken. There are two possible mechanisms by which the –OH groups of cellulose molecule form hydrogen bonds. One is by the interaction between suitably positioned OH groups in the same molecule (intramolecular). These are located among C2–OH, C6–OH, and C3–OH groups with endocyclic oxygen (Fig. 9.2). The other mechanism occurs when neighbouring cellulose chains (intermolecular) interact via their C3–OH and C6–OH groups (Fig. 9.2). Intramolecular hydrogen bonds between the hydroxyl group at the C3 and oxygen of the pyranose ring were first described in the 1960s by Liang and Marchessault and Blackwell et al. who claimed the existence of a second "pair" of intramolecular hydrogen bonds between the C6 and C2 of the neighbouring AGUs (Machessault and Liang 1960; Blackwell et al. 1977). The improvement of solubility of cellulose in water or organic and inorganic solvents is rarely observed by varying external factors such as humidity, temperature, pressure, etc. For such poor solubility, it may

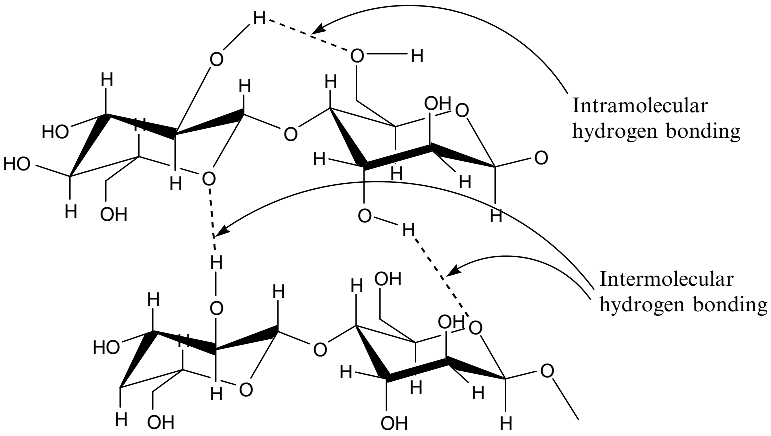


Fig. 9.2 Cellulose structures showing the intramolecular hydrogen bond and the intermolecular hydrogen bond

be assumed that intramolecular and intermolecular hydrogen bonding between the individual chains is very strong. But various water-soluble derivatives of cellulose have found various applications.

The plant kingdoms are the great sources of cellulose. Almost all plant cells are built by cellulose. But the percent of cellulose differs from plant to plant species. Cellulose is arranged in composite form with hemicelluloses and lignin in plant cell. It can be easily separated from other constituents because it is very stable in polar and nonpolar solvents. The purified cellulose and its derivatives have major contribution to various fields especially in pharmaceuticals, food, and cosmetics industries as edible food coatings, film coatings, thickener, binder, stabilizer and emulsifying agents, etc. For example, carboxymethylcellulose (CMC), cellulose acetate phthalate, and microcrystalline cellulose are frequently employed as excipients in tablets (Heng et al. 2001; Rathbone et al. 2003; Aulton et al. 1995).

9.1.1 Cellulose Extraction from Sawdust

Sawdust or wood dust is a by-product of sawmills produce during cutting, grinding, drilling, sanding, or otherwise pulverizing of wood; simply it composed of fine particles of wood. It is mostly used as fuel by direct combustion in rural as well as partially in urban area of Bangladesh. Proper utilization of sawdust is extremely needed not only for remedy environment pollution, but also from the economical point of view of giving value to this residue. Recently, efforts are being made in Bangladesh and India for commercial utilization of sawdust to manufacture particle board as well as to minimize environmental pollution. It contains 40–50 % of cellulose, 25–35 % of hemicellulose, and 20–30 % lignin, approximately (Ali et al. 2009). However, the chemical composition can vary with the age of the plant, climatic conditions, and

Table 9.1 Chemical composition and structural parameters of some natural fibers (Bledzki et al. 1996; Hon 1992)

Type of fiber	Cellulose (wt %)	Lignin (wt %)	Hemicellulose (wt %)	Pectin (wt %)	Wax (wt %)	Moisture content (wt %)
Jute	61–71.5	12–13	13.6–20.4	0.2	0.5	12.6
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0
Kenaf	31–39	15–19	21.5	–	–	–
Sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	11.0
PALF	70–82	5–12	–	–	–	11.8
Henequen	77.6	13.1	4–8	–	–	–
Coir	36–43	41–45	0.15–0.25	3–4	–	8.0
Sawdust	40–50	20–30	25–35	–	–	12.0

processing techniques (Sain and Panthapulakkal 2006). Bledzki et al. (1996), summarized that component or composition means values of plant fibers such as cellulose, hemicellulose, lignin, pectic matters, fatty and waxy matters, and water-soluble substances in Table 9.1.

Sawdust has great possibility to manufacture value-added products. It is found in the form of fine particle from mill which can be used directly for further processing. On the other hand, its low price attacked researcher to find beneficial products in various application. Ali et al. (2009) extracted acetic acid, formic acid and glycolic acid, aldehydes (acetaldehyde, formaldehyde), phenol and phenol derivatives, furfural, methyl furfural, hydroxymethyl furfural by hydrothermal treatment of sawdust. Alvarez et al. (2005) prepared sawdust-pitch-based composites to improve the thermal stability. Studies were also published that sawdust is important resource for many cellulose products such as pulp, paper, textiles, construction materials, particle board, as well as cellulose derivatives, such as cellulose esters (Serad 1993) and ethers (Majewicz and Padlas 1993). Several processes are generally concerned in the conversion of sawdust to cellulose: (1) scouring, (2) mercerization, and (3) bleaching of mercerized derivation with oxidizing agents namely hydrogen peroxide, sodium chlorite, etc. (Mondal and Khan 2008).

9.2 Derivatives of cellulose

The reactions occurred in cellulose structure are mainly the substitution reaction of three chemically active hydroxyl groups in each anhydroglucose unit at positions 2, 3, and 6. Reactivity of these hydroxyl groups depends on various parameters of the reaction medium where chemical functionalization is performed. The average number of hydroxyl groups substituted per anhydroglucose unit is known as the average degree of substitution (DS). The DS can vary between 0 and 3. If all three hydroxyl groups are replaced by the substituents, the maximum theoretical DS is 3.0, but practically it is impossible. The distribution pattern of substituent groups determines the properties of derivatives. The hydroxyl (–OH) groups of cellulose

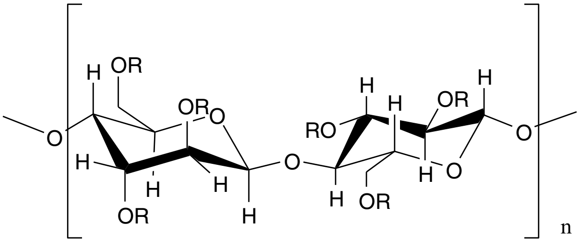


Fig. 9.3 Common structure of cellulose derivatives

EC: R= H; CH_3CH_2
NaCMC: R= H; $CH_2COO^-Na^+$
HEC: R= H; $CH_2CH_2(OCH_2CH_2)_mOH$
HPC: R= H; $CH_2CH_2(OCH_2CH_2CH_3)_mOH$
CA: R= H; -(CO)CH_3
CN: R= H; NO_3
CS: R= H; SO_3H

molecule took part in various substitution, oxidation, reduction, etc. reactions to prepare numerous useful derivatives mainly cellulose ethers and cellulose esters (Fig. 9.3, Table 9.2).

9.2.1 Cellulose Ethers

Cellulose ethers are important derivatives of cellulose. They are soluble in water and organic solvents. Cellulose ethers have various substituents, degrees of substitution, degrees of polymerization and even various mixed substituents, which make them suitable for a wide range of applications in various industries, such as the food industry, the recovery of oils, paper, cosmetics, pharmaceutics, adhesive, agriculture, ceramics, textiles, and construction (Brandt 1986). Cellulose is mercerized with aqueous alkaline solution to yield swollen alkali cellulose. The alkali cellulose is then etherified with the chemicals under alkaline conditions. Sodium hydroxide is often used as the alkali, though other alkalis have different influences on both mercerization and etherification (Krässig 1996). To synthesize mixed ethers, the various reagents may be reacted with cellulose simultaneously or in various stages. There are two important types of etherification depending on the consumption of alkali (Brandt 1986).

1. *The Williamson etherification*: An organic halide is used as the etherification reagent to react with the alkali cellulose. Alkali is consumed stochastically. At the purification stage, the residual alkali in crude methylcelluloses must be washed out as salts.
2. *The Michael addition*: The alkali functions as a catalyst during the addition of epoxides to the hydroxyl groups. No alkali is consumed, although sufficient alkali must be retained during the etherification process. The alkali in the crude products must be neutralized before the purification stage.

Table 9.2 Various ether derivatives of cellulose

Cellulose ether	Etherifying agent	Related compounds	Reagents	Group R′
Alkyl-	Alkylhalides	Methylcellulose	Methylchloride	$=H$ or $-CH_3$
		Ethylcellulose	Ethylchloride	$-CH_2CH_3$
		Ethyl methyl cellulose	Methylchloride and ethylchloride	$-CH_3$ or $-CH_2CH_3$
Carboxyalkyl-	Halogenated Carboxylic acids	Carboxymethylcellulose	Monochloroacetic acid	$-CH_2COOH$
Hydroxyalkyl-	Epoxides	Hydroxyethylcellulose	Ethylene oxide	$-CH_2CH_2OH$
		Hydroxypropylcellulose	Propylene oxide	$-CH_2CH(OH)CH_3$
Alkylhydroxyalkyl-	Alkylhalides and Epoxides	Methylhydroxyethyl cellulose	Methylchloride and ethylene oxide	$-CH_3$ or $-CH_2CH_2OH$
		Ethylhydroxyethyl cellulose	Ethylchloride and ethylene oxide	$-CH_2CH_3$ or $-CH_2CH_2OH$
		Methylhydroxypropyl cellulose	Methylchloride and propylene oxide	$-CH_3$ or $-CH_2CH(OH)CH_3$
Cyanoethyl-	Acrylonitrile	Cyanoethyl cellulose	Acrylonitrile	$-CH_2CH_2-CN$

The etherification can be carried out in heterogeneous or homogeneous systems as continuous or batch reactions. The cellulose ethers in heterogeneous system are produced by the following three steps: mercerization, etherification, and separation or purification. Simply, etherification reaction can be expressed by the following equation

$$\mathrm{R-OH+R'-Cl \rightarrow \ ROR' \ + \ \ HCl}$$

Where, R–OH represents one of the three alcohol groups in an anhydroglucose unit and the R′ is an organic radical of etherifying agents such as methyl ($-CH_3$), ethyl ($-CH_2CH_3$), or more complex structure.

9.2.1.1 Alkylcellulose

The traditional procedure for the preparation of alkyl cellulose is based on the Williamson etherification reaction using alkyl halide. Depending on the alkylhalides various types of alkylcellulose are produced by the following general reaction

$$\mathrm{Celulose} \xrightarrow{\text{Alkali}} \mathrm{Alkalicellulose} \xrightarrow{\text{Alky lhalide}} \mathrm{Alkylcellulose}$$

Methylcellulose

Methylcellulose (MC) is one of important cellulose ethers (Krässig 1996; Hon and Shiraishi 1991; Donges 1990; Coffey and Bell 1995). It has very wide applications. Building industry uses about 47 % of worldwide produced methylcellulose (about 70,000 tons/year) (Donges 1990; Greenway 1994; Greminger 1979; Greminger and Krumel 1981). Paints, wallpaper paste, cosmetics and pharmacy, detergents and polymer industries consume about 21 %, 14 %, 4 %, and 5 % of methylcelluloses, respectively, (Donges 1990). It has a wide application as a surfactant because its chain contains of both hydrophilic –OH and hydrophobic $-OCH_3$ groups (Donges 1990). It is also used in cement and gypsum formulations, aquatic paints, and wallpaper adhesives for its excellent water retention properties (Brandt 1986). Sometimes it may prescribe for treatment of eye illness. Methylcellulose is utilized as an additive of drugs, food, and cosmetics, in which methylcellulose functions as a component of coating, a drug release controller, a viscosity controller, a filler of tablet and capsule, etc (Donges 1990). Suida (1905) synthesized methylcellulose for the first time. Methylcellulose is synthesized by the Williamson etherification with iodomethane, methyl chloride, or dimethyl sulfate (Brandt 1986; Donges 1990; Ye et al. 2005). Commercially produced methylcelluloses have two types: (1) water-soluble methylcelluloses with degrees of substitution (DS) ranging from 1.4 to 2.0, (2) alkali-soluble methylcelluloses with degrees of substitution (DS) ranging from 0.25 to 1.0 (Brandt 1986). Methylcellulose is made in different viscosities ranging from 4 to 100,000 mPas in 2 % aqueous solution at 20 °C with 20 rpm. Methylcelluloses of different DS and viscosity satisfy their diverse applications.

During mercerization with concentrated alkali solution, pulp became swell, degrade, decrease the orderness, and finally form the alkali cellulose. Then the alkali cellulose easily reacts with methyl halide and produce methylcellulose. The nucleophilic substitution reaction of alkali cellulose and methyl halide is carried out through the interaction of the oxonium sodium hydroxide complexes with three accessible hydroxyls of the anhydroglucose unit. During methylcellulose synthesis from bleached pulp (sawdust pulp) rather than the pure cellulose, reaction is occurred by the mechanisms of William etherification and the macro-heterogeneous methylation (Timell and Purves 1951; Rebenfeld 1954). As a result, inhomogeneous and incomplete methylation can be found because of the difficulty of reagent diffusion, competitive reactions of lignin and hemicellulose, the inaccessible fibril interiors, and the crystalline cellulose interiors (Krässig 1996; Rebenfeld 1954). Synthesized methylcellulose is often comprised of unreacted fibrils, methylcellulose with an inhomogeneous distribution of the methoxyl group and salts.

Currently, the synthesis of methylcellulose focuses on the essential properties: the DS, the molecular weight (the degree of polymerization, DP), and the distribution of the methoxyl group along both the anhydroglucose unit and the methylcellulose molecule chain. The methylcellulose is dissolved in cold water at the range of DS 1.3–2.0 (Croon and Manley 1963). For a given DS, the molecular weight is the deciding factor of methylcellulose for its solubility and application (Timell and Purves 1951). Properties such as the number average molecular weight (M_n), the weight average molecular weight (M_w), the polydispersity (PD), and the degree of polymerization constitute the essential characteristics for the optimal synthesis and application of water-soluble methylcellulose. The molecular weight of methylcellulose needs to be maintaining within a particular range for various application by carefully selecting the raw materials and process parameters. Methylcelluloses of viscosities higher than 50,000 mPas in 2 % aqueous solution at ambient temperature are produced from cotton linters because cotton has a degree of polymerization as high as 10,000 (Brandt 1986). Methylcelluloses of lower viscosities are produced from sulfite-processed wood pulps (Brandt 1986). The pulps for production of methylcelluloses are required as almost free of lignin, highly purified, and high α-cellulose contents of more than 86 % (Brandt 1986). Sulfate-processed wood pulps are less used (Brandt 1986).

Ethyl Cellulose

Ethyl cellulose (EC) is a cellulose ether distinguished by its versatility. It is very tough, non-ionic, pH insensitive cellulose ether. It is soluble in many polar organic solvents and insoluble in water. Ethyl cellulose can be formulated into film former, thickener, stabilizer, and suspending agent for oral and topical applications when a non-ionic material is desired. Several researchers had reported the ability of ethyl cellulose to sustain the release of drugs (Mura et al. 1999; Friedman and Golomb 1982). It may be used as a taste-masking agent in some dietary food supplements and also as discoloration preventing agent of easily oxidizable substances such as ascorbic acid. Ethylcellulose is produced by the reaction of ethylchloride and alkali cellulose by the reaction:

$$\mathrm{R-OH+NaOH \rightarrow R-ONa+H_2O}$$

$$\mathrm{R-ONa+CH_2CH_3Cl \rightarrow R-O-CH_2CH_3\ +NaCl}$$

Where, R represents the cellulose radical. Complete substitution of all three groups would give the triethyl ether possessing a substitution value 3. However, triethylcellulose has no commercial significance, because it lacks strength and flexibility. EC is practically colourless, of low density, good thermal stability, low flammable and compatible with wide range of resins and plasticizers. It is readily soluble in various solvents like alcohols, esters, ketones, aromatic hydrocarbons, and chlorinated solvents. It is resistant to alkalies both diluted and concentrated and to salt solutions.

Ethyl Methyl Cellulose

Ethyl methyl cellulose is mixed ether of cellulose which is prepared from cellulose by treatment with alkali to prepare alkali cellulose and with dimethyl sulphate and ethyl chloride. Both the methyl and ethyl groups are attached to the anhydroglucose units by ether linkages.

$$\mathrm{R-OH + NaOH \rightarrow R-ONa + H_2O}$$

$$\mathrm{R-OH\ +\ dimethyl\,sulfate \xrightarrow{C_2H_5Cl} Enthyl\,cellulose}$$

9.2.1.2 Carboxyalkylcellulose

Carboxyalkylcellulose are important class of cellulose ether which is produced by the following reactions. In the first step, cellulose is suspended in sodium hydroxide to produce alkali cellulose, and then the alkali cellulose is reacted with halogenated carboxylic acids to produce respective type of carboxyalkylcellulose.

$$\mathrm{Cellulose \xrightarrow{Alkali} Alkali\,cellulose \xrightarrow[\text{carboxylicacid}]{\text{Halogenated}} Alkyl\,cellulose}$$

Carboxymethylcellulose

Carboxymethylcellulose (CMC) is nontoxic and it has various applications in food, pharmaceutical, and textile industries. Na-CMC is used as an emulsifying agent in pharmaceuticals and in cosmetics (Arion 2001). It is being used as an important ingredient in controlled drug-release formulation and in the manufacture of personal care products (Maile et al. 1990). It is also used in gels applied as protecting agent during heart, thorax, and cornea surgery (Pennell et al. 1992; Nomori and Horio 1997). CMC is generally added for paper quality improvement, as it forms inter-bonds with cellulose. The CMC film-coated cellulose fibers have improved the substantial property of paper for printing jobs (Xiaojia et al. 2009). Beside the wide use of CMC, it is used as drilling mud in oil industry (Dolz et al. 2007). In addition, CMC is employed as a dye thickener in textile industry (Fijan et al. 2009). The presence of a small amount of CMC in anti-dirt agents such as detergent and surfactant can protect fiber's surface from degradation (Mohanty et al. 2003). Raw cellulose, wood, paper cotton-linter, natural fibers (Lantana camara, banana plants, and sugar beet pulp) are the sources of CMC (Kirk and Othmer 1997; Togrul and Arslan 2003; Xiaojia et al. 2009; Jardeby et al. 2005; Varshney et al. 2006; Casey 1981). The key step in carboxymethylation reaction is the preparation of alkali cellulose. The accessibility of cellulose towards chemicals has been improved by swelling of fibers. Cellulose fibers became floppy by removing fatty, waxy, pectic matters, hemicelluloses, etc. in concentrated NaOH (Barba et al. 2002). CMC is formed by replacing the hydroxyl group of anhydrous-glucose unit with the carboxymethyl group of monochloroacetic acid. The hydroxyl group of cellulose shows high activity at alkaline conditions. For production of CMC, two consecutive steps of reactions are required (Xiaojia et al. 2009). Carboxymethylcellulose is produced of the reaction of alkali cellulose and monochloroacetic acid or sodium monochloroacetate under controlled conditions.

$$\mathrm{R-ONa + Cl-CH_2-COONa \rightarrow R-O-CH_2-COONa + NaCl}$$

Where, R represents the cellulose radical and R–O–CH_2–COONa is the sodium carboxymethyl cellulose. At the end of carboxymethylation, the reaction mixture contains a slight excess of sodium hydroxide, which is usually neutralized. Although the neutral point of CMC is pH 8.25, the pH is generally adjusted to about 7–7.5. If the pH to which the CMC is neutralized is 6.0 or less, the dried product does not have good solubility in water; solutions are hazy and contain insoluble gel particles. If the pH is 4 or below, the dried product is insoluble in water. A representative listing of the many applications for NaCMC is given below in Table 9.3 (Aqualon.com).

Table 9.3 Applications for NaCMC

Types of uses	Applications
Pharmaceuticals	Emulsion stabilizer, thickener, film-former
	Thickener, gelling agent, protective colloid, film-former
	High-strength binder
	Thickener, suspending aid
Cosmetics	Thickener, flavor stabilizer, suspending aid, binder
	Suspending aid, thickener, foam stabilizer, high water-binding capacity
Adhesives	Water-binding aid, adhesion, nonstaining
Detergents	Whiteness retention through soil suspension
Paper and paper products	High-strength binder, improves dry strength of paper
Textiles	Film-former

9.2.1.3 Hydroxyalkylcellulose

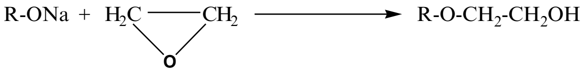
Hydroxyalkylcellulose is produced by the treatment of sodium hydroxide to prepare alkalicellulose; the alkalicellulose is then reacted with different etherifying agents depending on the required type of cellulose ether. Simply, such type of etherification reaction can be expressed by the following diagram

$$\text{Cellulose} \xrightarrow{\text{Alkali}} \text{Alkalicelluose} \xrightarrow{\text{Epoxides}} \text{Hydroxyalkylcellulose}$$

Hydroxyethylcellulose

A typical hydroxyethylation reaction involving alkalization and etherification with ethylene oxide shown below is used to produce hydroxyethylcelulose (HEC)

$$\text{R-OH} + \text{NaOH} \longrightarrow \text{R-ONa} + H_2O$$



$$\text{R-ONa} + H_2C\!-\!CH_2\,(\text{O}) \longrightarrow \text{R-O-}CH_2\text{-}CH_2OH$$

Where, R represents the cellulose radical.

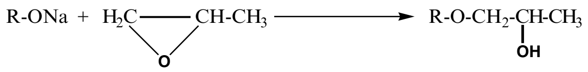
Table 9.4 Applications for hydroxypropyl cellulose

Types of uses	Applications
Pharmaceuticals	Thermoplastic binder, non-ionic, pH insensitive thickener, diffusion barrier flexible films, suspending agent
Cosmetics	Alcohol-soluble thickener, and film former emulsion stabilizer, thickener
Food	Stabilizer, whipping aid, protective coating and oil barrier, high gloss and color coatings, binder for molding and extrusion
Adhesives	Thickener, thermoplastic
Coating and printing	Thickener, binder-suspending agent
Aerosol	Stabilizer, foaming aid
Binder	Film-former, binder, binder-suspending agent

Hydroxypropylcellulose

Hydroxypropylcellulose is produced by reacting alkalicellulose with propylene oxide under controlled conditions. Simply, such type of etherification reaction can be expressed by the following equation:

$$\text{R-OH} + \text{NaOH} \longrightarrow \text{R-ONa} + H_2O$$



Where, R represents the cellulose radical. A representative listing of the many applications for hydroxypropylcellulose is given below in Table 9.4 (Aqualon.com).

9.2.1.4 Alkylhydroxyalkylcellulose

Methylhydroxyethylcellulose (MHEC), ethylhydroxyethylcellulose (EHEC), and methylhydroxypropylcellulose (MHPC) are most common types of alkylhydroxyalkylcellulose which are water-soluble, non-ionic cellulose ether that is produced by alkoxylation process with alkylchloride and epoxides. These are used in many industrial applications as water retention aids, protective colloids, thickening agents, binders, and stabilizers. The general formula of alkylhydroxyalkylcellulose preparation is shown below:

$$\text{Cellulose} \xrightarrow{\text{Alkali}} \text{Alkalicelluose} \xrightarrow[\text{Alkylhalides}]{\text{Epoxides}} \text{Hydroxyalkylcellulose}$$

9.2.1.5 Cyanoethylcellulose

Cyanoethylcellulose is produced when acrylonitrile is reacted with partially anionized hydroxyls groups of cellulose AGU in an aqueous alkaline medium.

$$\text{Cell-OH} + \underset{\text{Acrylonitrile}}{\mathrm{CH_2 = CH - CN}} \xrightarrow{\text{NaOH}} \underset{\text{Cyanoetylcellulose}}{\mathrm{Cell - O - CH_2 - CH_2 - CN}}$$

9.2.2 *Cellulose Esters*

Cellulose esters are synthesized from inorganic and organic acids or their anhydrides. Cellulose may be considered as a trivalent polymeric alcohol with three free hydroxyl groups, which are polar and can be substituted by nucleophilic groups in presence of strong acid. Cellulose is a semi-crystalline solid in which crystalline cellulose (about 67 %) and amorphous cellulose (about 33 %) form the elementary fibril. The crystal interior is not freely accessible to the reaction reagents. The strong hydrogen bonds and weak van der Wall's forces cause the molecular arrangement of cellulose and microstructure in the cellulose fibril, which both depend on the origin and previous physicochemical treatments. Accessibility toward reagents and reactivity of the alcoholic –OH groups also depend on the nature of the cellulose structure. Since cellulose is insoluble in all common solvents, cellulose esterification is usually carried out in heterogeneous slurries. This kind of reaction is usually a typical topochemical reaction. New reactive sites are formed during proceeding of reaction so that, most fibrils the cellulose fibers are took part in the reaction. Some yielded soluble derivatives and are even further reacted in a homogeneous phase. The following two reaction types can occur during the esterification of cellulose (Balser et al. 1986) (Table 9.5).

1. An intermicellar reaction: The esterification chemicals initially penetrate and diffuse into the amorphous regions between the crystalline cellulose micelles. This penetration and diffusion then continue from the surface to the inner parts of the micelles, which are attacked and gradually disrupted by these reagents. The reaction of cellulose and acids is faster than the penetration and diffusion. The total reaction is therefore determined by diffusion.
2. An intramicellar or permutoid reaction: The reagents penetrate and diffuse into all parts, together with the crystalline micelles in order that every cellulose molecules react nearly at the same time. The reaction speed is determined by the esterification equilibrium.

Both reactions may occur and finally merge, depending on the reaction conditions—especially the reaction solvents, the nature of the cellulose, the mole ratio of reagents, and the temperature (Balser et al. 1986). The esterification reactions are not carried out as stoichiometric reactions (Balser et al. 1986). The average degree of substitution of cellulose esters does not often reach the maximum (3). The degree of cellulose esters is

Table 9.5 Various ester derivatives of cellulose

Cellulose ester	Esterifying agents	Related compounds	Reagents	Group R′
Organic esters	Organic acids	Cellulose acetate	Acetic acid and acetic anhydride	H; $-(C{=}O)CH_3$
		Cellulose triacetate	Acetic acid and acetic anhydride	$-(C{=}O)CH_3$
		Cellulose propionate	Propionic acid	H; $-(C{=}O)CH_2CH_3$
Inorganic esters	Inorganic acids	Nitrocellulose (Cellulose nitrate)	Nitric acid or another powerful nitrating agent	H; $-NO_2$
		Cellulose sulfate	Sulfuric acid or another powerful sulfuring agent	H; $-SO_3H$

often below three. The primary hydroxyl group on the C-6 atom is more reactive than the neighboring hydroxyl groups on the C-2 and C-3 atoms of the anhydroglucose unit, which are less reactive because of steric hindrance (Balser et al. 1986). Over 100 types of cellulose esters are available but the most important ones are cellulose nitrate and cellulose acetate. Simple esterification reaction may be shown by the following equation:

$$R-OH+R'-COOH\longrightarrow R-COO-R'+H_2O$$

Where, R and R′ represent the cellulose radical and alkyl group, respectively.

9.2.2.1 Cellulose Acetate

Cellulose acetate is the generic term used to describe a variety of acetylated cellulose polymers. These include cellulose diacetate, cellulose triacetate, and the mixed esters of cellulose acetate propionate and cellulose acetate butyrate. Both cellulose diacetate and cellulose triacetate may be acetylated on one, two, or all three of the available sites on each glycopyranose ring. The degree of substitution, along with the solvents used during the manufacturing process, and plasticisers, such as triphenyl phosphate, which are usually used, determine the composition and properties of the acetate produced. Cellulose acetate was first produced in 1869 (Aubier 1996). It was used in the photographic and film industries in 1909 when the Eastman Kodak Company produced a small quantity of cellulose acetate sheet film, which was expected to replace unstable cellulose nitrate (Fordyce). However, due to technical limitations at the time, it wasn't until 1923 (Horvath 1987) that an adequate manufacturing process was found. This was used to produce 16 mm amateur motion picture film (home movies) on a large commercial scale. Kodak was the first company to introduce a cellulose acetate "Safety" film in sheet form. This material, known as cellulose diacetate, became brittle and shrunk within a short period, so modifications were made to increase its stability. Mixed esters, such as cellulose acetate propionate and butyrate, were used to produce 16 and 8 mm amateur motion picture film, sheet film, aerial film, and X-ray film. In the late 1940s, 35 mm film and microfilm were produced on cellulose triacetate. By 1951, production of cellulose nitrate in the USA had stopped, and motion picture film, microfilm, and negatives were being produced on triacetate film (Adelstein et al. 1992). Cellulose acetate was experimentally used in magnetic tape audio recordings in 1932 by chemists from AEG. The magnetic particles were suspended in a solution of cellulose acetate and acetone with which the cellulose acetate substrate was coated. Small scale commercial production commenced in 1936 at BASF in Germany; however, wartime shortages caused the substitution of the preferred substrate with PVC. Other manufacturers commenced producing cellulose acetate tape from 1946 until 1964, when the use of polyethelyne terapthalate (PET) rapidly replaced it. The new tape enabled thinner tape substrate suitable for use in the compact cassette. The factors responsible for the hydrolysis of the acetyl side groups from the main cellulose chain appear to be numerous and are typically difficult to fully identify. Anecdotal accounts abound with widely varying rates of cellulose acetate deterioration that cannot be attributed to differences in storage conditions. However, moisture, acids, and elevated temperature have all been shown to be crucial factors in controlling the rate of deacetylation. Deacetylation of cellulose acetate requires the presence of water. While removal of water would effectively prevent hydrolysis of the acetyl side group from occurring, some water is necessary to prevent the acetate film from contracting and becoming brittle. As well as humidity control, low temperature storage has been demonstrated to result in very significant reductions in the rate of cellulose acetate deterioration (Reilly 1993). Acetic acid generated on deacetylation gradually diffuses to the surface of the film. Initially, the free acid is generated slowly, the rate of reaction being governed primarily by temperature and relative humidity.

9.2.2.2 Cellulose Nitrate

The nitrate esters are produced by the reaction of the cellulose and a mixture of nitric acid, sulfuric acid along with water (Balser et al. 1986). The highly nitrated cellulose with DS ranging from 2.4 to 2.8 is used to produce explosives and flammable solids. The less nitrated celluloses are used to produce tapes of movies, adhesive, shellacs, and plastics. It is produced by reacting cellulose to nitric acid or other powerful nitrating agents in presence of sulfuric acid as a catalyst to produce nitronium ion, NO_2^+. Simply, this nitration reaction may be given by the following equation:

$$3HNO_3 + C_6H_{10}O_5 \xrightarrow{H_2SO_4} C_6H_7\left(NO_2\right)_3 O_5 + 3H_2O$$

9.2.2.3 Cellulose Sulphate

Cellulose sulphate is a water-soluble derivative. It may be synthesized through either homogeneous or heterogeneous sulphating process in various solvents starting from cellulose or cellulose derivatives (Zhang et al. 2010). Various sulphating agents such as SO_3, chloro sulphuric acid, and SO_3 are generally used in this process. DMF complex has been applied for the sulphating of cellulose (Baumann et al. 2000; Philipp et al. 1987; Wang et al. 2007) and possible solvents are pyridine, N,N-dimethylformamide (DMF), and dimethyl sulfoxide, N_2O_4. It is known that after the sulphating of cellulose the product CS shows improved enzymatic degradability and water-solubility (Saake et al. 2002). For these properties, CS has wide use in biotechnology and pharmaceutics (Dautzenberg et al. 1999). Cellulose sulfate has also antivirus and anticoagulant activity (Groth and Wagenknecht 2001). It is used to some infectious diseases like HIV.

9.2.3 *Oxidised Cellulose*

Oxidations of cellulose either partial or complete produce various functional groups such as aldehyde, carboxylic acid, and ketone groups. The reaction mainly depends on the nature of oxidizing agent and reaction conditions (Nabar and Padmanabhan 1950). Oxidised cellulose may be produced by the treatment of an oxidising agent, such as hydrogen peroxide, chlorine, chlorine dioxide, nitrogen dioxide, permanganate, persulfates, hypochlorous acid, hypohalites or periodates, dichromate-sulfuric acid, and a variety of metal catalysts, etc. (Simon and Wim 2010). It is used as an antihemorrhagic (Oto et al. 1999). Oxidation reaction can be charged the physical and chemical properties of cellulose. Varma and Chavan (1995) found lower crystallinity for 2,3-dialdehydecellulose and crystallinity decrease with the increase of oxidation reaction.

9.2.4 *Microcrystalline/Nanocellulose*

In literature nano-fibers are often referred as “nano-whiskers” or “microcrystals.” The term nano-fiber can be defined as long flexible particles consisting of elementary assemble of distinct polymer units that have diameters in order of tens of nanometers. A specific cellulose nanofiber has diameter in the range 2–20 nm (Azizi Samir et al. 2005; Liu et al. 2009). Native cellulose (cellulose I) has a Young’s modulus of 167.5 GPa which was found by the theoretical and experimental determinations of the stiffness of cellulose (Tashiro and Kobayashi 1991). The processes to produce cellulose at nanoscale have been developed by following two pathways:

1. Nanocrystals or whiskers found by the chemical hydrolytic treatment. Inorganic acids (H_2SO_4, HNO_3, HCl, etc.) are usually utilized to manufacture individualized rod-like cellulose nanocrystals/whiskers since the process discovered by

Rånby and Ribi (Rånby 1949; Rånby and Ribi 1950; Bondeson et al. 2006; Morandi et al. 2009; Candanedo et al. 2005; Araki et al. 2001; Berg et al. 2007).

2. Microcrystalline cellulose (MCC) prepared by mechanical treatment. Suspensions of cellulose fibrils named microfibrillated cellulose (MFC) can be produced by mechanical disintegration (Herrick et al. 1983; Turbak et al. 1983; Nakagaito and Yano 2004) of cell walls and chemical treatments (Zimmermann et al. 2004; Saito et al. 2006, 2007). Due to the huge possibility of cellulose nanoparticles or nanocellulose in different applications, interest is growing by scientists to develop nano-scale materials as they developed different processes to produce cellulosic nanoparticles. With the continuation, Saito et al. (2006, 2007) have suggested a procedure to get MFC based on TEMPO reaction and strong proficient mixing. They found 3–4 nm wide and few micrometers long individualized MFC. Aulin's group (2010) recommended similar strategy to form carboxymethylated MFC. The most important features of mechanical mixing for the production of MFC is that no additive is required. The enzymatic treatment methods have been proposed as an alternative to reduce production cost by decreasing the number of passes through the homogenizer. In addition, high aspect ratio MFC can be obtained by preserving junction sites of the network (Paakko et al. 2007). The enzymatic treatment process is not only very specific but also reduces environmental pollution rather than the use of hazardous chemicals. It is less corrosive compared to chemical treatments (Henriksson et al. 2007).

9.3 Conclusion

The novel aspect of this study was the proper utilization of the cellulose available in sawdust used as a raw material. The collections of many scientific surveys in synthesis and lots of factors were discussed. Various types of cellulose derivatives are being used in a considerable interest in pharmaceutical, cosmetics, paints, paper, and composite technologies due to their characteristics such as, no toxicity, biocompatibility, and high viscosity. Thus, to stop pollution causing synthetics, it is compulsory to continuous use and technology development of cellulose and its derivatives. Finally it can be concluded that the concept of sawdust biomass as raw material of cellulose is now of key importance to preserve money as well as our environment.

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Chapter 10
Upgrading of Oil Palm Biomass to Value-Added Products

Anli Geng

Contents

Abstract Indonesia and Malaysia account for about 85 % of the global palm oil production. Oil palm plantations in these two countries are producing about 200 million tons dry oil palm biomass and substantial amount of palm oil mill effluent (POME) which is rich in nutrients and carbohydrates. The solid oil palm biomass has been converted to a series of value-added products, such as solid fuels, biofertilizer, wood products, biocomposite, fiber mats and activated carbon, etc. POME, on the other hand, has been converted to biogas and biohydrogen for power generation. Recently, oil palm biomass has been explored as a possible feedstock for the production of biofuels, such as ethanol, butanol, syngas, and bio-oil. In addition, oil palm biomass has also been investigated for the production of value-added chemicals, e.g., volatile fatty acids, citric acid, levulinic acid, lactic acid, biodegradable

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plastics polyhydroxyalkanoates (PHAs), nanomaterials, and xylooligosaccharides. Although various value-added products have been investigated, the ultimate valorization of oil palm biomass will be possible if biorefinery approach is taken.

Keywords Oil palm biomass • Palm oil mill effluent • Value-added products • Biofuels • Bio-based chemicals • Biorefinery

10.1 Introduction

Global production of palm oil will reach 56 million metric tons in 2013, which has almost doubled over the past 10 years. By 2020, another 40 % growth is expected from its current levels and it will reach 78 million metric tons. In 2013, about 85 % of the global palm oil production is from Indonesia (29 million tons) and Malaysia (19 million tons) according to International Institute of Sustainable Development. With the rapid expansion of this industry, vast amount of oil palm biomass is generated. It was estimated that for one metricton of crude palm oil produced, approximately 4 tons of dry biomass are generated (Husin et al. 2002; Wahid et al. 2004; Yusoff 2006). Therefore, approximately 200 million tons of dry oil palm biomass is produced in Malaysia and Indonesia in 2013. Among the dry oil palm biomass, 75 % is left in the plantations as oil palm fronds (OPF) and oil palm trunks (OPT), and the remaining 25 % is generated in palm oil mills as empty fruit bunch (EFB), palm kernel shells (PKS), and mesocarp fiber (MF). In addition, significant amount of palm oil mill effluent (POME) is produced in palm oil mills (Tables 10.1 and 10.2).

Currently, majority of the oil palm biomass is returned to the field as biofertilizer to release its nutrients and replenish the soil, with a small increasing amount processed to wood products and bioenergy. In palm oil mills, EFB, PKS, and MF are burned for steam generation and power supply. POME is used for biogas production and power generation. Besides the above, oil palm biomass can also be potentially valorized to produce higher value products, such as pellets, biofuels, bio-based chemicals, and bio-based materials. This paper aims to review and discuss the potential routes to valorize oil palm biomass.

10.2 Direct Utilization of Oil Palm Biomass

Direct utilization of oil palm biomass refers to the utilization of such biomass in its polymer form without serious biomass decomposition. The major applications in such category are summarized in Fig. 10.1. This particularly refers to the solid oil palm biomass.

The most straight forward utilization of oil palm solid biomass is biofertilizer. For example, the major utilization of OPT and OPF is to shred them and return them to oil palm plantation as mulch. Young palms are planted directly onto the

Table 10.1 Types of oil palm biomass

Image	Biomass type	Description	Site of production
	Fronds (OPF)	Leaves of oil palm tree	Plantation
	Trunks (OPT)	Tree trunks available at end of plantation lifecycle	Plantation
	Brunches (EFB)	Remains after removal of palm fruits	Mill
	Shells (PKS)	Remains after palm kernel oil extraction	Mill
	Fiber (MF)	Remains after oil extraction from mesocarp	Mill
	Palm oil mill effluent (POME)	Liquid by-product from sterilization and milling process of fresh fruit bunch (FFB)	Mill

Table 10.2 Oil palm biomass availability in Malaysia in 2012

Biomass type	Availability[a] (million tons)
Fronds (OPF)	6.63
Trunks (OPT)	46.53
Brunches (EFB)	7.85
Shells (PKS)	4.77
Fiber (MF)	8.29
Palm oil mill effluent (POME)	66.27

Source: Malaysia Palm Oil Board (MPOB) 2012

[a]Dry weight

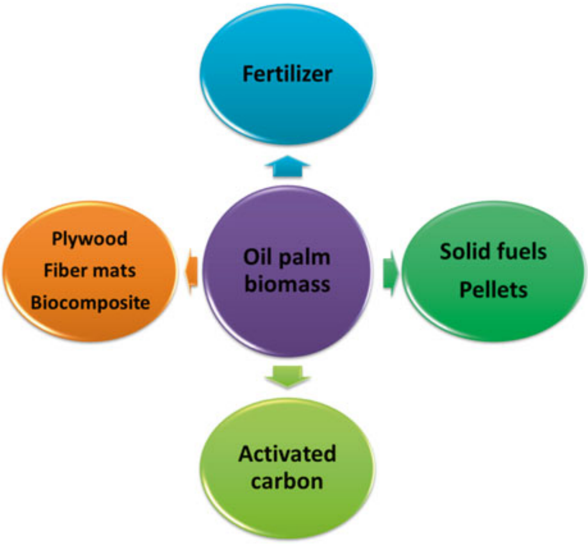

Fig. 10.1 Direct utilization of oil palm biomass

palm residue piles in order to increase the accessibility and efficiency of nutrient utilization. This way the palm oil yield was significantly improved compared with those planted in the area having no palm residue (Khalid et al. 2001). On the other hand, EFB is often composted to increase its digestibility and value as a biofertilizer (Oviasogie et al. 2010). EFB and its nutrients are mineralized into plant-available forms in the process of composting. In the meanwhile, pathogens are destroyed and disease infestation is suppressed by pressed partial sterilization. Mature compost is an excellent organic fertilizer and soil conditioner. When applied to and mixed into the soil, it can promote good soil composition, improve water and nutrient content, and assist erosion control. In the long term, it is beneficial to oil palm sustainable plantation.

Another common use of oil palm biomass is to use it as a renewable energy. For example, mesocarp fiber (MF) and palm kernel shells (PKS) generated by the palm oil mills are commonly used as solid fuels for steam boilers to generate electricity. This can generate enough energy to meet the energy demands of a palm oil mill, making it self-sufficient for energy supply in most palm oil mills. However, due to the incomplete combustion, dark smoke is produced while burning MF and PKS, causing environmental problems. On the other hand, most palm oil mills are using palm oil mill effluent (POME) for biogas production and POME-derived biogas is a good supplementary fuel for power generation in palm oil mills. It is likely to supply the excessive power generated from palm oil mills to the pubic grid.

In order to produce a more generic solid fuel, oil palm biomass such as OPT, EFB, MF, and PKS can be further processed to pellets, which are rich in energy and therefore are high-quality burning fuels for power plants. Palm pellets can substitute for coal and fuel oil as a burning biofuel, as well as bio-based raw material for industrial processes. Oil palm biomass pelleting is a relatively mature technology, which includes crushing, drying, pelleting, cooling, and packing. Due to the abundant resources of oil palm biomass in Malaysia and Indonesia, pellet manufacturers are gathered in this region and they are providing oil palm pellets to overseas markets, such as Europe and South Korea. Besides pelleting, oil palm biomass can be further processed through torrefaction to increase its energy capacity (Lu et al. 2012; Daud et al. 2013). In torrefaction raw biomass is heated in a nonoxidizing atmosphere in the temperature range of 200–300 °C. The main advantage of torrefaction is the amplification of the energy density of biomass.

Apart from fertilizer and renewable solid fuel application, a higher value utilization of oil palm biomass is to process it to wood products, such as plywood, fiber mats, biocomposite, and other bioproducts such as activated carbon. Plywood has been successfully produced from oil palm trunk in combination with the hardwood by the conventional plywood manufacturing process with modifications (Anis et al. 2003; Hashim et al. 2004). Empty fruit bunch is composed of 100 % organic fiber. It is hard and strong. It can be spun and woven into matting. Such palm fiber mats have the right strength and durability to protect the slopes from erosion, while allowing vegetation to flourish. They are commonly used as mulch and for erosion control. In addition, they are also used in highway/railway embankments, drainage channel banks, and in residential areas for beautification and landscaping. More recently, oil palm empty fruit bunch was investigated as a raw material for biodegradable polymer production. Hybrid biocomposite was prepared through the melt and blending techniques with poly(butylene adipate-co-terephthalate) (PBAT) (Siyamak et al. 2012), poly(3-hydroxybutyrate-co-38 mol%-3-hydroxyvalerate) [P(3HB-co-38 mol%-3HV)] (Salim et al. 2011), and polylactic acid (Mohamad Haafiza et al. 2009). The primary advantages of such oil palm fiber-based hybrid composites are its low densities, nonabrasiveness, and biodegradability. In addition, compared with the synthetic biodegradable plastics, such as polylactic acid (PLA), or polyhydroxyalkanoates (PHAs), the hybrid biocomposite made of natural biopolymers is more environmentally friendly and more cost-effective (Figs. 10.2 and 10.3)

In recent years, there has been an increasing interest in converting of oil palm biomass to activated carbon. Activated carbon can find wide applications as adsorbents, catalysts, or catalyst supports. Activated carbon is one of the most important adsorbents from an industrial point of view. It plays a vital role in removal various pollutants from gaseous and liquid phase mixtures. However, the usage of commercial activated carbon is restricting due to the use of non-renewable and expensive raw material such as coal. Therefore, in recent years, many researchers are trying to

Fig. 10.2 EFB compost at Sime Darby palm oil mill

Fig. 10.3 Palm oil mill effluent

Fig. 10.4 EFB pellets

produce low-cost-activated carbons using renewable and cheaper precursors, such as industrial and agricultural by-products. For example, oil palm empty fruit bunch was converted to activated carbon through a thermal carbonization process and it was successfully used for 2,4,6-trichlorophenol removal from wastewater (Hameed et al. 2009) and for its application in super capacitors (Farma et al. 2013). A comprehensive review on activated carbon from oil palm biomass was given by Rafatullah and his colleagues (Rafatullah et al. 2013). By reviewing about 200 recently published articles, it was demonstrated that activated carbons from oil palm biomass exhibited outstanding capabilities for pollutants removal from gas and liquid mixtures and the performance are comparable to those from their commercial counterpart. Therefore, converting of oil palm biomass to activated carbon may provide a good opportunity to small and medium enterprises (SMEs) to valorize oil palm biomass. The challenge might be the cost involved in activated carbon preparation from oil palm biomass as thermal carbonization process is expensive and energy intensive. Further research is necessary to assess the economic feasibility and the environmental impact of the activated carbons produced by oil palm biomass (Rafatullah et al. 2013) (Fig. 10.4).

10.3 Conversion of Oil Palm Biomass to Biofuels

Oil palm biomass is lignocellulosic material containing three main structural components: cellulose, hemicellulose, and lignin. It also contains extractives. The chemical compositions of different parts of oil palm biomass are summarized in Table 10.3.

Table 10.3 Composition of oil palm biomass (Hashim et al. 2011)

		Chemical composition (%)		
Parts of oil palm biomass	Extractives	Cellulose	Hemicellulose	Lignin
Oil palm bark	10.00	18,87	58.95	21.85
Oil palm leaves	20.60	44.53	3.17	27.35
Oil palm frond	3.5	47.76	35.37	20.15
Oil palm shells	–	29.70	18.00	53.40
Mid part of oil palm trunk	14.50	50.21	22.39	20.15
Core-part of oil palm trunk	9.10	43.06	7.67	22.75
Oil palm empty fruit bunch	3.21	50.49	29.6	17.84

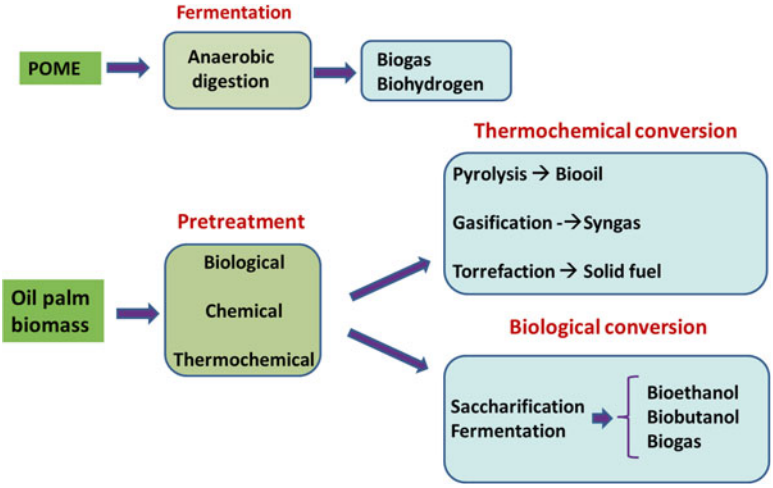

Fig. 10.5 Biofuel production from oil palm biomass

Over the past decade, oil palm biomass has been extensively explored as a feedstock for biofuel production. Generally speaking, oil palm biomass-based biofuel production-related activities can be summarized in Fig. 10.5.

10.3.1 Pretreatment of Solid Oil Palm Biomass

Similar to biofuel production from other lignocellulosic biomass, solid oil palm biomass conversion to biofuels can be classified into thermochemical conversion and biological conversion. Prior to each of the conversion technology, biomass pretreatment is necessary to reduce the recalcitrance of biomass and to enhance its converting efficiency. The purpose of pretreatment is to open its structure and increase its digestibility and subsequently the degree of conversion. Oil palm biomass pretreatment can be classified into biological pretreatment, physical pretreatment, chemical pretreatment, and physical–chemical pretreatment. For biological pretreatment, oxidizing enzymes and white-rot fungi were used to degrade the lignin content in EFB (Syafwina et al. 2002; Amin et al. 2010). Chemical method is the most often used pretreatment method for oil palm biomass, such as two-stage dilute acid hydrolysis (Millati et al. 2011), alkali pretreatment (Han et al. 2011), sequential dilute acid and alkali pretreatment (Kim et al. 2012), alkali and hydrogen peroxide pretreatment (Misson et al. 2009), sequential alkali and phosphoric acid pretreatment (Kim et al. 2012), aqueous ammonia (Jung et al. 2011a), and solvent digestion (Abdullah et al. 2011). However, it seems that alkali pretreatment is the most effective pretreatment method for oil palm biomass according to what is reported in the literature. Han and his colleagues investigated NaOH pretreatment of OPEFB for bioethanol production and a total glucose conversion rate (TGCR) of 86.37 % was obtained (Han et al. 2011). Lignin degradation might contribute to the effectiveness of alkali pretreatment and H_2O_2 posttreatment can further enhance such effects. Physical–chemical pretreatment such as ammonium fiber explosion (AFEX) (Lau et al. 2010) and superheated steam (Bahrin et al. 2012) was also effective in the increase of oil palm biomass digestibility.

10.3.2 Thermochemical Conversion of Solid Oil Palm Biomass

Thermochemical conversion of biomass refers to heating the biomass materials in the absence of oxygen to produce a mixture of gas, liquid, and solid. Such products can be used as fuels after further conversion or upgrading. It can be further classified as pyrolysis, gasification, and torrefaction. Pyrolysis refers to the thermal degradation of the biomass materials in the absence of oxygen conducted at 400–600 °C with short retention time. Its produces a mixture of liquids (water, oil/tars), solids (charcoal), and gases (methane, hydrogen, carbon monoxide, and carbon dioxide) and the composition of such mixture depends on the process parameters. Oil palm EFB fast pyrolysis was investigated using a bench top fluidized bed reactor with a nominal capacity of 150 g/L (Sulaiman and Abdullah 2011). It was found that higher temperature was more favorable for gas production. The bio-oil contained an organic phase predominated by tarry organic compounds (60 %) and an aqueous phase (40 %). The high viscosity of the organic phase and the high water content of the aqueous phase make bio-oil a challenging fuel for boilers and engines. It is worthwhile mentioning that Canada-based Dynamotive and Genting Bio-Oil Sdn Bhd (GBO) of Malaysia is collaboratively running a bio-oil pilot plant in Malaysia using oil palm EFB as the feedstock with the aim to commercialize this technology (Genting Group 2005).

Gasification process is an extended pyrolysis process conducted at elevated temperature range of 800–1,300 °C, which is more favorable to gas production. The gas stream is mainly composed of methane, hydrogen, carbon monoxide, and carbon dioxide. Biomass gasification offers a few advantages, such as less CO_2 emission, smaller footprint for equipment, easy combustion control, and high thermal efficiency. Gasifier design is very critical to ensure minimum energy consumption. Ogi et al. explored EFB gasification using an entrained-flow gasifier at 900 °C (Ogi et al. 2010). More than 95 % (C-equivalent) carbon conversion rate was obtained and the produced gas is rich in hydrogen making it suitable for liquid fuel synthesis. Oil palm EFB was proved to be an ideal candidate for biomass gasification. Oil palm EFB gasification was also investigated in a pilot-scale air-blown fluidized bed reactor (Lahijani and Zainal 2011). Compared to saw dust, at 1,050 °C, oil palm EFB had almost equivalent gas yield and cold gas efficiency. However, the produced gas had lower maximal heating values and higher carbon conversion. It was found that at high temperature, agglomeration was a major issue in EFB gasification. A bench scale fluidized-bed reactor was used for hydrogen-rich gas production (Mohammed et al. 2011a). The increase of temperature greatly enhanced the total gas yield. The gas yield reached the maximum value (~92 wt%) at 1,000 °C and mainly contained H_2 (38.02 vol.%) and CO (36.36 vol.%), making it suitable for further processing to other hydrocarbons. Oil palm EFB was an ideal biomass for gasification due to its high content of volatiles and in turn its high reactivity. At 700 °C, more than 90 % of oil palm EFB was decomposed (Mohammed et al. 2011b). A thermochemical analysis demonstrated that the heating value (HHV), specific heat (c), combustion rate (CR), combustion heat (Q) of the oil palm biomass displayed an increasing trend in the order of EFB, PKS, and MF (Nyakuma et al. 2013). Recently, both oil palm fronds (OPF) (Guangul et al. 2012) and oil palm trunk (OPT) (Nipattummakul et al. 2012) were investigated for gasification and syngas production and it was demonstrated both OPF and OPT were potential in syngas production. Therefore, we can conclude that all solid oil palm biomass are potential feedstock for biomass gasification and syngas production.

Torrefaction removes oxygen from biomass and therefore increases biomass energy density through the thermal process without oxygen. Through torrefaction, EFB, MF, and PKS were processed to potential solid fuels, with MF and PKS exhibited higher energy yield than EFB (Uemura et al. 2011a, b).

The above analysis suggests that thermochemical methods can convert almost all solid oil palm biomass to biofuels and gasification seems to be most suitable. Bio-oil application as a biofuel might be challenging due to its complex composition, high viscosity of the organic phase, and high water content of the aqueous phase.

10.3.3 Biological Conversion of Oil Palm Biomass

Biological conversion of oil palm biomass refers to the extraction of sugar from cellulose and hemicellulose, and then converting such sugar to biofuels through fermentation. It basically involves three major steps: pretreatment, saccharification, and fermentation. Biofuels obtained through oil palm biomass bioconversion include ethanol, butanol, biogas, and biohydrogen. Solid oil palm biomass is extensively studied as a potential feedstock for biofuel production, in particular, bioethanol production. On the other hand, palm oil mill effluent is often investigated for biogas and biohydrogen production.

EFB was pretreated by ammonium fiber expansion (AFEX) for cellulosic ethanol production (Lau et al. 2010). About 90 % of sugar yield was obtained after enzymatic saccharification. Up to 65 g/L glucose was obtained from the water extract of the AFEX-pretreated EFB (9 % solid loading) and it was fermented to ethanol within 24 h without the supplement of nutrients, suggesting its high ferment ability. An ethanol concentration of 18.6 g/L and a productivity of 0.11 g/L/h were obtained from aqueous ammonia soaking pretreated EFB (Jung et al. 2011a). This corresponds to an ethanol yield of 0.33 g ethanol/glucose. Han and his colleagues applied a pilot scale alkali pretreatment of EFB and through simultaneous saccharification and fermentation (SSF) processes, an ethanol titer of 48.54 g/L was obtained at 20 % (w/v) pretreated biomass loading (Han et al. 2011). By far, it is the highest ethanol titer from oil palm biomass. In total 410.48 g of ethanol were produced from 3 kg of raw EFB in a single run using this pilot scale facility. Aqueous ammonia method was also effective in oil palm trunk (OPT) pretreatment (Jung et al. 2011b), 95 % digestibility, and 13.3 g/L ethanol titer were obtained, corresponding to 78.3 % of the theoretical ethanol yield. Two-stage sulfuric acid pretreatment was also successfully applied to oil palm trunk to obtain bioethanol (Chin et al. 2010). Sime Darby Plantation and Mitsui Engineering and Shipbuilding of Japan announced a partnership that produced cellulosic ethanol from up to 1.25 metric tons of palm fruit waste per day in a pilot-scale project with an estimated 35–50,000 gal per year of ethanol (Biofuel Digest). This is the first and sole pilot-scale oil palm biomass to ethanol facility in the world and it was co-located with the Sime Darby's palm oil facilities at Selangor before (Biofuel Digest). Currently, this pilot scale cellulosic ethanol facility is with Tech Guan Group in Malaysia. The aim of the partnership between Mitsui and oil palm plantations in Malaysia is to gather data in support of a potential commercial scale-production facility. Cellulosic ethanol might be the first commercial biofuel from oil palm biomass, although it is not cost-effective compared to the first-generation bioethanol from sugarcane and corns. The advantage of the bioethanol is that it can be further processed to value-added chemicals such as ethylene, polyethylene, ethylene oxide, butanol, butene, butadiene, acetic acid, and ethyl acetate, etc., making cellulosic ethanol an attractive intermediate for value-added chemical production.

In terms of energy capacity and gasoline miscibility, butanol is better than ethanol as a biofuel. Although the advantages of butanol over ethanol are very well known, conversion of oil palm biomass to butanol is not fully explored, probably due to the low product concentration, low productivity, and low yield. EFB was pretreated by alkali followed by enzymatic hydrolysis. Approximately 20 g/L sugar was obtained and only about 1.262 g/L ABE (acetone: butanol: ethanol = 3:6:1) was attained using *Clostridium acetobutylicum* (Noomtim and Cheirsilp 2011). In another case, about 3.47 g/L ABE was obtained from EFB using *Clostridium butyricum* EB6 and it was found that cell growth was inhibited by the accumulated acid (5–13 g/L) (Ibrahim et al. 2012). Both of the above investigations obtained very low ABE concentration. Palm oil mill effluent (POME) has also been investigated as a substrate for butanol production and it was found that pretreatment is very essential for the increase of ABE concentration (Al-Shorgani et al. 2012). POME was pretreated with cellulolytic enzymes and XAD-4 resin, the production of ABE was increased to 4.29 g/L, corresponding to an ABE yield of 0.29 g/g. However, So far, there are no pilot scale facilities to convert oil palm biomass to butanol worldwide.

Palm oil mill effluent has high organic content and is therefore a potential substrate for biogas and biohydrogen production (Ji et al. 2013). Biogas generated from anaerobic digestion of POME can replace palm kernel shell (PKS) and mesocarp fiber (MF) as the boiler fuel for power generation. This way, excessive power generated at palm oil mills can be supplied to the pubic grid or nearby industries. Biogas production has been realized in a lot of palm oil mills (Ji et al. 2013). EFB has also been investigated for biogas production; however, pretreatment is necessary to improve its biogas yield (Nieves et al. 2011). Co-digestion of the pretreated EFB with palm oil mill effluent (POME) can further enhance the biogas production (O-Thong et al. 2012). Biohydrogen production is coupled with biogas production from POME in the anaerobic digestion process and its content was 57 % in the biogas produced (Vijayaraghavan and Desa Ahmad 2006). Pure culture of *Clostridium butyricum* EB6 was used and it seemed to be more favorable to biohydrogen production (Chong et al. 2009); biohydrogen production and productivity reached 3,195 mL H_2/L-medium and 1,034 mL H_2/L-medium/h, respectively. The produced biogas contained 60–70 % hydrogen. After cell immobilization in polyethylene glycol, the hydrogen production reached 5,350 mLH_2/L-POME, and the maximum H_2 production rate was 510 mL H_2/L-POME h (22.7 mol/L h) (Singh et al. 2013). Biohydrogen is produced in the commercial biogas production process as a co-product and pure culture biohydrogen production from POME has not been commercialized.

In summary, oil palm biomass has been extensively investigated for biofuel production, in particular EFB to bioethanol and POME to biogas. The highest ethanol titer, 48.54 g/L, was obtained by Han and his colleagues from alkali-pretreated EFB in a pilot scale reactor (Han et al. 2011) and a pilot scale cellulosic ethanol plant is currently run by Mitsui and Tech Guan Group, Sabah, Malaysia. The commercialization of oil palm biomass to ethanol technology largely depends on the process cost and ethanol yield; however, POME conversion to biogas has now become a reality in a lot of palm oil mills. Other than POME, prior to its bioconversion, the solid oil palm biomass such as OPT, OPF, PKS, MF, and EFB has to be pretreated to enhance their digestibility. While, alkali, aqueous ammonia, and dilute acid pretreatment methods were most often used in laboratory investigation, in industrial scale, steam explosion and hot water pretreatment are often reported, though they were not investigated in the lab scale for oil palm biomass bioconversion.

10.4 Conversion of Oil Palm Biomass to Bio-based Chemicals and Materials

Similar to biofuel production, conversion of oil palm biomass to bio-based chemicals can also be classified into two categories, i.e., thermochemical conversion and biological conversion. On the other hand, palm oil mill effluent (POME) can be

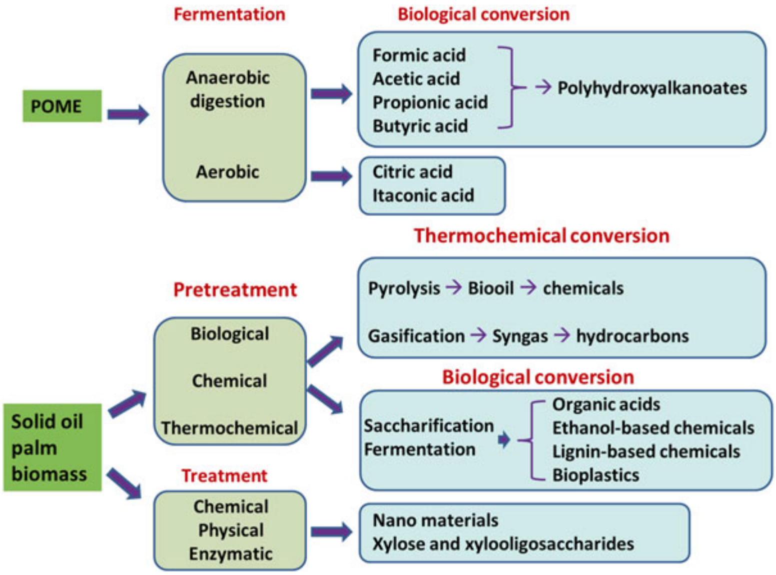

Fig. 10.6 Bio-based chemical and material production from oil palm biomass

converted to bio-based chemicals through anaerobic and aerobic fermentation. Substantial research has been done on the conversion of oil palm biomass to bio-based chemical and materials. It is summarized in Fig. 10.6.

10.4.1 Conversion of Palm Oil Mill Effluent to Bio-based Chemicals and Materials

Palm oil mill effluent (POME) is wastewater produced during the fresh fruit bunch sterilization and oil palm clarification (Borja et al. 1996). It has high chemical oxygen demand (COD), 100 times more than that for municipal wastewater. Raw POME contains 95–96%water, 0.6–0.7 % oil, and 4–5 % total solids (Wu et al. 2009). Reuse the effluent for biotechnological means not only can solve its environmental problems, but also create added value to palm oil mills. POME contains content of carbohydrate, protein, nitrogenous compounds, lipids, and minerals, making it an ideal fermentation media to produce some high value chemicals (Habib et al. 1997). Besides the intensive investigation of biogas and biohydrogen production, POME has also been explored as the feedstock to produce antibiotics, bioinsecticides, biopolymers (e.g., polyhydroxyalkanoates), organic acids, and enzymes so on and so forth (Wu et al. 2009). Among these, organic acids and polyhydroxyalkanoates are the two most extensively investigated fermentation products from POME.

10.4.1.1 Organic Acid Production from POME

A variety of organic acids, such as formic acid, acetic acid, propionic acid, and butyric acids, are produced in the anaerobic digestion of biological wastes (Mumtaz et al. 2008). The composition of such organic acids largely depends on the fermentation conditions. For example, acetic acid was predominant at higher pH, whereas formic acid was predominant at lower pH (Hassan et al. 1996). In addition, incorporating a sludge recycling system with the freezing–thawing method in the anaerobic treatment of POME was able to enhance organic acid production (Yee et al. 2003). Aerobic fermentation of POME has also been investigated to produce organic acids. POME with glucose and wheat flour as the co-substrates was used to produce citric acid using filamentous fungi *Aspergillus* strains with prolonged fermentation time (Jamal et al. 2005; Alam et al. 2008). More recently, it was found that cellulase digestion was an effective way to reduce the cost of citric acid production from POME (Nwuche et al. 2013). Itaconic acid was also produced from POME using an *Aspergillus* sp.; however, little itaconic acid could be obtained. Aerobic fermentation of POME for the production of either citric acid or itaconic acid not only depends on the fungal strains used, but also on the digestibility of POME. Enzymatic digestion is helpful in converting the polysaccharide components, such as cellulose and hemicellulose in POME, to fermentable sugars.

10.4.1.2 Polyhydroxyalkanoate (PHA) Production from POME

As mentioned above, a series of volatile fatty acids (VFAs), such as formic acid, acetic acid, propionic acid, and butyric acids, are produced in anaerobic digestion of POME. Such VFAs are potential platform chemicals for biofuel, chemical, and material production (Chang et al. 2010). Polyhydroxyalkanoates (PHAs) are 100 % biodegradable polymers that accumulate naturally in bacteria via fermentation from feedstock such as vegetable oils, sugar, or industrial wastes. It is likely to improve POME conversion efficiency and energy utilization further if bacterial PHA production can be integrated into the existing mill VFA-producing units (Mumtaz et al. 2010). Hassan and his research group have done so by combining the existing waste water treatment system with PHA production to achieve zero discharge for palm oil industry (Hassan et al. 2002). In POME anaerobic digestion, methanogenic activity was suppressed and organic acids were extracted. Such VFAs were then further separated, purified, clarified, and subsequently used for PHA production (Mumtaz et al. 2008; Sim et al. 2009). The effectiveness of PHA production from POME-derived VFAs depends on the VFA profiles, which in turn was determined by the pH value of the anaerobic process (Hassan et al. 1996). VFA concentration is also very critical and therefore VFAs need to be clarified and concentrated before their conversion to PHAs (Mumtaz et al. 2010). Several studies proved that polymers from POME-derived VFAs are comparable to those obtained from commercially available organic acids. In addition, PHA-producing microorganisms are also essential for the high-yield PHA production from such VFAs, where both pure culture and mixed culture have been investigated (Hassan et al. 2013). The advantage of using mixed microbial cultures is that anaerobic acidogenic fermentation (organic acid production) and aerobic PHA accumulation can be integrated to obtain simultaneous high COD removal and high PHA accumulation (Salmiati et al. 2007). However, it may increase the complexity of PHA recovery from cells. Therefore, further research and development on PHA production from POME should focus on the improvement of PHA content, volumetric productivity and quality while fulfilling the wastewater treatment objectives.

10.4.2 Conversion of Solid Oil Palm Biomass to Bio-based Chemicals and Materials

Apart from the palm oil mill effluent, palm oil mills and plantation generate tremendous amount of solid biomass such as oil palm frond (OPF), oil palm trunk (OPT), empty fruit bunch (EFB), palm kernel shell (PKS), and mesocarp fiber (MF), which contain significant amount of polysaccharides, such as cellulose and hemicellulose, and lignin (Table 10.3). Such solid oil palm biomass is the potential feedstock for bio-based chemical and material production. Similar to the case of biofuel production, both thermochemical and biological approaches can be used to convert solid oil palm biomass to bio-based chemical and materials (Fig. 10.6). Alternatively, like the case of POME, solid oil palm biomass can also be converted to a series of chemical materials through the VFA platform. Although over the past decade, such solid oil palm biomass has been extensively investigated for biofuel production, in particular, bioethanol production, only a few reports can be found on its conversion to bio-based chemicals and materials.

10.4.2.1 Thermochemical Conversion of Solid Oil Palm Biomass to Bio-based Chemicals

Oil palm biomass can be converted to bio-based chemicals through thermochemical processes. Oil palm EFB was pretreated using NaOH, H_2O_2, and $Ca(OH)_2$ to enhance its catalytic pyrolysis. Up to 90 wt% phenolic yields was obtained using Al-MCM-41 as the catalysts, whereas only 67 wt% phenolic yields were obtained for the untreated EFB (Misson et al. 2009). Phenols took up to 81 % of the liquid oil fraction of the pyrolysis product for the treated EFB. Besides phenol, the liquid oil also contained alcohols, acids, aldehydes, ketones, alkanes, alkenes and esters, etc. Such bio-oil fraction can be further upgraded to biofuels or bio-based chemicals. Lignin is a potential substitute for the expensive petroleum-derived phenolic compounds as it is an amorphous polymer composed of phenyl propane. EFB was converted to lignin through liquefaction process using ionic liquid and the highest lignin yield of 26.6 % was achieved at the optimum condition (Sidik et al. 2013). Lignin can be further converted to aromatic-based biochemical and biofuels through depolymerization in aqueous alkaline solution (Beauchet et al. 2012). Depending on the reaction conditions four fractions of products were obtained: (1) gas (mainly CO_2); (2) small organic compounds (methanol, acetic acid, formic acid, etc.); (3) aromatic monomers (up to 19.1 wt% of lignin); (4) oligomers (polyaromaticmolecules) and modified lignin (45–70 wt%). At high severities (315 °C) pyrocatechol was most abundant (up to 25.8 % selectivity). Using a hybrid catalyst comprising of modified zeolite and metal halide, EFB has also been converted to levulinic acid and up to 55.2 % oflevulinic acid yield was attained (Yaaini et al. 2012).

10.4.2.2 Biological Conversion of Solid Oil Palm Biomass to Bio-based Chemicals

Besides thermochemical conversion, biological conversion of the solid oil palm biomass to bio-based chemicals has also been investigated. As mentioned earlier, ethanol can be produced from oil palm biomass and such ethanol can be further processed to value-added chemicals such as ethylene, polyethylene, ethylene oxide, butanol, butane, butadiene, acetic acid, ethyl acetate, etc. In addition, oil palm biomass can also be converted to other chemicals through fermentation. Citric acid production from EFB was investigated through solid state fermentation using *Aspergillus niger* strains and up to 369 g citric acid was obtained from 1 kg dry EFB (Bari et al. 2009, 2010; Alama et al. 2010). Citric acid yield obtained using EFB was quite comparable to that obtained using other agricultural residues, such as rice straw. This suggests that citric acid production is an economic way to add value to such oil palm biomass. Lovastatin is a potent drug to lower the blood cholesterol levels and it was the first accepted statin as a hyper cholesterolemic drug by United States Food and Drug Administration (USFDA) (Tobert 2003). More recently, through solid state fermentation using *Aspergillus terreus*ATCC 20542, EFB was used to produce lovastatin and the yield of 70.17 mg lovastin/kg dry EFB was obtained when EFB was cofermented with soybean meal (Jahromi et al. 2012). Although the yield of lovastatin is low, it proves that it is possible to valorize such oil palm biomass to high value chemicals, such as pharmaceuticals. Bio-based chemicals can also be obtained by chemical or enzymatic hydrolysis of the oil palm biomass followed by bioconversion of the hydrolyzate. EFB was hydrolyzed using dilute H_2SO_4 and H_3PO_4 followed by over-liming using $Ca(OH)_2$. Such EFB hydrolyzate (containing mainly xylose) was used for lactic acid production using *Bacillus coagulans* JI12 and 59.2 g/L of lactic acid was produced within 9.5 h, with a lactic acid yield of 97 % and a productivity of 6.2 g/L/h (Ye et al. 2013). In a recent report, the enzymatic EFB hydrolyzate (containing mainly glucose and xylose) was used for polyhydroxybutyrate (PHB) using *Bacillus megaterium* R11 (Zhang et al. 2013). PHB content reached about 60 % in cell dry weight and 12.48 g/L PHB was obtained from EFB hydrolyzate containing 60 g/L sugar with PHB productivity of 0.260 g/L/h. Unlike EFB, oil palm frond (OPF) contains free sugars and OPF juice can be obtained by pressing the OPF using a sugarcane pressing machine (Zahari et al. 2012; Mohd Zahari et al. 2012). Such OPF juice contained a mixture of sugars such as glucose, sucrose, and fructose, where the glucose accounts for 70 %. OPF juice was used for PHB production, 2.72 g/L and 5.0 g/L of PHB was respectively obtained using *Cupriavidus necator* CCUG 52238 T (Zahari et al. 2012) and *Cupriavidus necator* CCUG52238 (Mohd Zahari et al. 2012). Further improvement of PHB production from OPF juice might be done through the use of high-content PHB-accumulating microbial strains and the optimization of fermentation conditions.

10.4.2.3 Value-added Material Production

In addition to bio-based chemicals, oil palm biomass has also been investigated for value-added material production. Sulfur-free chemical treatments were applied to oil palm EFB to generate cellulose pulps (Ferrer et al. 2012). Nanofibrillated cellulose (NFC) and nanopaper were produced from such cellulose pulps through microfluidization and over-pressing. The NFC grades compared fairly well with those produced from bleached wood fibers. Oil palm trunk (OPT) and oil palm frond (OPF) were used to produce fibrous materials (FM) and alkali-treated fibrous residues (FR) (Fung et al. 2010). The soluble fraction from alkali treatment of fibers was electrospun into nanofibers. Such nanofibers were further developed into nano encapsulants for drug delivery. As mentioned earlier, currently mesocarp fiber and palm kernel shell are mainly used as solid fuels for boilers in palm oil mills. After combustion, approximately 5 % ash is produced and such oil palm ash (OPA) can be further utilized for high-value material production. After high-energy ball milling, OPA was converted into a nano-structured materials and nano particles. The nano-structured OPA was suitable to be used as reinforcement for nanocomposites fabrication.

10.4.2.4 Xylose and Xylooligosaccharides Production

Sugar and sugar oligomers can be obtained from hydrolysis of solid oil palm biomass. As mentioned earlier, the key components of lignocellulosic biomass are cellulose, hemicellulose, and lignin (Table 10.3). Xylose is the main monomeric sugar in hemicellulose. Through chemical and biochemical processes, xylose can be used as a substrate for the production of a wide variety of compounds (Almeida e Silva et al. 1995), such as xylitol (Zhang et al. 2012). Xylitol can be used as an alternative sweetener and an anticariogenic agent. Dilute H_2SO_4 was used to treat oil palm empty fruit to extract xylose (Rahman et al. 2007). Xylose yield of 91.27 % and selectivity of 17.97 g/g were obtained under the optimal conditions. H_2SO_4 seemed to be better than H_3PO_4 in the recovery of xylose from oil palm EFB (Tan et al. 2013). Higher titer of xylose can be obtained if the solid loading can be further increased. Besides xylose, xylose oligomers or xylooligosaccharides (XOs) can also be obtained from hemicellulose. XOs are indigestible xylose-based oligomers. XOs have also been used in food ingredients, pharmaceuticals, feed formulations, and agricultural products (Vazquez et al. 2000; Moure et al. 2006). Oil palm fronds

[OPF] were investigated to produce XOs through auto hydrolysis followed by enzymatic treatment (Sabiha-Hanim et al. 2011). Autoclaving of palm fronds at 121 °C for 60 min recovered 75 % of the solid residue, containing 57.9 % cellulose and 18 % Klason lignin. The autohydrolyzate contained 14.94 % hemicellulose, corresponding to a fractionation efficiency of 49.20 %. The autohydrolyzate was hydrolyzed using 8 U of endoxylanase at 40 °C for 24 h and a solution containing 17.5 % xylooligosaccharides and 25.6 % xylose was generated. These results clearly indicate that OPF is a potential resource for XOs production. Oil palm EFB has also been investigated for xylooligosaccharides, in particular, xylobiose, production by chemical and enzymatic method (Lakshmi et al. 2012). Oil palm EFB was pretreated chemically and was then hydrolyzed using FXY-1 xylanase. A maximum 262 mg of xylobiose was produced from 1.0 g of pretreated EFB fiber corresponding to a xylobiose yield of 78.67 g/100 g (based on xylan in the pretreated EFB fiber). Further improvement in the yield of XOs might be obtained through thermochemical methods (Otieno and Ahring 2012).

10.5 Conclusion and Future Perspective

Oil palm biomass, including solid oil palm biomass and palm oil mill effluent, is a potential feedstock for value-added fuel, chemical, and material production. While the use of solid oil palm biomass as a fertilizer and mulch for oil palm plantation is well established, processing it to pellets, wood products, fiber mats, biocomposite, and activated carbon can bring more value to such biomass. Oil palm biomass pelleting, wood products, and fiber mats processing are relatively straight-forward, mature, and has been commercialized, whereas technology on biocomposite and activated carbon from oil palm biomass needs to be further improved to make it cost-effective. Despite the fact that biogas production from POME has been realized, biofuel production from oil palm biomass has not been commercialized though cellulosic ethanol and bio-oil technology are being demonstrated at the pilot scales. Commercialization of biofuel technology highly depends on the technology improvement and subsequent cost reduction. Citric acid production is probably the most mature bio-based chemical technology from oil palm biomass and it is quite commercializable as much similar citric acid yield was obtained using oil palm empty fruit bunch when compared to the use of other agricultural residue, such as rice straw. Although intensive research has been done on the conversion of POME to polyhydroxyalkanoate (PHA), due to the complexity of the process, low PHA content, and consequently low PHA yield, such process might not be commercialized in the near future. Similar to cellulosic ethanol technology, biological conversion of oil palm biomass to bio-based chemicals through saccharification followed by fermentation faces the problems of high cost due to the recalcitrance of the solid oil palm biomass. Biomass pretreatment and enzymatic saccharification should be improved to reduce the process cost. Alternatively, higher value chemicals, such as pharmaceutical products, can be produced from such processes to make them more economically feasible. Higher value products, such as nanomaterials, were produced using oil palm biomass; however, it is still at the initial stage. Although only a few studies reported the production of xylose and its oligomers from oil palm biomass, it is possibly a good technology to be commercialized as xylooligosaccharides can be used as ingredients in food and health-promoting products; therefore having higher value. Malaysia government is willing to mobilize 20 million tons of dryoil palm biomass for high value use (AIM 2011). However, it is unclear what high-value products can be firstly produced commercially from such biomass. Biorefinery of oil palm biomass to multiple value-added products, such as xylooligosaccharides, ethanol and ethanol-based chemicals, lignin and lignin-based chemicals, as well as animal feed or fertilizer from the fermentation residue, might be an ultimate solution.

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Chapter 11

Polylactic Acid-Based Kenaf Biomass Synthesized via Ring Opening Polymerization

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Abstract An extensive effort was made by many industries to shrink the usage of petroleum-based product or synthetic fiber owing to raising consciousness in the environmental issues. Realizing this phenomenon, research works on biodegradable polymers from natural fibers and production of eco-friendly products are geared towards replacing the existing petroleum-based products. One of the promising polymers is polylactic acid (PLA) and it has good mechanical and thermal properties like other thermoplastic such as polyolefin. The uniqueness of the current research is that PLA was synthesized in house through polymerization of lactic acid (LA) obtained from a simple fermentation product of kenaf biomass (KB). KB was introduced as the raw material in chemical pretreatment process to liberate glucose which was then used as the carbon sources in microbial fermentation via *Lactobacillus rhamnosus* to produce lactic acid. Lactic acid produced was purified before being polymerized via ring opening polymerization (ROP) method. The PLA obtained was characterized and analyzed using Fourier transform infrared (FTIR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

Keywords Polylactic acid • Ring opening polymerization • Kenaf biomass • Fermentation • Pretreatment

11.1 Introduction

Biodegradable polymers are widely used in the mass production applications. Basically they can be used not only for packaging, fibers, and films, but also in biomedical applications (Tuominen et al. 2002). The important features that need to be upheld by these polymers in order to be used in these applications are that they can easily degrade or biodegradable, nontoxic, and safe to the earth and environment. In addition, in medical world, polymers should be bioresorbable and also biocompatible. Thus, the polymers should be investigated thoroughly in order to fulfil the above requirements.

One of the possible polymers that can fulfil all the criteria needed in this matter is polylactic acid (PLA). PLA is a polymer produced from polymerization of lactic acid, which is a simple product of fermentation process. Theoretically, PLA belongs to aliphatic polyesters family which is produced from α-hydroxy acids. These acids include polyglycolic acid or polymandelic acid and were considered as biodegradable and compostable (Garlotta 2002). PLA is a thermoplastic, which possesses certain properties such as high strength and modulus that is produced from renewable resources for medical and packaging applications. It is easily processed into required parts, film, or fibers (Hartmann 1998).

Beside that PLA can also be broken down or decomposed either by simple hydrolysis of the ester bond or by the absence of enzyme which is used as a catalyst in this hydrolysis process. The rate of degradation is reliant on the size and shape of the particle, the isomer ratio, and the temperature of the hydrolysis process (Hartmann 1998; Garlotta 2002). Recently, the biodegradable and biocompatible plastics manufacturer such as PLA has gained more focus in finding a replacement for the plastic due to the fluctuating of oil price (Yen et al. 2009). Thus, the alternative approach in optimizing the production of PLA is by enhancing the synthesis methods. In general, there are two methods to produce the PLA which are polycondensation and ring-opening polymerization (ROP) methods (Avella et al. 2009).

Lactic acid (LA), scientifically known as 2-hydroxy propionic acid ($CH_3CHOHCOOH$), is the basic building monomers or blocks in PLA. Lactic acid, also known as milk acid, is a hydroxy carboxylic acid which was first discovered in the year 1780 by a Swedish chemist Carl Wilhelm Scheele (Hartmann 1998; Narayanan et al. 2004). Basically, lactic acid has been used in broad field of applications such as in food, pharmaceutical, and cosmetic industries. Nowadays, due to the alarming environment issue, lactic acid is emerging into polymer industry since it offers good feedstock potential for the biodegradable polymer (Narayanan et al. 2004). Besides, the lactic acid production has a good prospect and attraction in the research and development area.

The current demand of lactic acid has significantly increased due to its potential as a monomer for production of biodegradable polymer (PLA) which can be used as substitute for synthetic polymers derived from petroleum resources (Wee et al. 2004). According to Åkerberg and Zacchi (2000), the world production of lactic acid yield is approximately 50,000 tons/year and the commercial price of lactic acid is depending on the grade of the food sources used in the mass production. Thus, the price of commercial lactic acid is in the range~~s~~ of USD 1.40 kg for 50 %–USD 1.90 kg for 88 % food grade lactic acid. Due to this enormous demand, many companies had readily made a huge investment in lactic acid production. Cargill, Inc. in Minneapolis, USA, is one of the six companies that announced their involvement in developing PLA polymer. Cargill, Inc. is the largest company operating the PLA facilities.

In general, there are two methods to produce the PLA which are polycondensation and ring-opening polymerization (ROP) methods (Avella et al. 2009). However, the production of lactic acid using biological fermentation route is more preferable compared to chemical synthesis since it offers great advantages where it may be able to reduce the environmental burden, decrease consumption of petroleum resources as well as use cheap polysaccharide. Indeed, chemical synthesis can give a great harm not only to human body but also to the environment (Wee et al. 2004; Åkerberg and Zacchi 2000). This biological fermentation method is also more preferable since cheap polysaccharide and renewable raw materials such as starch or cellulose (Åkerberg and Zacchi 2000) are abundantly available locally.

As stated by Narayanan et al. (2004) and Maas et al. (2008), lactic acid is produced commercially via microbial or biological fermentation of the carbohydrates glucose, sucrose, lactose, and starch or maltose is derived from feedstock such as whey, potato, and barley malt. However, these feedstocks are not consistent with market production as the price seems to be gradually increased parallel to their high demand of food supplies.

In order to counteract these feedstock problems, new resources that are cheap, sustainable, and eco-friendly to replace the existing raw materials for lactic acid or feedstock need to be investigated by researchers. While searching for the alternative raw materials, the researchers found that the natural resources have fulfilled the essential criteria (John and Thomas 2008). Basically the natural resources can be divided into several categories depending on their origins which are plant-, animal-, or mineral-based resources. However, the plant fiber is more preferable as it consists of cellulose (John and Thomas 2008).

One of the potential natural resource-based plants is kenaf biomass. Kenaf, scientifically known as *Hibiscus cannabinus. L*, is a warm season annual crop. Kenaf is actively cultivated since it grows faster with the height reaching up to 8–20 ft. It is being developed as a non-wood fiber crop, which contains long soft bast fibers contributing 30–40 % of the dry weight of the stem. The central core of the stem contains a weakly disbursed pith cells surrounded by a thick cylinder of short woody fibers. Other supporting characteristics of kenaf are the low cost of its productions and the convenient availability of this source.

The use of PLA had increased tremendously from time to time and it had been used in many industries especially in food packaging. However, the price of PLA is very expensive and it is reliant on the commercial price of lactic acid since lactic acid is the basic building monomers of PLA. As mentioned before, the commercial raw material used in lactic acid production is derived from feedstocks such as starch, beet sugar, whey, and barley malt. Nonetheless, these feedstocks are not sufficient since they must compete with the demand in other fields, especially in food processing industry and in daily consumption. This situation had led to the increase of lactic acid price. Besides, the price of lactic acid is also depending on the grade of the feedstocks used in the lactic acid productions. Therefore, it is necessary to explore a reliable, less expensive raw material and to optimize the bioconversion conditions in order to ensure the success in the commercialization of PLA. While searching for the alternative raw materials which are not only cheap but also compatible to the environment, it is found that the natural resources especially biomass (plant fiber) such as kenaf had fulfilled the criteria.

The main aim of this study is to synthesize PLA from kenaf biomass. Basically, this study was divided into three major parts which are chemical pretreatment process, fermentation process as well as the purification and polymerization process. Glucose which is the carbon source of the PLA construction was liberated from the kenaf biomass using chemical pretreatment process since kenaf biomass has very complex structure that contains three major components which are lignin, cellulose, and hemicelluloses. Then, the fermentation of lactic acid via *L.* rhamnosus was carried out using the glucose produced. Next, the polymerization of PLA process via ring-opening polymerization (ROP) method was conducted using the lactic acid produced from the kenaf biomass, and finally, the PLA produced was analyzed and characterized in order to determine its properties.

11.2 Materials and Methods

11.2.1 Sample Preparation

Kenaf biomass, also known as kenaf core, was obtained from Kenaf Natural Fiber Industries (KFI) Sdn. Bhd., Kelantan, Malaysia. Kenaf biomass is the waste from the separation process of kenaf bast and core. In general, one stalk of kenaf stem

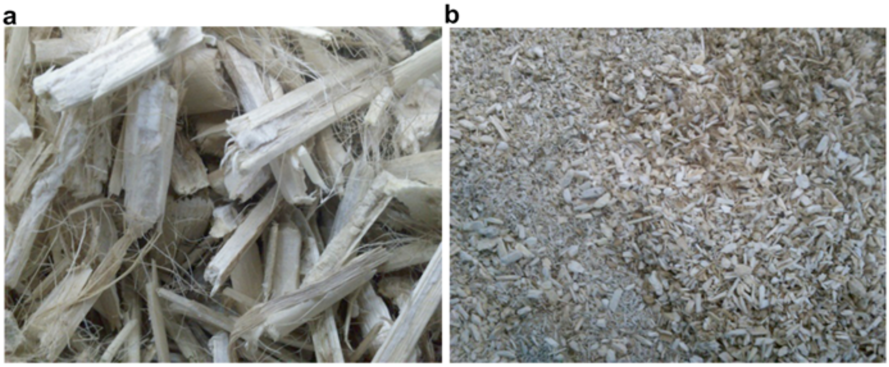

Fig. 11.1 Kenaf biomass (**a**) before being crushed and (**b**) after being crushed

Table 11.1 Parameters used in chemical pretreatment process

	Level		
Parameter	Low	Medium	High
Mixing time (min)	30	45	60
Temperature (°C)	160	180	200

generates about 70 % of core. Kenaf core or biomass was crushed using Hitop SY-20 crusher and sieved with Analysette 3 PRO siever into 100 μm mesh size. Figure 11.1 shows kenaf biomass before and after being crushed.

11.2.2 Chemical Pretreatment Process

This process starts with the screening of the solvents in order to select the best solvent for the glucose production. In fact the choice of the most suitable solvent is very important and crucial. Thus, determination of the best solvent used was carried out by using acid and alkaline solution. In this process, there were three solutions used which are 2 % (v/v) of sulfuric acid (H_2SO_4), 2 % (w/v) of sodium hydroxide (NaOH), and 2 % (v/v) of ammonium sulfate $(NH_4)_2SO_4$. All these solutions were prepared in 100 mL working volume. For the screening process, the mass of kenaf biomass, speed, mixing time, and temperature were held as constants (3 g, 100 rpm, 45 min and 180 °C, respectively). These screenings of the solvent process were carried out using Heidolph MR 3001 hot plate.

After obtaining the most suitable and significant solvents that can liberate high glucose concentration, 11 runs of experiments were designed using two parameters which are the mixing time and temperature. The main aim of this process is to attain the best condition that can liberate maximum glucose concentration. Table 11.1 shows parameters for the experiments that were carried out with two replications. The chemical pretreatment process was conducted using Heidolph MR 3001 hot plate with 100 rpm of agitation speed and 3 g of kenaf biomass.

Table 11.2 Media composition and concentration for fermentation

	Level	
Nutrient (g)	Low	High
Peptone	0	2
Yeast extract	0.8	2.5

11.2.3 Inoculum Preparation and Fermentation Process

Fermentation of lactic acid process was conducted in shake flask via *Lactobacillus rhamnosus* as its microorganism. The fermentation process starts by inoculating *L. rhamnosus* in de Man, Rogosa and Sharpe (MRS) media. Basically, the preparation of inoculum was started by transferring the stock culture into MRS broth as described in Bergey's Manual of Systematic Bacteriology (English et al. 1994). After the growth of culture, the microbes (*L. rhamnosus*) were transferred to a plate of MRS agar. The plate culture was incubated at 37 °C for about 48 h in order to allow sufficient growth of colonies. Next, a single colony of *L. rhamnosus* was inoculated into 10 mL MRS broth media which was then incubated at 37 °C for 24 h followed by; 1 mL of inoculum transferred into bijou bottle containing 9 mL media. Cultures were incubated for 10 h at 37 °C before being transferred into shake flask (Kandler and Weiss 1986).

The fermentation process of shake flask was carried out in order to determine the superlative media composition that produces the highest lactic acid concentration. In this process, the medium culture that was prepared in 100 mL consists of hydrolyzed glucose, lactose 5 g, Tween 80 0.25 mL, K_2HPO_4 0.5 g, $C_2H_3NaO_2$ 1.25 g, $(NH_3)_2SO_4$ 0.5 g, $MnSO_4$ 0.0125 g, and $MgSO_4$ 0.05 g, and certain nutrients such as peptone and yeast extract were varied in order to obtain optimum growth of the bacteria. Two different media compositions used are shown in Table 11.2.

The initial pH of the media in the shake flask was adjusted to pH 6 by adding sodium hydroxide (NaOH) or hydrochloric acid (HCl). All the media were sterilized at 121 °C for 20 min. The fermentation process was conducted for 3 days at 37 °C with 150 rpm agitation speed. The experiments were conducted for 11 runs with three replications in order to obtain good quality results.

11.2.4 Purification and Polymerization Processes

The purification process was carried out using IKA® RV 10 digital rotary distiller. In this process, the lactic acid obtained from the fermentation process was hydrolyzed and purified before being polymerized. The purification process was carried out with continuous magnetic stirring which was at 6 rpm and refluxing at 60 °C. Purification process was performed under the vacuum atmosphere which was at 8 m bars for 3 h. During the process, the temperature was gradually increased by 5 °C up till 60 °C in order to avoid the degradation of lactic acid as well as to evade lactide sublimation without using drying agent (Orozco et al. 2007).

After purification of lactic acid, the lactic acid samples were polymerized into polylactic acid (PLA) via ring-opening polymerization (ROP) method. In this polymerization process, the container used was pretreated before being used in this process. This pretreatment process was conducted at room temperature where the container was soaked in the mild acid (H_2SO_4) for overnight. After 24 h, the container was washed using distilled water for several times before rinsing with acetone. Essentially, the main reason the container was rinsed with acetone is to avoid the existence of water molecule in the container. Subsequently, the container was dried in the controlled atmosphere (oven) for 24 h at 120 °C. The polymerization process was carried out after the container was being treated.

The polymerization process was started by cooling down the treated container up till room temperature using dry nitrogen gas, N_2. Next, 3.6 g of the dehydrate lactic acid and 0.5 mL of freshly prepared stannous chloride ($SnCl_2$) in diethyl ether were transferred into the container under the nitrogen (N_2) ambiance. The excess amount of N_2 was evacuated using vacuum pump for about 5 min before being appropriately sealed. Then, the container was placed in the oven for 1 h at 160 °C. After one hour, the container was removed from the oven and placed speedily in the refrigerator in order to cease the polymerization process (Kaitian et al. 1996). Finally, the PLA produced was dissolved in ethanol and filter using filter paper before being dried in the oven for 24 h at 60 °C.

11.2.5 Analysis and Characterization

The total glucose and dextrin content as well as the existence of lactic acid was analyzed using high pressure liquid chromatography (HPLC) (Agilent model 1200 series) which comprised a quaternary pump with auto-sampler injector, micro-degassers, column compartment equipped with thermostat, and a diode array detector. The column used was a ZORBAX Eclipse XDB-C18, buffer used was deionized water/acetonitrile (1:99 v/v), and the column used for separation was allowed at a flow rate of 1.0 mL/min for 15 min with the temperature of 25 °C and the injection volume of 1 μL.

The molecular weight of the PLA was analyzed using gel permeation chromatography (GPC) (Waters model 4000 series) which was equipped with RI detector analysis carried out using two types of column which are PLgel Mixed B (500–10,000,000 Da) and PLgel individual pore (up to 4,000 Da). Both of these columns were placed in series and operated at flow rate of 1 mL/min for 45 min. The temperature of columns was maintained at 25 °C and the eluent which used as a buffer was ~~is~~ *N*-Methyl-2-pyrrolidone (NMP). The polydispersity (PD) index was a measurement of the broadness of the polymer molecular weight distribution.

In this study, there were several characterizations that took place in order to determine the chemical bonding, thermal stability, and thermal degradation. Perkin Elmer (Spectrum -100) Fourier transform infrared (FTIR) spectroscopy was used to indicate and determine the chemical bonding or functional groups that existed in PLA. The PLA samples were analyzed by four scans with the resolutions of spectrum in the range of 4,000–450 cm^{-1}.

The thermal stability analysis was carried out using Mettler Toledo 823E differential scanning calorimetry (DSC). DSC was used in order to analyze and determine the glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and energy absorbed during phase change. For DSC analysis, about 5 mg of PLA produced was pressed into the sample capsule before it began to heat up. DSC was run by using the fastest heating ramp to reach 190 °C and the fastest cooling rate down to −50 °C in order to remove the thermal history (Orozco et al. 2007). The temperature range was 24–300 °C with a heating rate of 10 °C/min.

Q Series thermogravimetric analysis (TGA) was conducted based on the ASTM D3850. TGA was used to determine the degradation/hydration, weight loss in materials, decomposition as well as the thermal stability. TGA measurement was subjected to the temperature of the controlled or surrounding atmosphere. The temperature range for TGA was 24–800 °C with a heating rate of 10 °C/min.

11.3 Results and Discussion

11.3.1 Chemical Pretreatment Process

This study started with the production of glucose which is acting as the carbon source in producing PLA monomer that is lactic acid. Basically, kenaf biomass (plant fiber) has a very complex structure since it contains three major elements in it. These three major elements are lignin, hemicelluloses, and celluloses. Thus, in order to liberate and obtain the glucose from the kenaf biomass, it needs to be treated to remove the lignin and hemicelluloses contents, to reduce crystallinity of cellulose, and to increase porosity. This process is known as the chemical pretreatment process.

Basically, there were three solvents or chemicals used in this chemical pretreatment in order to determine the most significant solvent that can liberate maximum glucose production. The solvents or chemicals used in this study were sulfuric acid (H_2SO_4) as the acid solvent and the sodium hydroxide (NaOH) and ammonium sulfate ($(NH_4)_2SO_4$) as the alkaline solvents. Each type of these solvents was either acid or alkaline solvent. These solvents have their own purposes and utility as well as their own advantages and disadvantages in treating the natural fibers. These natural fibers were used as raw materials in this study and the treatment process was carried out to break down complex structures as well as to rupture their cellulose bonding into a simple structure which is glucose.

Therefore, in order to find the most suitable and the best solvents that can reduce the crystallinity of the cellulose bonding as well as can remove the lignin and hemicellulose bonding, the acid and alkaline chemicals or solvents used were screened. In this screening process of solvents, there are three different types of

Table 11.3 Average glucose concentration from screening the best pretreatment solvents

Solvent	Replicate 1 (g/L)	Replicate 2 (g/L)	Average glucose concentration (g/L)
$(NH_4)_2SO_4$	0.225	0.230	0.2275
H_2SO_4	1.051	0.968	1.0095
NaOH	0.458	0.721	0.5895

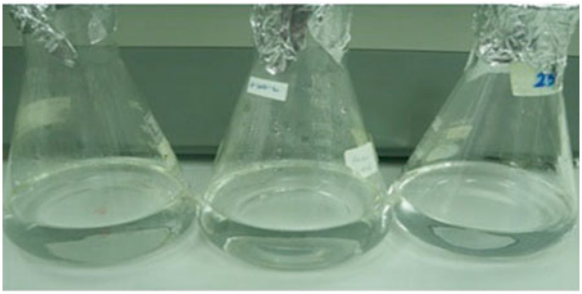

Fig. 11.2 The color of the solvents before the pretreatment process

Fig. 11.3 The color of the solvents after the pretreatment process

solvents (H_2SO_4, NaOH, and $(NH_4)_2SO_4$) used in this pretreatment process. Previously, a study carried out by Nurhafizah et al. (2011) had proven that the two most significant parameters that were affecting the production of glucose from kenaf biomass are the mixing time and temperature. Thus, these two parameters were used during the screening process of solvents as fixed conditions in order to distinguish the most significant solvent that produced maximum glucose concentration. Basically, the process parameters were fixed at 180 °C for 45 min on the hot plate with the ratio of the raw material (kenaf biomass) to solvent of 3 g of kenaf biomass in 100 mL solvent which is 0.3:10. The result of screening of solvents was obtained from HPLC and the average of glucose concentration was calculated and recorded in Table 11.3, while the color changes in the solvents were observed as shown in Figs. 11.2 and 11.3.

Figure 11.3 shows the color changes that occurred when the kenaf biomass was treated with three different solvents or chemicals. The color in each solvent changed from colorless to yellowish or brownish in which NaOH solvent resulted in darker brown solution compared to $(NH_4)_2SO_4$ and H_2SO_4. Besides, the dark brown showed in NaOH solution indicated high production of reducing sugar (mixture of sugar).

Table 11.4 Results of glucose and dextrin concentration for pretreatment process

Run	Mixing time (min)	Temperature (°C)	Glucose (g/L)	Dextrin (g/L)
1	30	180	0.366	38.48
2	60	180	0.754	43.009
3	30	160	0.334	39.617
4	45	200	0.457	40.165
5	45	180	0.388	38.385
6	60	200	3.397	50.777
7	45	180	0.439	39.335
8	30	200	0.374	39.295
9	60	160	0.531	37.553
10	45	180	0.62	41.944

It also signified that the sugar produced was burned. Principally, these color changes indicated that hydrolysis or pretreatment reaction had occurred in each solvent. Due to this reason, HPLC was used in order to determine the concentration of glucose in all solvents. The results in Table 11.1 show that the highest conversions of glucose were obtained by H_2SO_4, which is 1.0095 g/L, and followed by NaOH and $(NH_4)_2SO_4$,which are 0.5895 g/L and 0.2275 g/L, respectively. Even though NaOH produced high reducing sugar; however, the glucose produced was half of the glucose produced in H_2SO_4. Therefore, H_2SO_4 was used for further treatment since it gave the highest glucose conversion.

Thus, by using H_2SO_4 as the main solvent and mixing time and temperature as the variables, 11 runs of experiments with fixed agitation speed were designed to find the conditions that can give the maximum glucose production as shown in Table 11.4. The main reason of this agitation speed is to circulate the heat received from the hot plate across the entire acid solution as well as to control the solution temperature.

Table 11.4 shows the attained glucose and dextrin results after the pretreatment process. From Table 11.4, it was found that Run 6 gave the highest glucose and dextrin concentrations which are 3.397 g/L and 50.777 g/L, respectively, where the mixing time and temperature used are the highest. Meanwhile, Run 3 produced the lowest glucose which was around 0.334 g/L; however, the concentration of dextrin was considerably high which was 39.617 g/L compared to Run 9 which gave the lowest dextrin production which was 37.553 g/L. Table 11.3 clearly shows the drastic change in the production of glucose. According to Torget et al. (2000), the higher the temperature, the less time will be needed for pretreatment. However, different phenomenon occurred in the study where the higher the mixing time and temperature needed in this pretreatment process the higher glucose and dextrin concentrations produced. Figure 11.4 shows peak obtained from high pressure liquid chromatography analysis which indicated the production of glucose and dextrin. From the figure it showed that the first peak which is around 2.821 min belongs to dextrin, while the second peak which is about 4.275 belongs to glucose.

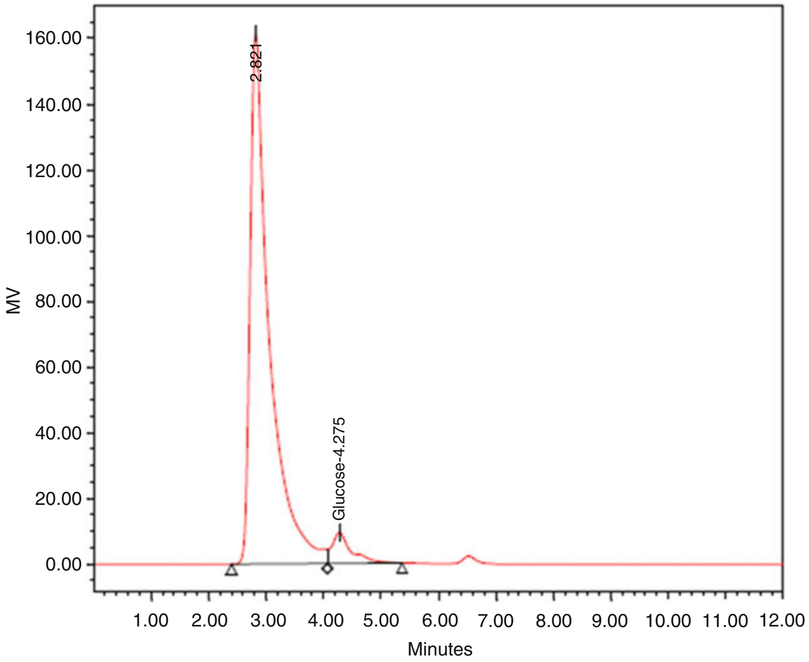

Fig. 11.4 Peak obtained from HPLC analysis

11.3.2 Fermentation Process

The fermentation process was carried out after obtaining the best conditions or parameters that can produce maximum glucose production. In this process, the glucose produced during the pretreatment process was used in the media prepared which served as the carbon source in the lactic acid production. The main aim of this fermentation process is to determine the best media composition that could produce the maximum amount of lactic acid concentration. By using hydrolyzed glucose or the glucose obtained from pretreatment process, 11 runs of experiments were carried out as tabulated in Table 11.5 by varying the amount of protein compositions which are peptone and yeast extract as the limiting parameters.

From the table it was found that Run 5 gave the maximum yield of lactic acid concentration which is 10.851 g/L obtained when 2 g of peptone and 2.5 g of yeast extract were used as the nutrients. Meanwhile, Run 3 produced the lowest yield of lactic acid concentration which is 1.069 g/L when using only 0.8 g of yeast extract as its protein sources. From Table 11.5, it can be concluded that as the amount of peptone decreases (0 or 1 g), the yield of lactic acid concentration is also decreased. The yield of lactic acid obtained in this study can be considered as high compared to the study conducted by Wee and Ryu (2009) which also used lignocellulosic material as its raw material. According to Wee and Ryu (2009), the production of lactic acid using lignocellulosic material as its raw material yielded

Table 11.5 Results of lactic acid concentration from fermentation process

Run	Peptone (g)	Yeast extract (g)	Lactic acid (g/L)
1	2	0.8	6.945
2	1	1.65	3.488
3	0	0.8	1.069
4	1	1.65	4.375
5	2	2.5	10.851
6	1	0.8	1.389
7	1	2.5	3.178
8	0	1.65	1.072
9	2	1.65	6.091
10	1	1.65	4.169
11	0	2.5	3.679

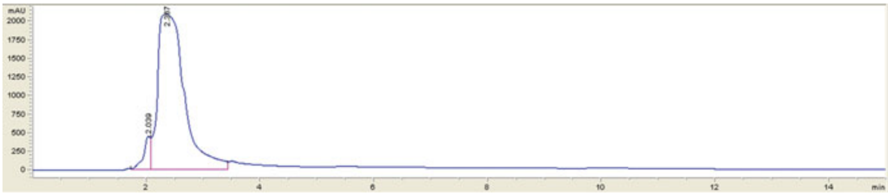

Fig. 11.5 Lactic acid peak obtained from HPLC analysis

quite low lactic acid which was around 0.9 g/g. Figure 11.5 shows the lactic acid peak attained from HPLC analysis. From the figure, it showed that the peak for lactic acid was found at 2.367 min.

FTIR analysis was used to determine or identify not only the functional groups that exist in the samples or substances, but also to determine whether they are organic or inorganic. In fermentation process, the FTIR analysis was conducted to investigate the existence of similar chemical bonding or functional group between the commercial lactic acid and lactic acid produced via fermentation process and also to compare the lactic acid produced. Figure 11.6 shows that both of these lactic acids produced have almost similar peak with each other. The main differences that can be seen in Fig. 11.6 are the sharpness of the peak and some of the peaks do not appear or exist in the lactic acid produced from fermentation process.

Figure 11.6 shows that both of the lactic acids have the hydroxyl or O–H bond which is essentially overlapping with the alkanes or C–H stretch (Gonçalves et al. 2010). Gonçalves et al. (2010) also mentioned that both of these functional groups existed at the wave number of 3,800–2,500 cm^{-1}. The existence of the O–H and C–H stretch bonds in lactic acid produced from fermentation process is indicated by the 3,273.90 cm^{-1} and 2,835.11 cm^{-1}, respectively. As for the commercial lactic acid, the O–H and C–H stretch bonds existed at wave number of 3,384.66, 2,988.84, and 2,944.11 cm^{-1}. The existence of both of these functional groups in the commercial lactic acid is because of the purity of the lactic acid used which is about 88 %.

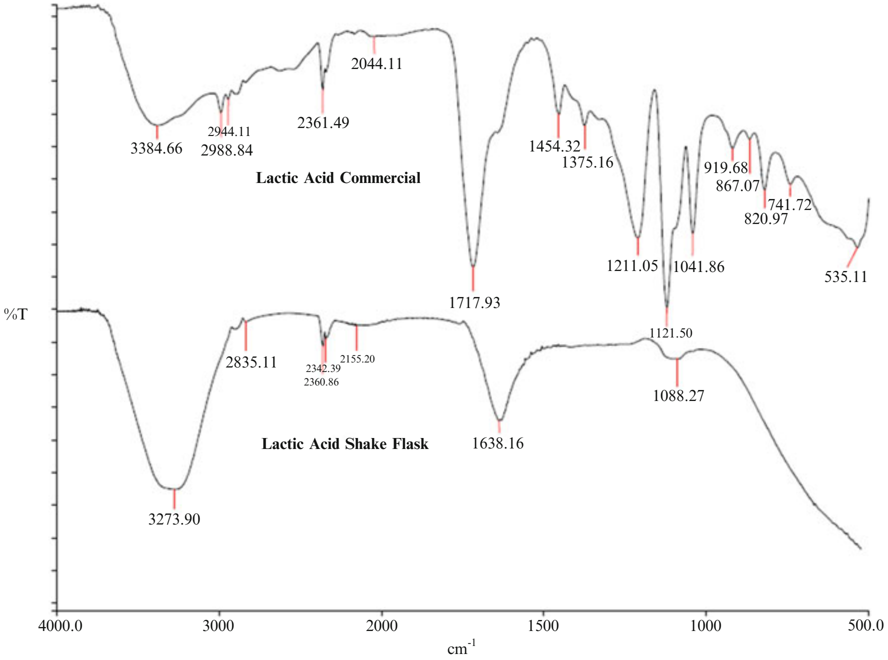

Fig. 11.6 FTIR spectra for lactic acid analysis

Besides, the carbonyls group which is C=O stretch is also present in both spectra. As for commercial lactic acid, this functional group appeared at 1,717.93 cm^{-1} which belongs to carboxylic acid group, while the wave number for lactic acid produced from fermentation process is at 1,638.16 cm^{-1} which is considered as amide group. The final similar bonds between these two lactic acids were the indication of the alcohol; an ether group with C–O bond and C–O–C symmetrical. Both of these bonds appeared at 1,121.50 cm^{-1} and 1,088.27 cm^{-1} wave number which are present in commercial lactic acid and lactic acid via fermentation process, respectively.

11.3.3 Polymerization Process

Polymerization process was carried out after the lactic acid obtained from the fermentation process was purified. Purification of lactic acid is to ensure that the lactic acid used in the polymerization process was not only 100 % pure but also free from water. The existence of water in lactic acid reduces the molecular weight of the PLA produced. This purification process was conducted under vacuum condition for 3 h at 60 °C. Purification process was carried out at lower temperature to avoid the degradation of lactic acid as well as lactide sublimation (Orozco et al. 2007).

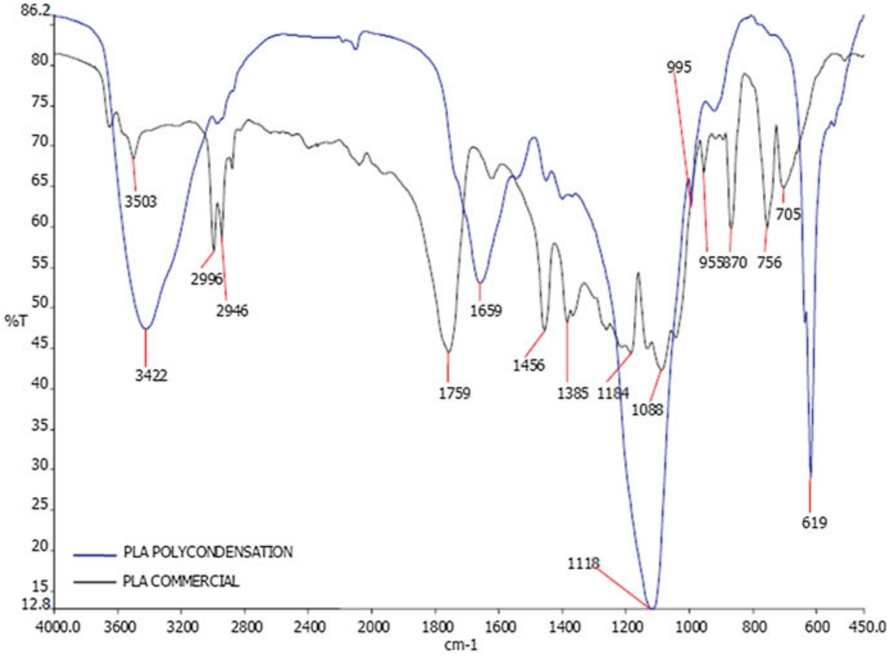

Fig. 11.7 FTIR spectra for PLA analysis

After the purification of lactic acid, the polymerization process took place. This polymerization method was carried out through ring-opening polymerization (ROP) method. There were several types of chemicals used as catalysts in ROP method. In this study, however, the catalyst used was stannous chloride ($SnCl_2$). The ROP method was carried out at 160 °C for 1 h. During the polymerization process, all the apparatuses used were properly sterilized using N_2 gas to cool down the container used after being pretreated to remove the O_2 gas that was present in the container. After 1 h, the container was placed in the refrigerator in order to terminate the polymerization process.

The FTIR analysis was carried out to determine the functional groups and chemical bonding that exist in the PLA produced as well as to reconfirm whether or not the production of PLA was achieved. Similar to lactic acid, the FTIR analysis for PLA was also carried out for the two types of PLA; commercial PLA and PLA produced via ROP method. The similarities and differences occurred were observed and recorded. Figure 11.7 shows the spectrum of commercial PLA and PLA produced via ROP method. Figure 11.7 illustrates almost similar pattern of curves for both PLAs. Similar to FTIR spectrum for lactic acid analysis, both of these spectra show almost similar pattern. The only differences were the sharpness and intensity of the peak and there were some peaks that do not exist in PLA via ROP method but available in commercial PLA.

Based on Fig. 11.7, there was a broad peak of strong hydroxyl (O–H) bonds present in the PLA via ROP method spectra which was at wave number of 3,422 cm^{-1}.

Meanwhile there was a small hydroxyl bond peak found and present in PLA commercial spectra at 3,503 cm^{-1}. Besides, alkanes (C–H stretch) groups also present in PLA commercial at the wave numbers of 2,996 and 2,946 cm^{-1} which cause asymmetric and symmetric stretching vibrations. Figure 11.7 also shows the carbonyl (C=O) group and alkene (C=C) group in both of the spectra which are present at the wave number of 1,759 cm^{-1} for commercial PLA and 1,659 cm^{-1} for PLA via ROP method. Furthermore, there were aromatic groups appeared in both of the PLA spectra approximately at 1,650–1,450 cm^{-1}. Commercial PLA and PLA via ROP method also illustrated the alcohol or ester group (C–O) and dialkyl group (C–O–C stretch) around 1,300–1,000 cm^{-1} region. The $CH=CH_2$ was emerged in both of the PLA spectra at 955 cm^{-1} for commercial PLA and 995 cm^{-1} for PLA via ROP method. According to Gonçalves et al. (2010), the regions between 870 and 688 cm^{-1} can be attributed to the amorphous and crystalline phases.

Gel permeation chromatography (GPC) was used out in order to determine the molecular weight of the polymer produced and in this study the polymer or to be exact the biopolymer produced was PLA. The determination of molecular weight is very important in the production of any polymers and biopolymers. According to Palacio et al. (2011), the main reason that the molecular weight of any polymers or biopolymers need to be determined is due to the fact that the molecular weight of polymers or biopolymers had huge and enormous influence on the size, degradation time, colloidal stability, surface functionality, morphology as well as the interaction with the active agents. Figure 11.8 shows the peak formed and created during the GPC analysis.

Figure 11.8 shows the molecular weight chromatograph or peak of the PLA from kenaf biomass that had been obtained via ROP method; meanwhile Table 11.6 shows the summary of the number of molecular weight (Mn), weight of the molecular weight (Mw) as well as the polydispersity index (PDI). Viéville et al. (2011) mentioned that normally the polydispersity is measured and calculated by the polydispersity index (PDI). Viéville et al. (2011) also mentioned that the PDI can be defined as the ratio of the mass average molar mass (Mw) or also known as the weight average of the molecular weight (Mw) to its number averaged of the molar mass or molecular weight (Mn) as shown in Eq. (11.1). Besides, Rogošić et al. (1996) also mentioned that the PDI which is measured or calculated by the width of molecular weight distribution (MWD) is a very important index.

$$\mathrm{PDI} = \frac{\mathrm{Mw}}{\mathrm{Mn}} \tag{11.1}$$

Based on Fig. 11.8, the peak that occurred in the range of 13.05–20.1 min indicated the molecular weight of PLA produced via ROP method. The maximum peak occurred at the retention time of 15.825 min. Based on Table 11.6, the Mw of the PLA produced from kenaf biomass via ROP method was very high which is 4,196,922 g/mol, meanwhile the Mn of the PLA produced is 241,529 g/mol. This higher Mw and Mn indicated that the PLA produced had a long chain and also due to its high temperature during processing. According to Callister (2007), the molecular

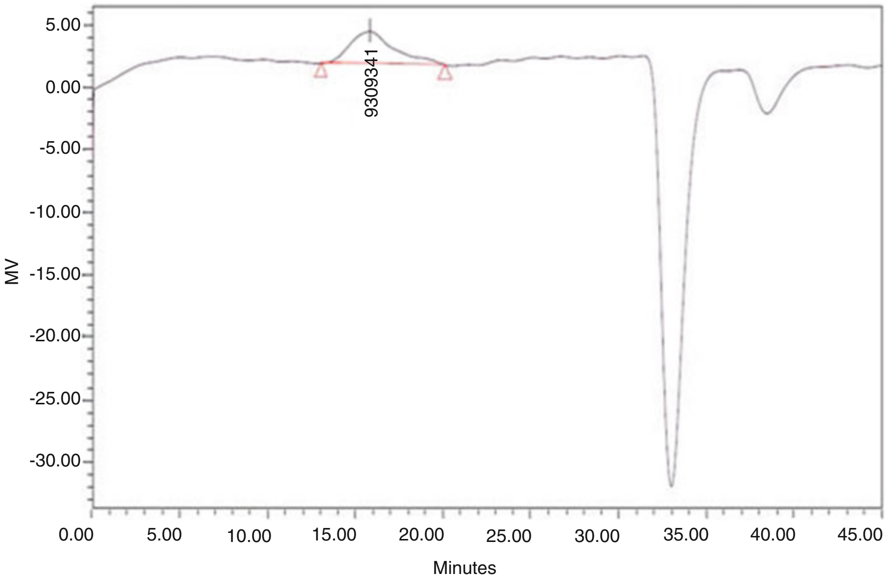

Fig. 11.8 Molecular weight chromatograph from GPC analysis

Table 11.6 The molecular weight and the polydispersity index (DPI) of the PLA produced via ROP method

	Mn (g/mol)	Mw (g/mol)	PDI
PLA produced via ROP method	241,529	4,196,922	17.4

weight of the polymer is normally affected by the melting and softening temperature. Callister (2007) also mentioned that as the molecular weight is increasing, the melting temperature or melting point is also increased. In addition, Orozco et al. (2007) mentioned that the catalyst used in the polymerization process, in this case the ROP method, does not have any influence not only on the broadness of the MWD, but also on the polymer chain length. Besides, Orozco et al. (2007) stated that if the PDI value is close to 2, then the degree of polymerization is almost 1. Since the PDI value in this ROP method is higher than 2, which is 17.4, it is indicated that the PLA produced via ROP method has high degree of polymerization.

DSC analysis was conducted to determine the thermal stability of the commercial PLA and PLA produced via ROP method. The DSC is used in order to determine the temperature and heat flow connected with the transition phase in materials. In the DSC analysis, the heating and cooling rates may affect the results. Thus, it is preferable to use low heating and cooling rates in order to avoid any circumstances occurred as well to produce better results.

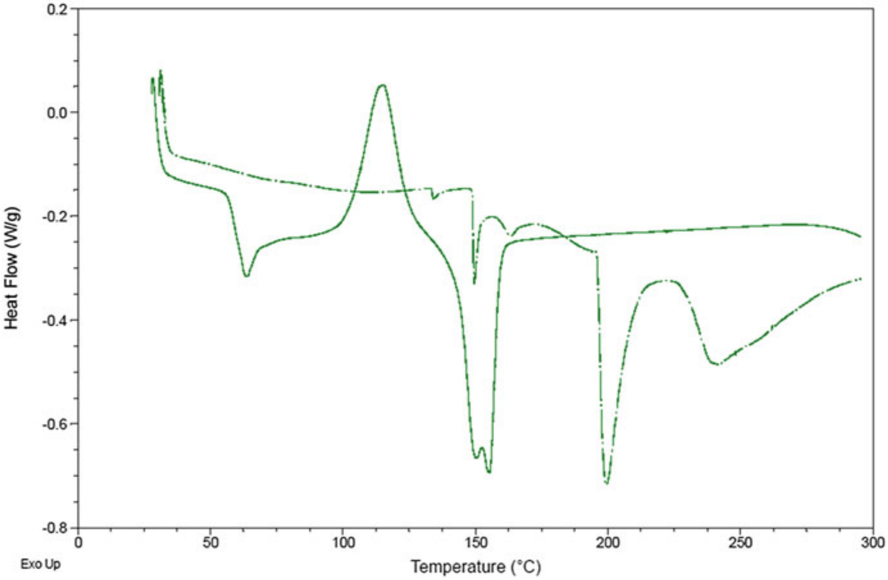

Fig. 11.9 DSC thermogram for PLA analysis

Figure 11.9 illustrates the glass transition temperature (T_g), the crystallization temperature (T_c), and the melting temperature (T_m) of the commercial PLA and PLA produced via ROP method. Figure 11.9 clearly shows the differences between both of these thermograms. Based on Fig. 11.9, the glass transition temperature (T_g) for the commercial PLA is around 65 °C, while the T_g value for the PLA produced via ROP method occurred at 149.51 °C. The crystallization temperature (T_c) for PLA produced via ROP method cannot be seen clearly, while the T_c for commercial PLA was approximately at 125 °C. As for the melting temperature (T_m), PLA produced via ROP method showed high T_m compared to commercial PLA which is at 199.43 °C a, while T_m for commercial PLA was in the range of 140–160 °C. According to this thermogram, the PLA produced via ROP method was shifted a bit from the PLA commercial. This phenomenon might be occurred due to the impurities that exist in the produced PLA. Based on the previous study conducted by Kaitian et al. (1996), T_g value was in the range of 20–57 °C, while the T_m value is in the range of 124–126 °C. Kaitian et al. (1996) mentioned that if the T_g value is low, it is an indication of low molecular weight of PLA. Thus, from the T_g value for PLA produced via ROP method, it is proven that the molecular weight, Mw, for PLA produced via ROP method is high and thus proven through the GPC analysis as shown above.

Thermogravimetric analysis (TGA) is one of the most widely used of thermal methods. Principally, the TGA analysis is based on the measurement, quantity, and amount of the weight loss of the materials or substances as a function of temperature. Commonly, the TGA curve was plotted based on the percentage weight loss versus temperature used. In this TGA analysis, there were two types or characteristics

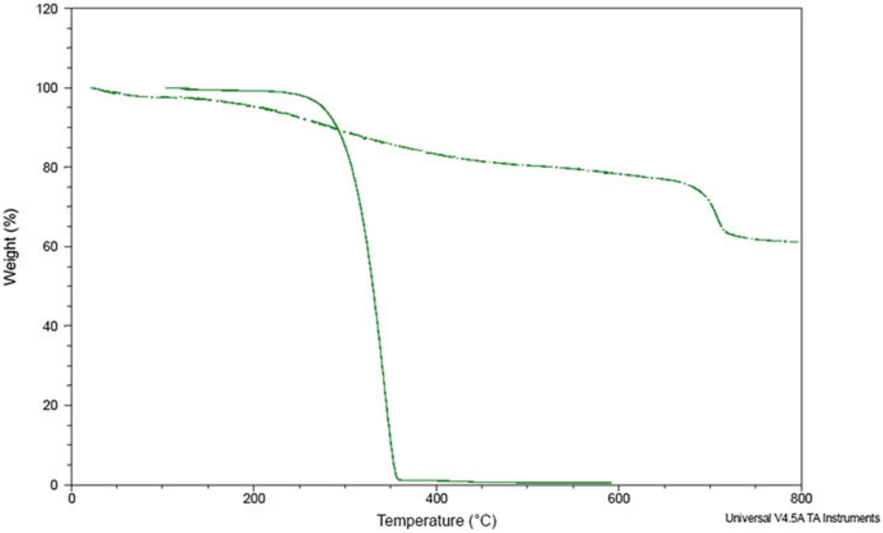

Fig. 11.10 TGA curve for PLA analysis

of temperature which are initial temperature or the lowest temperature (T_i) and the final temperature or the temperature where the decomposition process completed (T_f). The difference between T_f–T_i is termed reaction interval or decomposition temperature range. Figure 11.10 illustrates the TGA curve between commercial PLA and PLA produced via ROP method. The rate of decomposition of commercial PLA is faster compared to the PLA produced via ROP method. Based on Fig. 11.10, it can be seen that although the decomposition process of PLA produced via ROP method started earlier, it took high temperature to be degraded or decomposed unlike commercial PLA which started to decompose at temperature of around 250 °C and completed degradation at temperature of around 350 °C. Meanwhile the decomposition and degradation processes for PLA produced via ROP method started at temperature in the range of 20–50 °C and completed the process at temperature in the range of 750–800 °C.

11.3.4 Concluding Remarks

In short, there were several steps took placed in order to synthesize the PLA from kenaf biomass. Figure 11.11 shows the flow or the overview of all the processes that took place in this study. Basically there were three main processes that had been conducted through this study which are chemical pretreatment process, fermentation process, and polymerization process. In this study, kenaf biomass was used as the raw ~~materials~~ in the production of glucose. Since kenaf biomass has a complex structure, it needs to be treated in order to remove the hemicelluloses and lignin

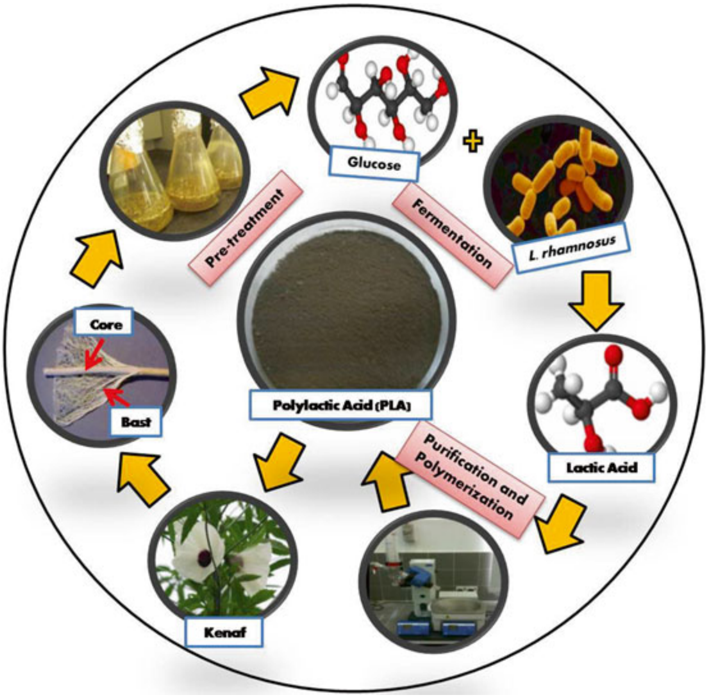

Fig. 11.11 Overview of the flow of the synthesis of PLA from kenaf biomass

content as well as to reduce the crystallinity of the cellulose content. Then, the fermentation process was carried out using the hydrolyzed glucose which acts as the carbon source in the lactic acid production. This biological fermentation was carried out for 3 days at 37 °C using *L. rhamnosus* as its microbial organism. The lactic acid obtained from the fermentation process was purified before being polymerized into PLA via ROP method. Finally, the PLA produced via ROP method was analyzed and characterized in order to investigate its properties and behavior. Basically, the processes involved in this study are interconnected with each other and the amount of time took to accomplish this study is 7 days.

11.4 Conclusions

Based on the characterization done, this study has successfully synthesized PLA from kenaf biomass via ring-opening polymerization (ROP) method. The process started with chemical pretreatment to produce maximum glucose concentration followed by fermentation process and finally polymerization process. In chemical pretreatment process, three solvents which are H_2SO_4, NaOH, and $(NH_4)_2SO_4$ were used in order to determine the most significant solvents that can liberate high glucose concentration. H_2SO_4 shows the maximum glucose concentration which is 1.0095 g/L followed by NaOH (0.5895 g/L) and $(NH_4)_2SO_4$ (0.2275 g/L). Thus, H_2SO_4 was used in designing 11 runs of experiments and it was found that the maximum production of glucose and dextrin occurred at Run 6 when the mixing time was at 60 min and the temperature was at 200 °C which are 3.397 g/L and 50.777 g/L, respectively.

After the production of glucose, the fermentation process was carried out using protein sources which are peptone and yeast extract as the parameters. In this fermentation process, the highest yield of lactic acid which is 10.851 g/L was produced at Run 5 with 2.0 g of peptone and 2.5 g of yeast extract. The obtained lactic acid was purified and polymerized into PLA. The PLA produced via ROP method was investigated for its chemical bonding and compared with the commercial PLA. The molecular weight, Mw of the PLA produced via ROP method, was determined using GPC analysis and the molecular weight for the PLA is 4,196,922 g/mol with 17.4 polydispersity index (DPI). From the DSC analysis, the PLA produced possessed a glass transition temperature (T_g) at 149.51 °C and melting temperature (T_m) at 199.43 °C. TGA analysis demonstrated slow decomposition rate of the PLA produced compared to commercial PLA. Further research should be carried out sequentially to produce good results especially in lactic acid and PLA production.

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Chapter 12
Chemical Functionalization of Cellulosic Fibers for Green Polymer Composites Applications

Manju Kumari Thakur, Aswinder Rana, and Vijay Kumar Thakur

Contents

Abstract During the last few decades, synthetic polymers have emerged as new potential viable alternative to traditional metallic and ceramic materials due to their inherent properties such as flexibility, light weight, corrosion resistance, and easy processing. However, these synthetic polymers also pose some serious threats to our environments due to the toxic and hazardous chemicals associated during their synthesis and afterward their end use applications. Although these synthetic polymers

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have benefited the human being to a great extent, recently efforts are being made to reduce their use. The prime reason for this is the increasing environmental awareness and health concerns. All these concerns have led to intensive research on natural polymer-based materials derived from different biorenewable resources. Among bio-based polymers, cellulose fibers offer a very high potential as biodegradable biorenewable material. However, the presence of hydrophilic groups on natural cellulosic fibers limits their applications in everyday use. In order to overcome the disadvantages associated with these fibers, graft copolymerization is the most trusted tool to alter their properties for targeted applications. So in the present book chapter we report some of our studies on the chemical functionalization of natural cellulosic fibers through free radical-induced graft copolymerization technique.

Keywords Biofibers • Environments • Surface functionalization • Physicochemical properties

12.1 Introduction

Petrochemical based materials have revolutionized human life since last century. Among various petrochemical-based products, polymers represent one of the most significant materials (Averous 2004; Wong et al. 2007). Bakelite is known as the first synthetic polymer synthesized a century ago and afterward a number of synthetic polymers have been synthesized and used as materials in different fields (Bledzki and Gassan 1999; Hagstrand and Oksman 2001; Singha and Thakur 2010, 2012). These synthetic polymers have emerged as new alternative to traditional metallic and ceramic materials due to their inherent properties such as flexibility, light weight, corrosion resistance, and easy processing. These polymers have nevertheless attracted a vast amount of attention due to the special properties mentioned above and their applications (Dhakal et al. 2007). In spite of their advantages, these synthetic polymers also possess some serious threats to our environments due to the toxic and hazardous chemicals associated during their synthesis and afterward their end use applications (Amash and Zugenmaier 1998; Wambua et al. 2003; Hasipoglu et al. 2005; Thakur et al. 2013a, b, c, d, e). There is no doubt that these synthetic polymers have benefited the human being to a great extent, but recently efforts are being made to reduce their use as a result of the increasing environmental awareness and health concerns (Debapriya and Adhikari 2004; Dufresne et al. 1997). These concerns have led to intensive research on biopolymer-based materials for a number of applications starting from biomedical to defense. Among different kinds of bio-based polymers, cellulose fibers offer a huge potential to be used as an alternative to the synthetic fibers (Klemm et al. 2005; Kabir et al. 2012). These fibers are also often referred to as vegetable fibers (Dufresne et al. 1999). Different kinds of fibers can be extracted from the plants/trees and are classified on the part of the plant they are extracted from (Montford and Small 1999; Ouajai and Shanks 2009; Panthapulakkal et al. 2006). These fibers offer the advantages of being biodegradable, renewable, economic, non-carcinogenic, and eco-friendly to name a few over their synthetic counterparts (Shanks et al. 2006; Thakur and Singha 2010a, b). Various kinds of natural fibers have been used by the people right from the early civilization till today in a number of house hold applications and most recently to industrial application such as for carpet backing, packaging, hessian, bags, canvas, tar felts, etc. (Shibata et al. 2013; Thakur et al. 2011a, b). One of the most common uses of natural fibers in present industrial application is their use as reinforcement in polymer matrices (Thakur et al. 2011a, b, 2012a, b, c, d). However, the presence of several hydrophilic groups on the lignocellulosic fibers limits their applications in automotive (Thakur et al. 2013a, b, c, d, e). In order to overcome the disadvantages associated with these fibers, graft copolymerization is the most trusted tool to alter their properties for targeted applications (Thakur et al. 2012a, b, 2013a, b, c, d, e). So in present book chapter we report some of our research work carried out in the direction of chemical functionalization of lignocellulosic biofiber through free radical-induced graft copolymerization technique.

12.2 Chemical Functionalization of Cellulosic Fibers

Natural *Hibiscus sabdariffa cellulosic fibers* used in this study were obtained from local resources available in Himachal Pradesh (India). These fibers were obtained from the Hibiscus plant by the traditional water retting method and were thoroughly cleaned with continuously flowing fresh tap water. The natural *Hibiscus sabdariffa cellulosic fibers* were then dried in a hot air oven at 70 °C for 24 h, followed by final extraction in soxhlet with acetone for a period of 96 h to remove any impurities and waxes that may hinder the graft copolymerization process (Thakur et al. 2013a, b, c, d, e). These fibers were then designated as raw *Hibiscus sabdariffa cellulosic fibers*. Different chemical sand solvents were used as received from their vendors.

12.2.1 Mercerization

Mercerization is one of the imperative techniques frequently used to initially stimulate the different functional groups on the surface of cellulosic fibers. In the present work also, the *Hibiscus sabdariffa biofibers* were activated for further reaction through graft copolymerization using mercerization method (Thakur et al. 2013e; Thakur and Singha 2011).

12.2.2 Graft Copolymerization Synthesis

Surface modification of lignocellulosic natural *Hibiscus sabdariffa fibers* using the graft copolymerization synthesis to prepare *Hibiscus sabdariffa biofibers copolymers* was carried out by putting an identified quantity of the mercerized *Hibiscus* *sabdariffa biofibers* in known quantity of water in a flask (Thakur and Singha 2011). These fibers were kept for activation for 24 h prior to the initiation of synthesis process (Thakur et al. 2013a, b, c, d, e). Subsequently the ammonium per sulphate initiator and Methylmethacrylate monomer were added in a definite amount into their action flask. The chemical reaction was then carried out for a definite time interval in an autoclave. Different reaction parameters that significantly affect the degree of grafting were then optimized. Soxhlet extraction using acetone was employed to remove the homo-polymer formed during the reaction. The percentage grafting (P_g) of mercerized *Hibiscus sabdariffa fibers* was calculated using the formula shown below (Thakur et al. 2012a, b, c, d, 2013e)

$$\text{Percent grafting}\left(P_g\right)=\frac{W_g-W}{W}\times 100$$

where W is the weight of raw fiber; W_g is the weight of grafted fiber.

12.2.3 Physico-chemical Tests

Both the raw and grafted *Hibiscus sabdariffa fibers* were then subjected to their swelling behavior study in different solvents, e.g., water, methanol; isobutyl alcohol and dimethyl formamide (Thakur and Singha 2011; Thakur et al. 2013a, b, c, d, e). The increase in the initial weight of the fibers kept in a particular solution was then used to calculate the percent swelling as shown in the equation below:

$$\text{Percent swelling}\left(P_S\right)=\frac{W_f-W_i}{W_i}\times 100$$

The amount of moisture absorbed in both the raw/grafted *Hibiscus sabdariffa fibers* exposed to different humidity level was studied in humidity levels ranging from 20 to 90 % using the equation given below:

$$\text{Percent moisture absorbance}\left(\%M_{abs}\right)=\frac{W_f-W_i}{W_i}\times 100$$

where W_f and W_i refer to the final and initial weight of raw/grafted *Hibiscus sabdariffa fibers* (Thakur and Singha 2011)

Different chemicals such as acids (HCl) and bases (NaOH) have also the effect on the chemical resistance of the fibers. The analysis of acids (HCl) and bases (NaOH) solution of 1 N concentration was studied in terms of weight loss using the equation below:

$$\text{Percent chemical resistance}\left(P_{cr}\right)=\frac{T_w-W_{aci}}{T_w}\times 100$$

Where T_w and W_{aci} refer to the total and initial weight after certain interval, respectively.

12.2.4 Characterization

The structural changes in the *Hibiscus sabdariffa biofibers* before and after graft copolymerization were verified using the Perkin-Elmer system RXI spectrometer in the range of 4,000–500 cm^{-1} with 2 cm^{-1} resolution (Thakur et al. 2012a). Scanning electron micrographs (SEM) of the raw/grafted *Hibiscus sabdariffa biofibers* were recorded on Electron Microscopy Machine (LEO 435 VP). Thermal stability of the raw and *Hibiscus sabdariffa fibers* was analyzed on a thermal analyzer (Perkin Elmer) using thermo gravimetric analysis (TGA) in nitrogen atmosphere (heating rate of 10°C/min) (Thakur and Singha 2011).

12.3 Results and Discussion

In all the biorenewable cellulosic polymers such as *Hibiscus sabdariffa biofibers*, the C_2, C_3, and C_6–OH/C–H_2 groups along with other groups acts as the prime center for grafting of monomer chains (Thakur and Singha 2011; Thakur et al. 2013e). The mechanism for grafting onto *Hibiscus sabdariffa biofibers* is explained in Scheme 12.1 (Thakur and Singha 2011)

12.3.1 Analysis of Different Reaction Parameters on the Degree of Grafting

The influence of different reaction parameters, namely monomer concentration, pressure, solvent, time, and initiator, on percentage grafting (Pg) has been studied, and the results are presented in Figs. 12.1, 12.2, 12.3, 12.4, and 12.5.

12.3.1.1 Effect of Solvent

Amount of water used as solvent in the grafting has been found to influence the degree of grafting percentage of grafting. It was found to increase with the increment in the amount of water up to 110 mL and then decreases (Fig. 12.1). With increase in the amount of water, there was dilution of the reaction that lowered

INITIATION

$$ {}^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \longrightarrow 2SO_4^{-\,*} \tag{1}$$

$$ 2SO_4^{-\,*} + H_2O \longrightarrow HSO_4^{-} + {}^{*}OH \tag{2}$$

$$ \text{Cell-OH} + SO_4^{-*} \longrightarrow \text{Cell-O}^{*} + HSO_4^{-} \tag{3}$$

$$ \text{Cell-OH} + {}^{*}OH \longrightarrow \text{Cell-O}^{*} + H_2O \tag{4}$$

$$ M + {}^{*}OH \longrightarrow {}^{*}M\text{-}OH \tag{5}$$

$$ M + SO_4^{-*} \longrightarrow {}^{*}M\text{-}SO_4^{-} \tag{6}$$

$$ M + MW \longrightarrow {}^{*}M \tag{7}$$

$$ \text{Cell-OH} + MW \longrightarrow \text{Cell-O}^{*} \tag{8}$$

PROPAGATION

$$ \text{Cell-OH} + {}^{*}M\text{-}OH \longrightarrow \text{Cell-O-M}^{*} + H_2O \tag{9}$$

$$ \text{Cell-O-M}^{*} + nM \longrightarrow \text{Cell-O-}(M)_n\text{-}M^{*} \tag{10}$$

$$ \text{Cell-O}^{*} + nM \longrightarrow \text{Cell-O-}(M)_{n-1}M^{*} \tag{11}$$

$$ {}^{*}M\text{-}OH + nM \longrightarrow HO\text{-}(M)_n\text{-}M^{*} \tag{12}$$

TERMINATION

$$ \text{Cell-O-}(M)_n\text{-}M^{*} + M^{*}\text{-}(M)_n\text{-O-Cell} \longrightarrow \text{Cell-O-}(M)_n\text{-}M_2\text{-}(M)_n\text{-O-Cell} \tag{13}$$

$$ \text{Cell-O-}(M)_{n-1}\text{-}M^{*} + M^{*}\text{-}(M)_{n-1}\text{-O-Cell} \longrightarrow \text{Cell-O-}(M)_{n-1}\text{-}M_2\text{-}(M)_{n-1}\text{-O-Cell} \tag{14}$$

$$ \text{Cell-O-}(M)_n\text{-}M^{*} + {}^{*}OH \longrightarrow \underset{\textbf{(Graft copolymer)}}{\text{Cell-O-}(M)_{n+1}\text{-OH}} \tag{15}$$

$$ HO\text{-}(M)_n\text{-}M^{*} + {}^{*}M\text{-}(M)_n\text{-}OH \longrightarrow \underset{\textbf{(Homopolymer)}}{HO\text{-}(M)_n\text{-}M_2\text{-}(M)_n\text{-}OH} \tag{16}$$

Scheme 12.1 Mechanism of the graft copolymerization reactions

the monomer concentration as well as various hydrogen abstraction reactions (Thakur et al. 2012a).

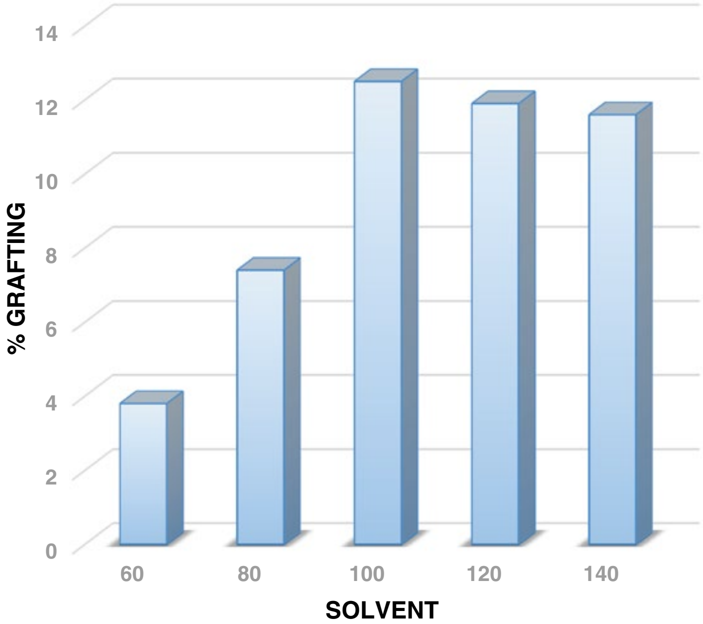

Fig. 12.1 Optimization of solvent amount for graft copolymerization onto *Hibiscus sabdariffa fibers*

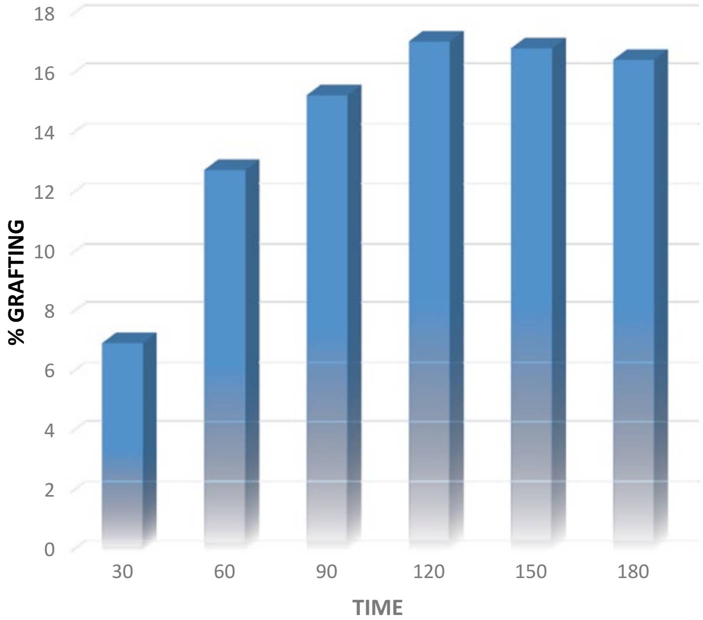

Fig. 12.2 Optimization of reaction time for graft copolymerization onto *Hibiscus sabdariffa fibers*

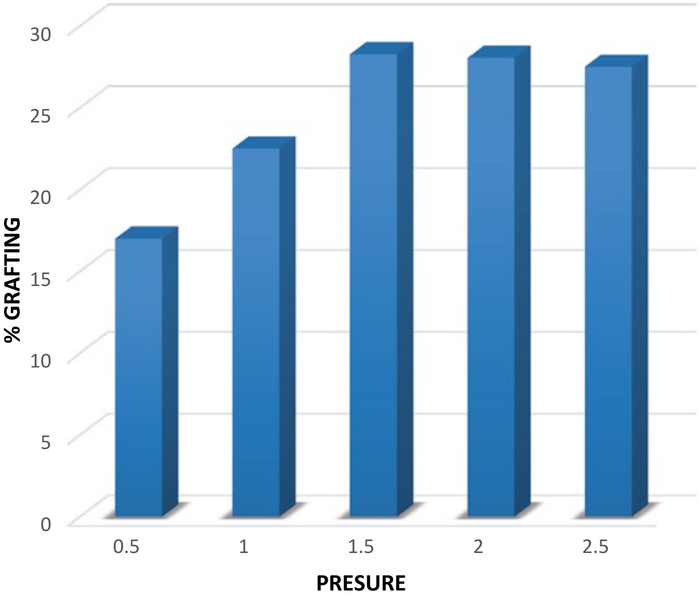

Fig. 12.3 Optimization of pressure for graft copolymerization onto *Hibiscus sabdariffa fibers*

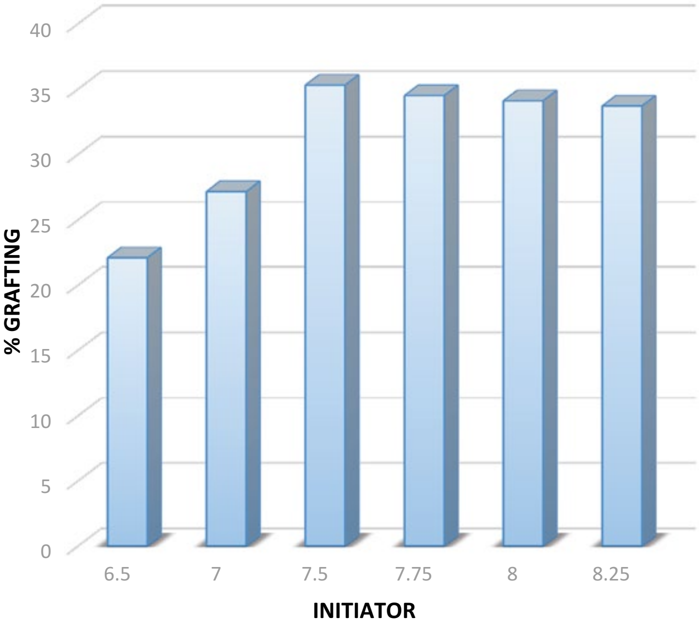

Fig. 12.4 Optimization of initiator ratio for graft copolymerization onto *Hibiscus sabdariffa fibers*

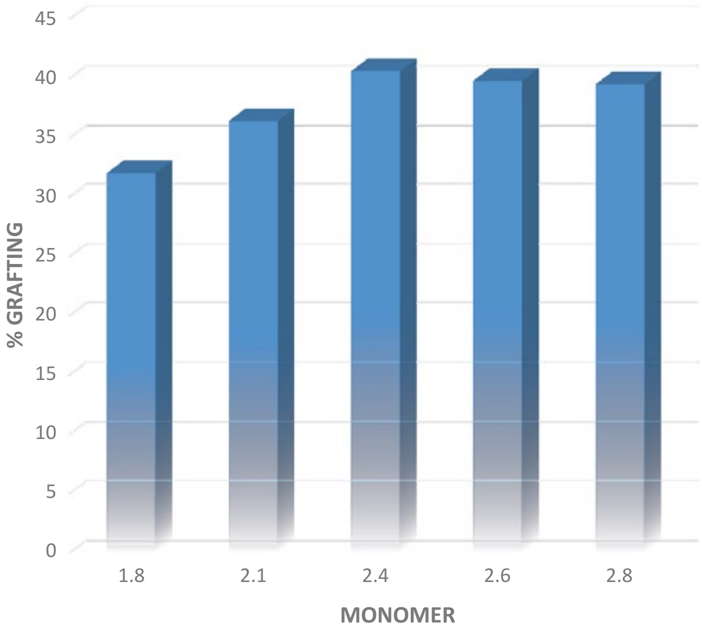

Fig. 12.5 Optimization of monomer for graft copolymerization onto *Hibiscus sabdariffa fibers*

12.3.1.2 Effect of Reaction Time

During the graft copolymerization synthesis reaction, the maximum degree of grafting was observed at 120 min (Fig. 12.2). The increase in time beyond 120 min caused a decline in grafting degree. This behavior was attributed to the occupation of reaction site with increase in time that caused the formation of the homopolymer in higher amount compared to graft copolymer and resulted in the low degree of grafting (Thakur et al. 2013e).

12.3.1.3 Effect of Pressure

Similar to other parameters, pressure also plays an imperative role in controlling the overall percentage of grafting. At a pressure of 1.5 kg cm^{-2}, the maximum degree of grafting was observed. However, further increase in pressure resulted in decreased degree of grafting (Fig. 12.3).

12.3.1.4 Effect of Initiator Concentration

Along with monomer concentration, the amount of initiator also plays an important role. To achieve the maximum degree of grafting under the influence of pressure, more quantity of initiator was used in comparison to the grafting in air/microwave (Fig. 12.4). Due to increase in more radicals with increase in the amount of the initiator, higher degree of grafting was obtained. However, once the optimum concentration has been reached, auxiliary escalation in the initiator concentration results in the domination of the termination overgraft copolymerization, leading to the decreased percentage of grafting (Thakur et al. 2013e).

12.3.1.5 Effect of Monomer Concentration

Grafting of MMA on mercerized *Hibiscus sabdariffa biofibers* has been studied in the aqueous reaction mixture. The addition of a trivial amount of MMA in the reaction mixture resulted in the increased degree of grafting of *Hibiscus sabdariffa biofibers* up to a certain value and afterward it decreased (Fig. 12.5). This behavior is quite obvious in cellulose-based graft copolymers and could be explained on the basis that with an increase in monomer concentration beyond optimum concentration, there is more homopolymer formation as compared to graft copolymer thus, resulting in the low grafting percentage (Thakur et al. 2013e).

12.3.2 Structural Characterization

The raw and grafted *Hibiscus sabdariffa fibers* were characterized through FTIR, SEM, and TGA analysis techniques to determine the successful grafting of monomer. Similar to the grafting of MMA on to *Hibiscus sabdariffa fibers* in AIR as medium, the graft copolymerization was also successful under pressure (Thakur et al. 2011a). The FTIR spectra of raw/grafted *Hibiscus sabdariffa fibers* in air medium are shown in Figs. 12.6 and 12.7 shows the spectra of the fibers under pressure. The broad peaks at 3,426, 2,927.3, 1,423.0, and 1,038.0 cm^{-1} in the raw *Hibiscus sabdariffa fibers* were due to bonded OH groups and –CH$_2$, C–C, C–O stretching, respectively, (Fig. 12.7). However, an additional peak at 1,733 cm^{-1}in grafted fibers corresponding to carbonyl group (>C=O) confirmed the grafting of the PMMA chains onto the raw fibers (Fig. 12.7). The spectra of the grafted fibers in both the mediums are nearly same with the little variation in the peaks' position and the intensity providing strong evidences of the MMA monomer grafting (Thakur et al. 2011a).

Scanning electron microscopy of both the raw and grafted natural cellulosic fibers (Fig. 12.8) also confirmed the successful grafting of MMA onto the fibers. SEM photographs clearly show the covering of the raw fibers by the MMA monomer (Fig. 12.9a, b) similar to the grafting in the air as medium (Fig. 12.9b) (Thakur et al. 2011a).

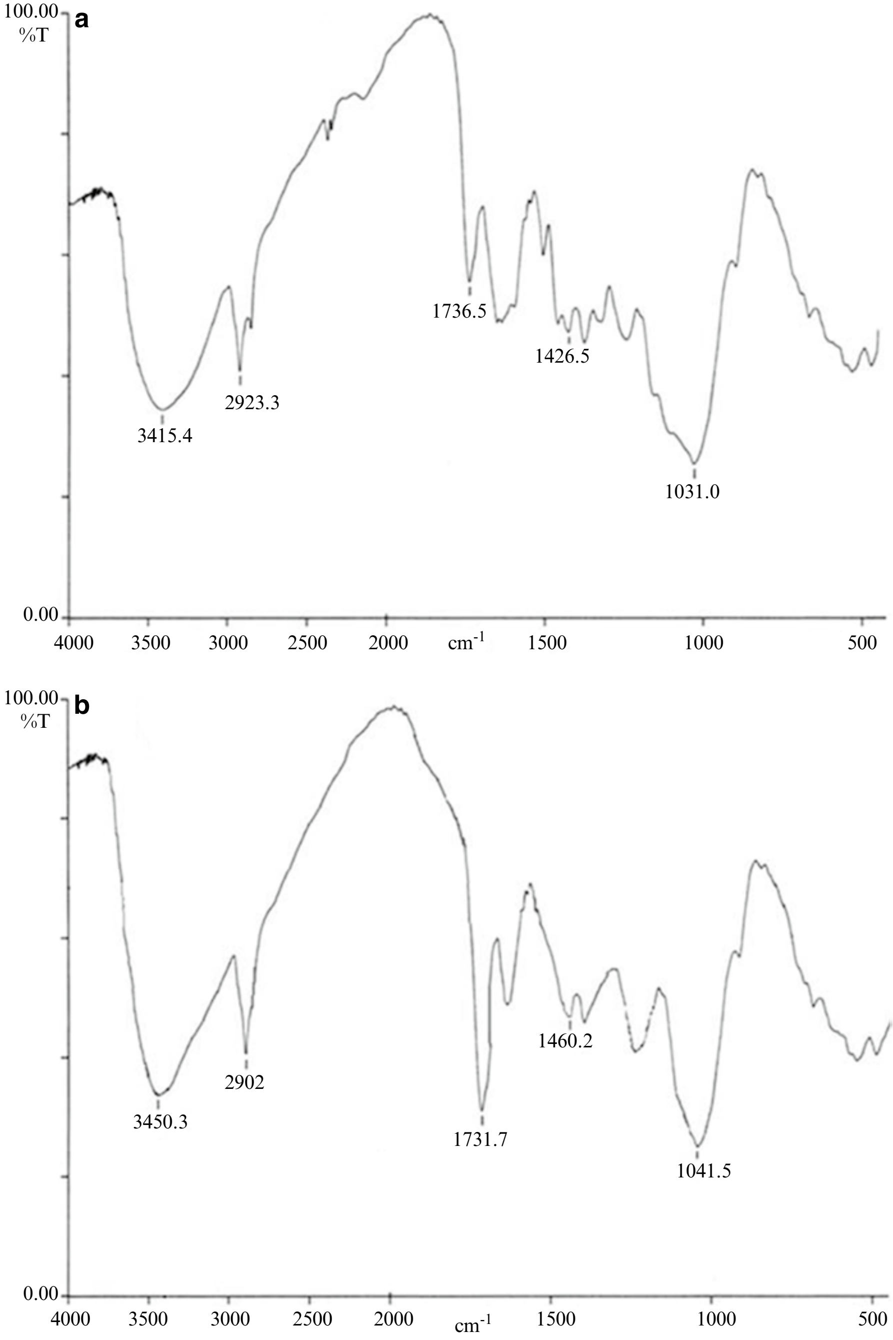

Fig. 12.6 FTIR spectra of (**a**) raw *Hibiscus sabdariffa fibers* and (**b**) poly (MMA)-grafted *Hibiscus sabdariffa fibers* (in *Air* grafting). Reprinted with permission (Thakur et al. 2011a). Copy right 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

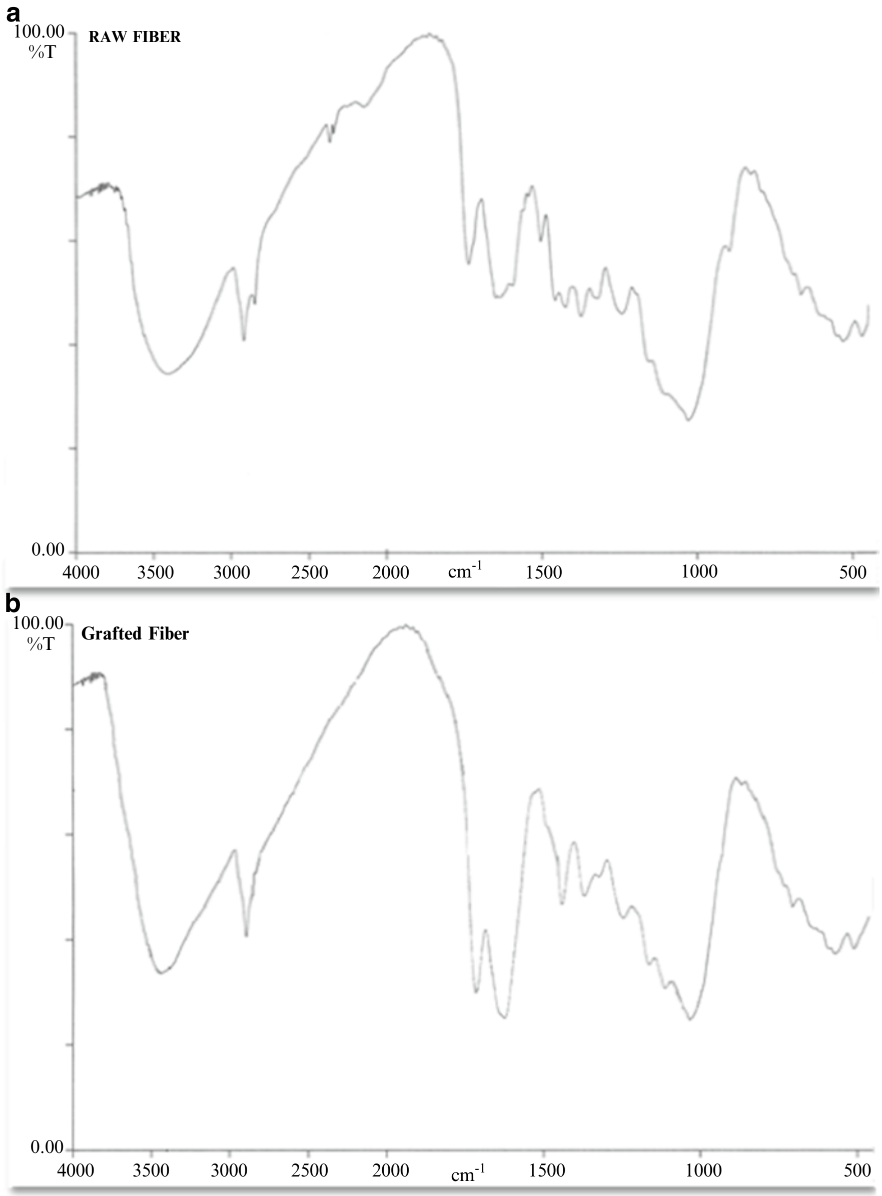

Fig. 12.7 FTIR spectra of (**a**) raw *Hibiscus sabdariffa fibers* and (**b**) poly(MMA)-grafted *Hibiscus sabdariffa fibers* (under *Pressure* grafting)

Figure 12.10 also shows the TGA thermo grams for the raw and grafted fibers. It is quite evident that the fibers grafted *under pressure* also follow the same trend of thermal stability as that of grafted fibers in air as reaction medium.

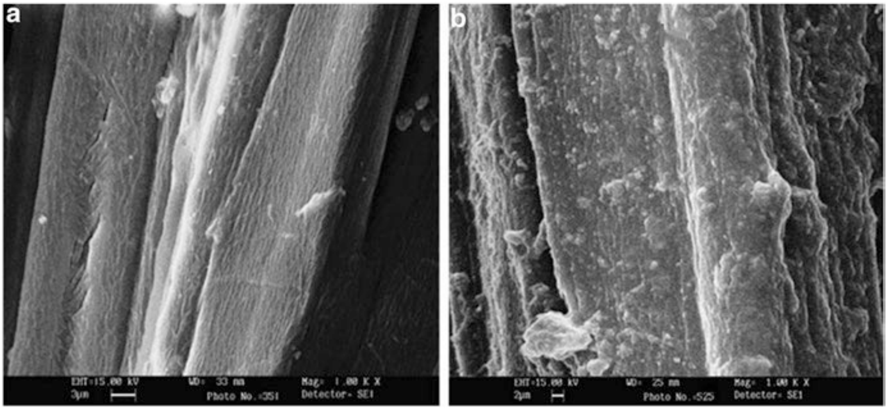

Fig. 12.8 SEM micrographs of (**a**) raw *Hibiscus sabdariffa fibers* and (**b**) poly(MMA)-grafted *Hibiscus sabdariffa fibers* (under *Pressure* grafting)

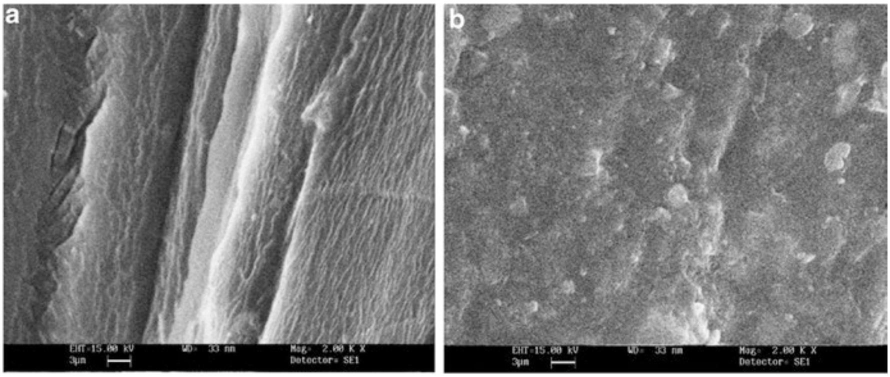

Fig. 12.9 SEM micrographs of (**a**) raw *Hibiscus sabdariffa fibers* and (**b**) poly(MMA)-grafted *Hibiscus sabdariffa fibers* (in *Air* grafting). Reprinted with permission (Thakur et al. 2011a). Copy right 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

12.3.3 Physico-chemical Study

It is evident from figure (Fig. 12.11) that the raw/grafted *Hibiscus sabdariffa fibers* show different swelling in different solvents. The fibers were found to exhibit higher swelling in water followed by CH_3OH, iso-BuOH, and DMF (Thakur et al. 2011a). The higher number of OH and CH_2OH groups in the raw *cellulosic fibers* caused a very high water absorption in raw *Hibiscus sabdariffa fibers*. However, in case of grafted fibers, the swelling behavior shows the trend DMF>CH_3OH>H_2O>iso-BuOH. This trend varied as a function of percentage as with increase in grafting, there were more hydrophobic groups present in the cellulosic fibers that resulted in

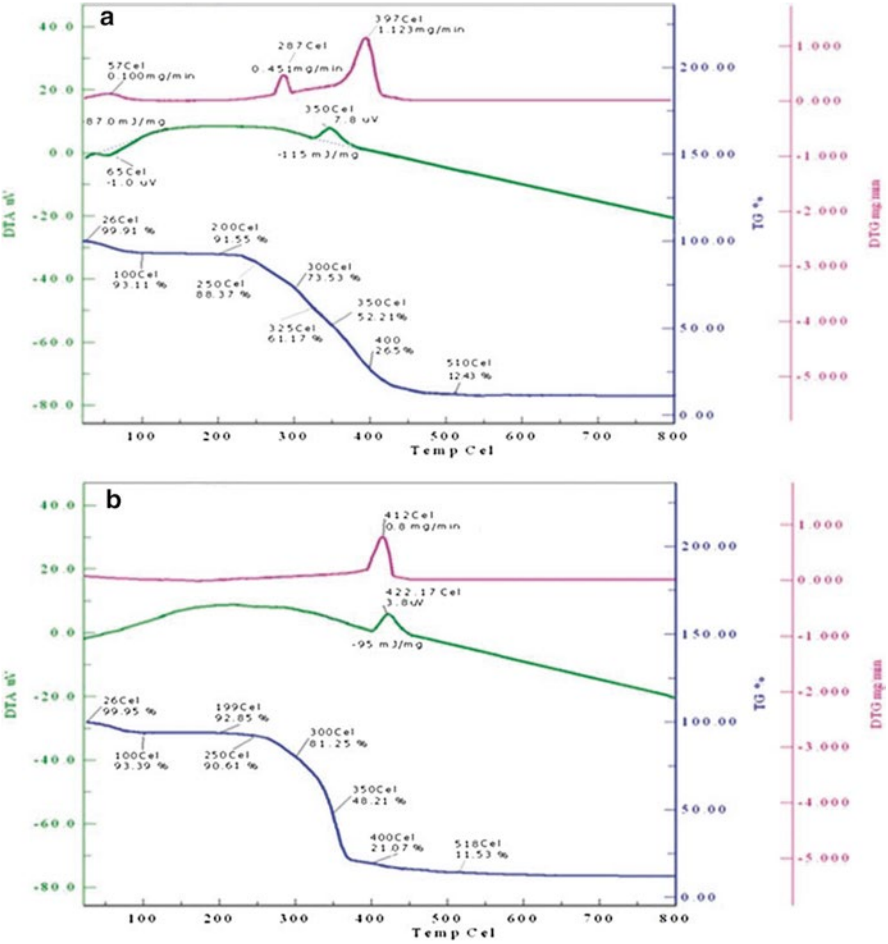

Fig. 12.10 TGA/DTA/DTG thermogram of (**a**) raw *Hibiscus sabdariffa fibers* and (**b**) poly(MMA)-grafted *Hibiscus sabdariffa fibers* (in *Air* grafting). Reprinted with permission (Thakur et al. 2011a). Copy right 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

decreased water absorption. Figure 12.12 shows the moisture absorbance of raw and MMA-grafted *Hibiscus sabdariffa fibers*. The moisture absorbance behavior was studied at diverse humidity using fibers with different percentage of grafting. Similar to the swelling behavior of fibers, the moisture absorbance (M_{abs}) was found to decrease with the increased degree of grafting due to the attachment of higher number of poly (MMA) chains onto the fibers backbone (Thakur et al. 2011a). The chemical resistance of the raw fibers was also found to increase with increase in the degree of grafting. For example, the grafted *Hibiscus sabdariffa fibers* showed an enhanced chemical resistance in solution of concentration 1 N HCl and 1 N NaOH,

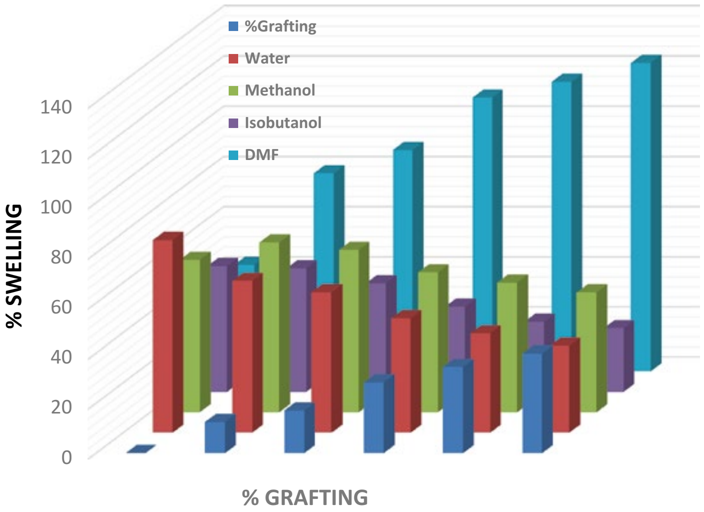

Fig. 12.11 Swelling behavior of raw and grafted *Hibiscus sabdariffa fibers* in different solvents

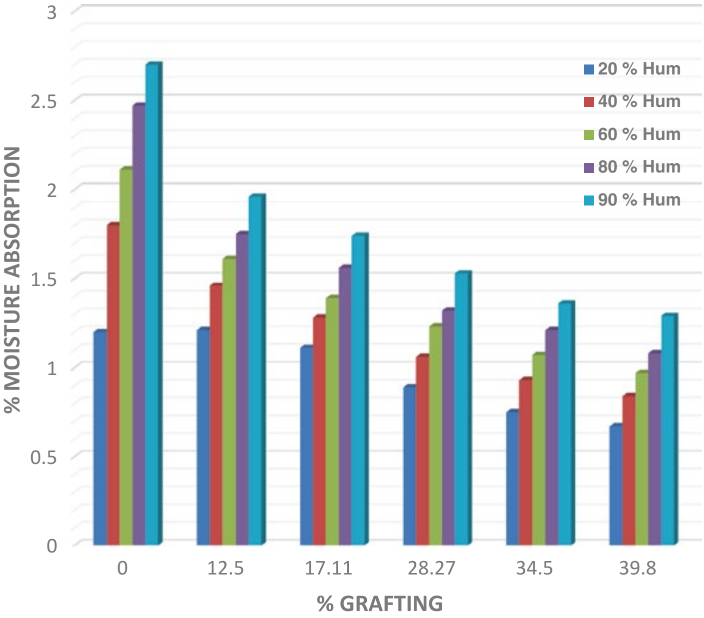

Fig. 12.12 Moisture absorbance behavior of raw and grafted cellulosic *Hibiscus sabdariffa fibers* at different humidity levels

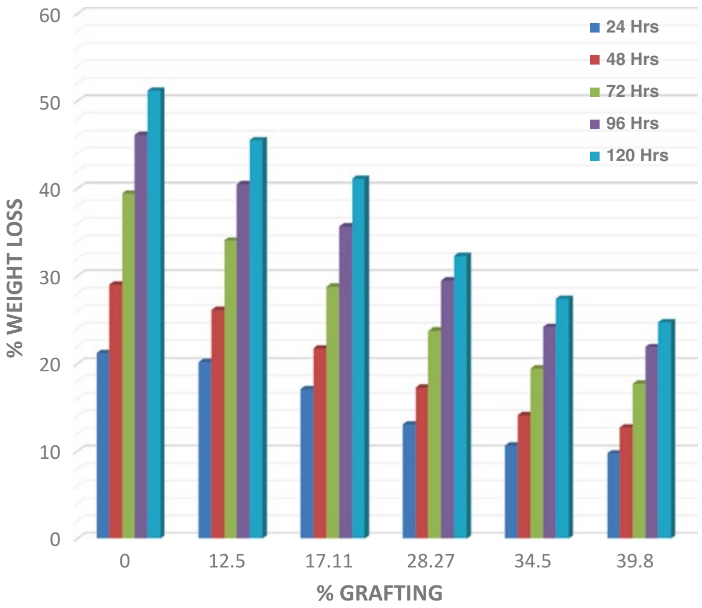

Fig. 12.13 Acid resistance behavior of raw and grafted cellulosic *Hibiscus sabdariffa fibers* in 1 N HCl at different time intervals

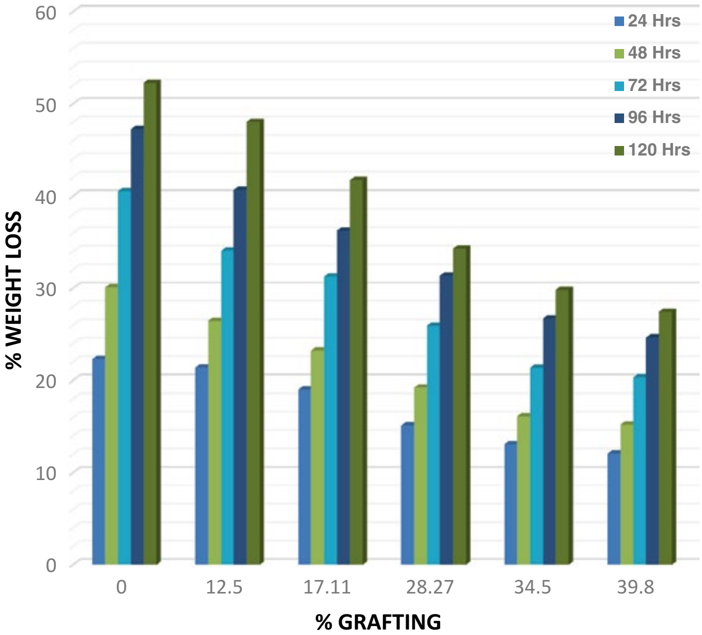

Fig. 12.14 Base resistance behavior of raw and grafted cellulosic *Hibiscus sabdariffa fibers* in 1 N NaOH at different time intervals

respectively, (Figs. 12.13 and 12.14) due to the hydrophobic nature of PMMA (Thakur et al. 2011a).

12.4 Conclusions

Hibiscus sabdariffa biofibers belong to the category of lignocellulosic fibers and are having hydrophilic nature due to the presence of hydroxyl groups. The hydrophilic nature of these fibers results in poor compatibility with the hydrophobic polymer matrices limiting their use for successful end applications. Therefore, functionalization of these fibers is required to overcome these difficulties. Hence, from the research work reported in the present chapter it is quite clear that pressure-induced synthesis is also a viable technique to modify the surface properties of the fibers. *Hibiscus sabdariffa biofibers* grafted using this technique showed enhanced physico-chemical properties.

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Chapter 13
Kapok Fiber: Applications

Yian Zheng and Aiqin Wang

Contents

Abstract Kapok fiber is obtained from the seed hairs of kapok trees (*Ceiba pentandra*) and belongs to a natural cellulosic fiber. Kapok fiber is consisted of abundant hollow microtubes with the unique structure of void content as high as 80–90 %. Conventionally, kapok fiber is used as the stuffing for pillows, bedding, and some soft toys. Owing to excellent buoyancy and air-filled lumen, kapok fiber is also utilized as the buoyant material (such as life preservers) and insulation materials against sound and heat. Due to better warm retention property, kapok fiber can blend with other fibers to achieve the required apparel textiles. Kapok fiber contains wax layer on its surface, which affords this fiber to show excellent hydrophobic–oleophilic characteristics, and accordingly, this fiber has received much attention in

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recent years as the oil-absorbing material. Featured with natural microtubes structure, kapok fiber can also be used as a desirable template material or supported candidate such as for catalyst carriers. This chapter provides a summary of recent applications of kapok fiber, with special attention to some fields being developed.

Keywords Kapok fiber • Application • Oil-absorbing material

13.1 Introduction

Kapok is a silky fiber that encloses the seeds of kapok trees (*Ceiba pentandra*) and the color is yellowish or light-brown with a silk-like luster. In contrast to cotton fiber, the kapok fiber is single-celled plant hairs. Owing to its hollow air-filled lumen and high void content, kapok fiber is conventionally used as stuffing for insulation against sound and heat, and for bedding, pillows, life preservers, and other water-safety equipments because of its excellent buoyancy. Due to the unique features, kapok fiber-based materials have opened the possibilities for various new application fields. Figure 13.1 shows the representative relationship between structure, properties, and applications for kapok fiber.

13.2 Applications of Kapok Fiber

13.2.1 Apparel Textiles

In the early years, kapok fiber is considered unfit for textile fabrics. However, the weavability can be enhanced by blending with other fibers. Generally, the addition of kapok fiber into the fabrics or wadding will improve the warm retention though

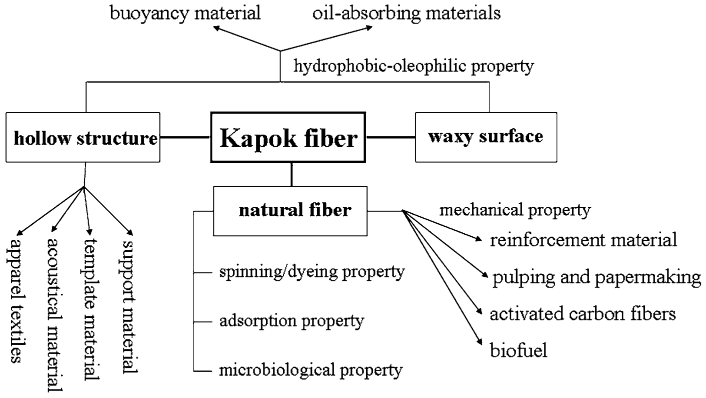

Fig. 13.1 Representative relationship between structure, properties, and applications for kapok fiber

the compression elasticity may be affected (Cui et al. 2010; Wei et al. 2008). The kapok/cotton fabric had met the basic requirements on apparel textiles, showing better performance than cotton fabric in air permeability, warmth retention, and durability, especially the warmth retention of plain woven kapok/cotton fabric. However, its wear resistance and crease recovery were slightly poorer than those of cotton fabric. Therefore, it is suggested for kapok/cotton fabric that loose texture, for example satin, should be chosen for summer, and plain weave should be selected for winter, by which cavities of kapok fibers can be fully utilized for realizing reasonable air permeability and warmth retention (Han et al. 2010). In addition, the kapok blended fabrics are observed with better hygroscopicity and moisture guide properties (Lou 2011). Comparative analysis showed that addition of kapok fibers into viscose/polyester blend fabric improved the warm retention, anti-ultraviolet radiation, and crease recovery. And also, the fabric was more likely to accumulate charge but with fast charge dissipation (Hong et al. 2012).

13.2.2 Buoyancy Material

Owing to large hollow structure and waxy surface, kapok fiber shows excellent hydrophobic–oleophilic characteristics. As the water drops are deposited onto the surface of kapok fiber, the intrinsic hydrophobic nature of fiber will cause a repelling force which will prevent the water drops from spreading onto the surface of kapok fiber (Fig. 13.2). Additionally, more wrinkles with the height of several nanometers are decorated on the cylindrical microtube of kapok fiber, and this micro-nano-binary structure will also produce positive contributions for its hydrophobic–oleophilic characteristic. Combining hydrophobic–oleophilic characteristic with lightest quality, kapok fiber aggregates ideally are applied as the life-saving supplies.

From previous studies, the optimal density of kapok fiber aggregates with 5 cm height is 0.015 g/cm^3. Accordingly to the common international standard, this 5 cm height corresponds to 0.5 kPa hydraulic pressure for evaluating buoyancy materials. The kapok aggregates with this density show excellent resistance to the outer hydraulic pressure and can keep a constant capacity up to 5 kPa. Compared with some artificial buoyancy materials, the optimal density of kapok fiber aggregates is at least 20 times lower. For example, this density is 0.3 g/cm^3 for life jacket foam and 0.37–0.42 g/cm^3 for poly (vinyl chloride) (PVC), polyurethane (PU), polystyrene (PS), or PE foam. The resulted high buoyancy multiple implies that kapok fiber aggregates show an excellent buoyancy performance and are expected to be an ideal buoyancy material (Zhang et al. 2013). However, the buoyancy would decline after the material is being used or stored for a long time, as it would be compressed due to fiber migration. Consolidating kapok fiber into webs with low-melting point fiber can improve the buoyancy behavior of the kapok fiber assembly, obtain a compression resistance even better than the kapok/three-dimensional crimped hollow polyester fiber assembly and provide higher buoyancy factor (Xiao et al. 2005). To improve the uneven structure, a processing way of combined action of air carding and mechanical blending can be employed to replace the hand padding (Shi et al. 2009).

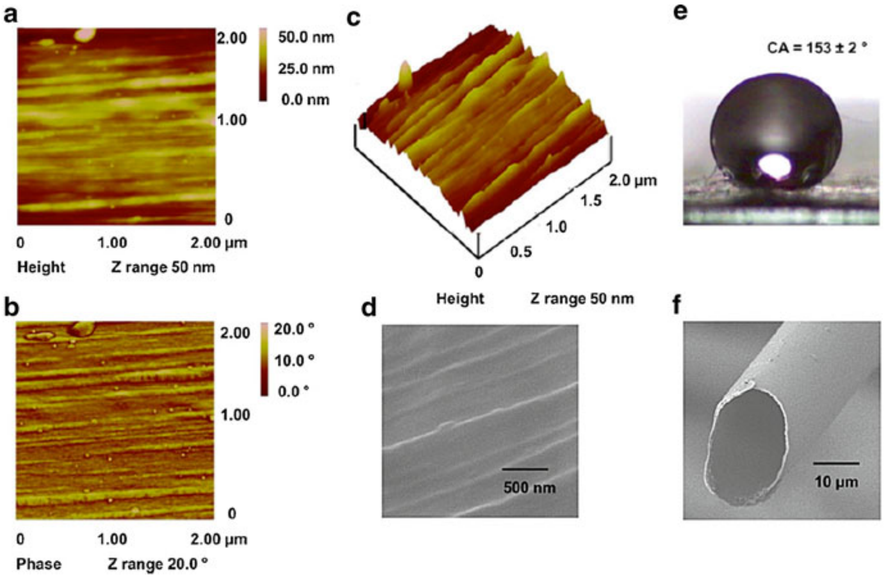

Fig. 13.2 (**a–d**) are the AFM height image, phase image, the according three-dimensional view, and the SEM image, of the outer surface of a kapok fiber, respectively. Nano-scaled wrinkle on the surface can be clearly seen. (**e**) CA of a water droplet on kapok fiber films is measured to be 153 ± 2. (**f**) SEM image of a natural kapok fiber with micro-scaled diameter (Zhang et al. 2013) Copyright 2013, reproduced with permission from Elsevier

13.2.3 Acoustical Material

Noise pollution is the disturbing or excessive noise that may bring heavy damage and great stress on the activity and balance of human or animal life, such as hearing impairment, disturbance of sleep, psychophysiological and mental health, and so on. Therefore, it is necessary and important to develop economical and environment-friendly acoustical materials to control the noise pollution. Traditional acoustical materials generally include fibers, foams, perforated panels, membranes, and their composites.

Different from other fibers, kapok fiber has large lumen and thin cell walls. The special structure of kapok fiber is expected to be beneficial for the sound absorption since it increases the chance of friction between sound waves and fibers. Some studies reveal that the kapok fiber has excellent acoustical damping performance and the sound absorption coefficients of kapok fibrous assemblies are significantly affected by the bulk density, thickness, and arrangement of kapok fibers but less dependent on the fiber length. Compared with assemblies of commercial glass wool and degreasing cotton fibers, the kapok fiber assemblies with the same thickness but much smaller bulk density may have the similar sound absorption coefficients (Xiang et al. 2013). The kapok fiber can also be combined with other fibers, such as polypropylene fiber to obtain a composite with sound absorptive property.

The values of sound absorption coefficient and noise reduction coefficient obtained indicate that the kapok fiber composites possess very good sound absorption behavior in the frequency range 250–2,000 Hz (Veerakumar and Selvakumar 2012). Furthermore, kapok fiber possesses some ecological characteristics such as environment-friendly, biodegradable, renewable, safe fiber handling, and low energy consumption. Combined with excellent chemical stability, it can be concluded that kapok fiber is a promising light and environment-friendly sound absorption material for potential applications in noise reduction field.

13.2.4 Oil-Absorbing Materials

Over the production, storage, and transportation of oils, there are always possible risks of oil spillage. Oil spills often result in immediate and long-term environmental damage, especially for marine areas since the spilled oils can form a thin coating over the hundreds of nautical miles. This is a major problem on the coastal environment and marine resources, and has created public and government awareness and concern. To minimize the possible environmental impacts in the event of oil spillage, some oil spill remediation products have been developed for the cleanup and recovery of oil spills, including but not limited to dispersants, solidifiers, demulsifiers, gelling agents, absorbents and biological agents, etc. Mostly, polypropylene fiber-based oil sorbents are used to clean up oil spills. However, this synthetic material will present serious environmental problems owing to their non-biodegradable characteristics at the end of usage.

Kapok fiber, a natural, inexpensive, hydrophobic–oleophilic agricultural product, is then considered to be a better alternative to those widely used synthetic materials. Owing to its hollow lumen and thick wax layer, kapok fiber exhibits high hydrophobic–oleophilic characteristics, and this intrinsic nature makes kapok fiber have high oil retention and reusability. Additionally, in the mixture of oil and water, the polypropylene fiber-based oil sorbents tend to sink just after 3 min, while this phenomenon cannot occur for the kapok fiber assemblies (Rengasamy et al. 2011). Compared to polypropylene, kapok fiber is relatively cheaper, and can be recovered from spent bedding, pillows, soft toys, and life preservers for reuse as the oil sorbents. Due to its eco-friendly properties, kapok fiber can be ultimately applied for biomass energy recovery and accordingly, no secondary wastes can be produced during its usage as a result its biodegradability (Lim and Huang 2007a).

Featured with lower density, higher porosity, greater specific surface area, and hydrophobic–oleophilic characteristics, kapok fiber is now receiving great attention as the filter product for deep-bed filtration in achieving oily water separation. Through the kapok-packed filter column, a series of pictures are taken to describe a typical diesel/water separation process when the oily water passed (Fig. 13.3). During the oil/water separation process, the dynamic behavior can be classified into four stages, i.e., infiltration, separation, displacement, and equilibrium. For the kapok filters, the optimum packing density was determined to be 0.07 g/cm^3, and

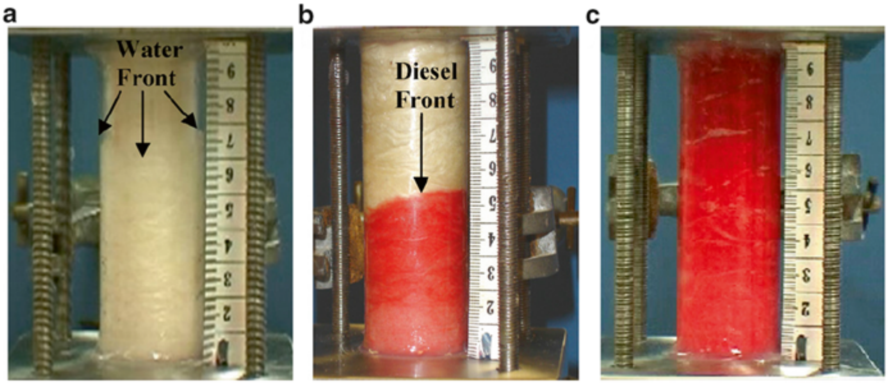

Fig. 13.3 Observation of the 2.5 % diesel/water separation by kapok filter with packing density of 0.07 g/cm^3: (**a**) water front advancement, (**b**) diesel front advancement, and (**c**) filter column at breakthrough (Lim and Huang 2007b) Copyright 2007, reproduced with permission from Elsevier

with an increase in packing densities and oil concentration, the hydraulic conductivities will decrease (Huang and Lim 2006). During this process, the kapok filters can also reduce the COD and turbidity of effluent for the oily water (Rahmah and Abdullah 2010), and can retain stable after 15 cycles of reuse with only 30 % of sorption capacity reduction (Abdullah et al. 2010). Owing to its impressive hydrophobicity, kapok fiber shows poor affinity to water and good affinity to all kinds of oils. This fiber shows a high adsorption capacity for diesel oil (31 ± 0.81 g/g) (Zhou et al. 2010), and can selectively absorb abundant amount of oil (40 g/g) from an oily water in both freshwater and seawater (Hori et al. 2000). Even in the well-mixed oil–water media, kapok fiber shows its effective oil-absorbing performance. In that case, the kapok fiber shows overwhelmingly high oil-to-water sorption (O/W) ratios ranging from 19.35 to 201.53, far superior to sugarcane bagasse, rice husks, and synthetic sorbent (lower O/W ratios of 0.76–2.69) (Ali et al. 2012). Given the mechanical property, an oil-absorbing composite material by mixing pig hair with kapok fiber has been developed. Flexibility of pig hair is larger than the kapok fiber, making the composite show a higher elasticity (Liu et al. 2012).

Kapok fiber is a highly effective oil-absorbing material and its sorption mechanism can be proposed as follows. Owing to its hollow structure and waxy surface, the kapok fiber has intrinsic larger effective pore volume for oil entrance and higher adherence ability for oils against escape. Due to the better compatibilities between the oils and the wax layer of the kapok fiber, the oils are firstly adsorbed by the interactions and van der Waals forces between the oils and the waxy surface. Subsequently, the oils previously entered the kapok assemblies will penetrate into the kapok lumens via internal capillary movement. During the entire process, two dominant factors that contribute to the oil absorption and retention within the kapok assemblies should be taken into account: one is the oleophilicity of the kapok fiber and the other is the physical characteristics of oils such as density, viscosity, surface tension (against air), and contact angle with the kapok surface (Lim and Huang 2007a).

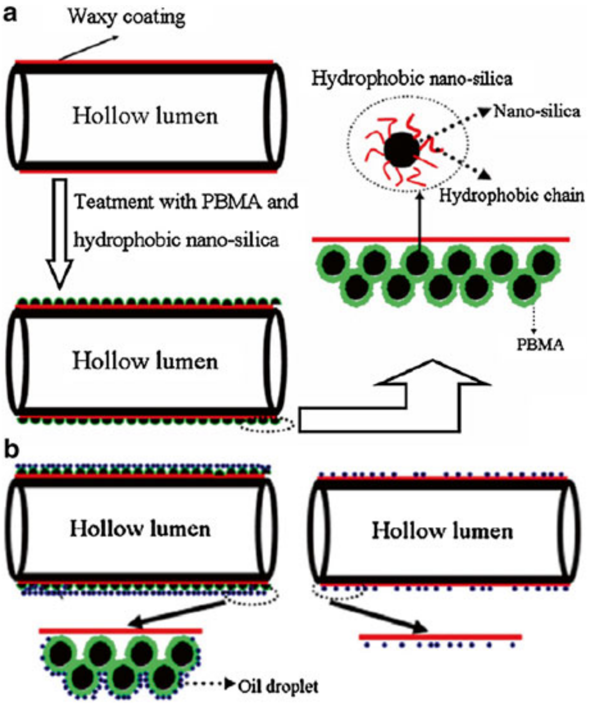

Fig. 13.4 (**a**) Schematic representation of transition from raw fiber to coated kapok fiber with surface of nanometric roughness and low surface energy and (**b**) Schematic mechanism of oil droplet on surface of raw and coated kapok fiber (Wang et al. 2013d) Copyright 2013, reproduced with permission from Elsevier

For the oil absorption and retention, the hydrophobic–oleophilic characteristic of the surface of kapok fiber has made great contributions. To find more chances for the application of kapok fiber in oil spillage control, kapok fiber can be amenable to surface modification by giving appropriate treatment. To enhance the oil absorbency, kapok fiber can be modified with materials with low surface free energy to obtain hydrophobic surface, by which the resulting kapok fiber can be afforded with new lipophilic properties. Using polybutylmethacrylate (PBMA) and PS as the modification agents, Wang et al. (2013a) prepared two kinds of oil absorbers via a facile solution–immersion process and found that PBMA- and PS-coated kapok fibers show higher oil-absorbing capacities than raw kapok fiber for gasoline, diesel, soybean oil, and paraffin oil and the oil sorption capacity can reach up to 80 times their weight. In addition, the kapok fiber can be used as the filler to construct a kind of network with a low crosslinking and a loose structure for synthetic sorbent materials in order to improve the oil absorbency (Wang et al. 2013b). Grafting copolymerization or esterification modification is also useful to increase the hydrophobicity of kapok fiber to enhance its oil sorption capacity (Wang et al. 2012a, 2013c).

Furthermore, the oil sorption capacity of kapok fiber can be improved by transforming its silky surface into rough surface by constructing hierarchical micro- or nanostructures (Wang et al. 2013d). As schemed in Fig. 13.4, with the assistance of hydrophobic–hydrophobic effect, hydrophobic nano-silica is firstly dispersed into the PBMA solution, and the resulting mixture is then coated on the surface of kapok

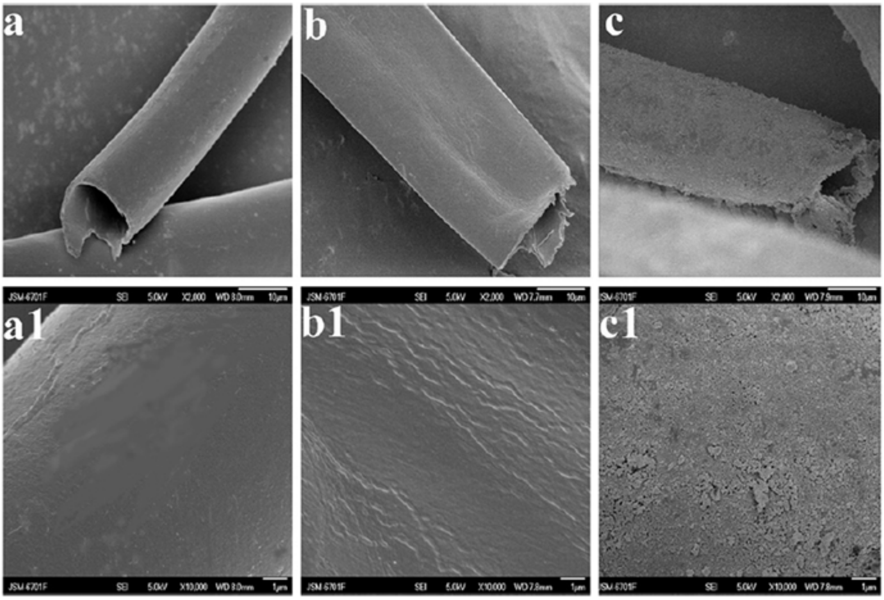

Fig. 13.5 SEM micrographs of (**a**, **a1**) raw, (**b**, **b1**) treated, and (**c**, **c1**) superhydrophobic kapok fiber (Wang et al. 2012b) Copyright 2012, reproduced with permission from Elsevier

fiber, by which a new surface with hierarchical micro and nanostructures is formed. This rough surface, which appears from the combination of more silica nanoparticles and PBMA deposit sediment with low surface energy, can provide more hydrophobic micro-areas that will facilitate the oil retention in kapok fiber. Therefore, more oils can be entrapped into the kapok fiber, which are not easily escaped from the constructed surface of kapok fiber. From hydrophobicity into superhydrophobicity, the surface of kapok fiber can also be coated by a facile incorporation of silica nanoparticles and subsequent hydrolyzation of dodecyltrimethoxysilane (DTMS) for hydrophobic modification (Wang et al. 2012b). As shown in Fig. 13.5, the raw kapok fiber shows a smooth and waxy surface, while the $NaClO_2$-treated kapok fiber exhibits a rough surface with subtle textures and wrinkles. This is attributed to the fact that after $NaClO_2$ treatment, the coverage of inherent plant wax layer on kapok fiber has been removed and more cellulose hydroxyl groups have been exposed to transform the fiber surface from hydrophobic to hydrophilic. Different from raw and $NaClO_2$-treated kapok fiber, the surface of hydrophobical modification of kapok fiber is covered with dense silica nanoparticles and among these nanoparticles, no any interstices can be observed from the SEM images. Though more silica nanoparticles are found on the external surface of kapok fiber, they do not block the internal hollow lumen, allowing those open lumens to retain their intrinsic oil sorption capacity. Compared with raw kapok fiber, this modified fiber shows an excellent oil sorption capacity and an improvement of 46.6 and 20.2 % have been reported for diesel and soybean oil. Furthermore, this coated fiber exhib-

Table 13.1 Kapok fiber-based oil-absorbing materials

Materials	Systems	Oil type, absorbency (g/g) or removal ratio (%)	References
Raw kapok fiber	Static	Machine oil, 40	Hori et al. (2000)
Raw kapok fiber	Static	Diesel oil, 31 ± 0.81	Zhou et al. (2010)
Raw kapok fiber	Static	Diesel oil, 19.35; crude oil, 25.71; new engine oil, 60.51; used engine oil, 49.94	Ali et al. (2012)
Raw kapok fiber	Static	Toluene, 30.4; chloroform, 40.2; xylene, 29.2; *n*-hexane, 21.1; gasoline, 34.1; diesel, 38.9; soybean oil, 50.6; paraffin oil, 54.3	Wang et al. (2012c, 2013a)
Raw kapok fiber	Static	Diesel oil, 36; hydraulic oil, 43; engine oil, 45 at 0.02 g/cm^3	Lim and Huang (2007a)
Raw kapok fiber	Static	Diesel oil, 36.7; used engine oil, 50.8; new engine oil, 47.4 at 0.02 g/cm^3	Abdullah et al. (2010)
Raw kapok fiber	Static	High density oil, 12.6; diesel oil, 11.8 with the porosity of 0.95	Rengasamy et al. (2011)
HCl-treated kapok fiber	Static	Toluene, 35.5; chloroform, 51.8; xylene, 34.8; *n*-hexane, 25.2	Wang et al. (2012c)
$NaClO_2$-treated kapok fiber	Static	Toluene, 36.4; chloroform, 52.3; xylene, 35.5; *n*-hexane, 26.2	Wang et al. (2012c)
PBMA-coated kapok fiber	Static	Gasoline, 59.5; diesel, 64.9; soybean oil, 83.2; paraffin oil, 80.3	Wang et al. (2013a)
PS-coated kapok fiber	Static	Gasoline, 62.3; diesel, 67.8; soybean oil, 80.3; paraffin oil, 83.3	Wang et al. (2013a)
PBMA/SiO_2 coated kapok fiber	Static	Diesel oil, 64.5; soybean oil, 87.1; crude oil, 68.3; 150SN, 77.9; 20cst, 82.3	Wang et al. (2013d)
Acetylated kapok fiber	Static	Diesel oil, 34.1–35.9; soybean oil, 49.8–53.9	Wang et al. (2013c)
Superhydrophobic kapok fiber	Static	Diesel oil, 46.9; soybean oil, 58.8	Wang et al. (2012b)
kapok-*g*-polystyrene	Static	Chloroform, 65.4; toluene, 43.2	Wang et al. (2012a)
PBMA/KF composite	Static	Toluene, 14.6; chloroform, 26.0 with 8 % KF	Wang et al. (2013b)
Raw kapok fiber	Deep-bed filtration	100 % for diesel/water mixture and >99.4 % for hydraulic oil/water mixture	Huang and Lim (2006)
Raw kapok fiber	Deep-bed filtration	>99 % in 2.5 % diesel/water influent	Lim and Huang (2007b)

its excellent oil/water selectivity for cleaning up oils over the water. Table 13.1 summarizes some kinds of oil-absorbing materials based on kapok fiber including raw, pretreated and modified.

13.2.5 Template Material

With kapok fiber as the natural fine template, Zhang et al. (2010) have successfully fabricated a series of microtubes with high length/diameter ratio and controllable morphology. This facile fabrication method has been used for the preparation of many kinds of organic and inorganic materials with controllable wall thickness. Using kapok fibers as the matrix, kapok fiber/magnetic nanocomposites and kapok fiber/CdS nanocomposites are prepared through in situ composition (Tang et al. 2008, 2012), which has a significant guiding role to the preparation and structure characterization of cellulose/inorganic nanocomposites based on plant cellulose resources. Besides, kapok fiber can guide the growth orientation of polyaniline via in situ rapid polymerization of aniline. The resulting material exhibits a unique kapok fiber-aligned morphology and a faster adsorption rate for an adsorbate (Zheng et al. 2012a, b).

13.2.6 Support Material

Kapok fiber is a natural cellulosic fiber which is consisted of abundant microtubes with round hollow structure. Kapok fiber has large hollow structure and contact surface area, and such structure characteristics allow the catalyst to be accessible to the surface of kapok fiber and then a highly effective catalytic reaction can be occurred. Therefore, kapok fiber is expected to be a desirable candidate for catalyst carriers and recovery. Fan et al. (2012) use polyacrylonitrile (PAN) coating to change the surface of kapok fiber from hydrophobic to hydrophilic and improve the adsorption ability for catalytic nanoparticles via a cetyltrimethylammonium bromide (CTAB) assisted self-assembly method. During this process, the amount of CTAB can affect the deposition of PAN coating on the fiber surface (Fig. 13.6). Subsequently, the PAN coated kapok fiber can be used as the support for Au nanoparticles, and the resulting material shows promising catalytic ability for reduction reaction of 4-nitrophenol in the presence of $NaBH_4$.

Kapok fiber can also adsorb an extractant during the metal solvent extraction and behave as the support for the impregnated metal adsorbent. Higa et al. (2011) employed 2-ethylhexyl phosphonic acid mono-2-ethylhexy ester as the extractant to obtain a solvent impregnated kapok fiber, with the findings that the kapok fibers possess a higher impregnation ability for the extractant than conventional solvent impregnated resins, such as crosslinked polystyrene and crosslinked polymethacrylic ester, and thus solvent impregnated kapok fibers have a higher adsorption ability for Eu(III) with the maximum adsorption of 0.685 m mol/g. By comparing bis(2-ethylhexyl)phosphoric acid (D2EHPA) impregnated kapok fiber (SIF) with D2EHPA impregnated resin using XAD7HP as the support (SIR) and solvent extraction with D2EHPA dissolved in a nonpolar organic solvent (SX), the removal percentage of Bi(III), Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II), and Zn(II) from an aqueous nitrate medium was evaluated, with the findings that SIF is more advantageous over SIR and SX according to the amount of D2EHPA necessary for achieving a certain removal percentage. Therefore, kapok fiber-supported SIF will find potential applications in metal-containing wastewater treatment (Huynh and Tanaka 2003).

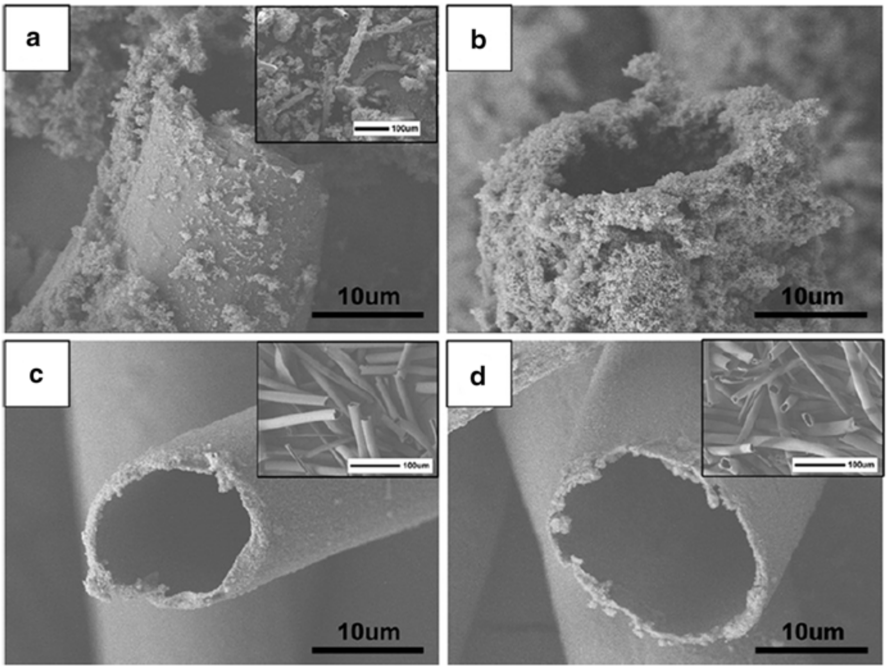

Fig. 13.6 SEM images of the prepared kapok–PAN composite microtubes using varying amounts of CTAB: (**a**) 4.0, (**b**) 7.5, (**c**) 15.0 and (**d**) 30.0 mg, respectively. The amount of AN was fixed at 1.5 mL. *Insets* are the tubes in a low magnification, and the scale bar is 100 μm (Fan et al. 2012) Copyright 2012, reproduced with permission from Elsevier

13.2.7 Reinforcement Material

Plant fibers as the easily renewable sources have attracted much attention in recent years. They are rich in cellulose and cheap in price, and have shown potential application as reinforcements to thermoset and thermoplastic polymer matrices. Plant fibers contain an abundant of hydroxyl groups, making them be highly polar. Accordingly, plant fibers can interact with the resin matrices to form hydrogen bonds. However, those hydroxyl groups are hindered from reacting with resin matrices because of the coverage of the surface of plant fibers with pectin and wax layer, which will result in mechanical interlocking adhesion between the surface of plant fibers and resin matrices. To expose the reactive hydroxyl groups and construct a rough surface, plant fibers generally suffer from a physical and/or chemical treatment or modification.

Alkali treatment is generally used to remove lignin, pectin, wax, and natural oils covering the outer surface of the plant fibers to improve the surface and mechanical properties for further application. In this case, sodium hydroxide has been widely used for treating the surface of plant fibers. By NaOH treatment, the chemical composition of cellulose in kapok fiber cannot be significantly affected, but the crystalline cellulose will be reduced as a result of partial transform of cellulose I to cellulose II. This process is known as alkalization (mercerization) (Mwaikambo and Ansell 2002). Acetylation is another attractive method for modifying the surface of kapok fiber, making it more hydrophobic. With and without an acid catalyst, acetyl groups can be grafted onto the cellulose structure of plant fibers to reduce the hydrophilic tendency. Alkalization and acetylation can successfully change or modify the structure of natural plant fibers to improve the performance of plant fiber composites for better adhesion to resin matrices (Mwaikambo and Ansell 1999; Mwaikambo and Bisanda 1999).

As one kind of important lignocellulosic plant fibers, kapok fiber has been used as the reinforcement material in polyester matrix by hybridizing with glass and sisal fabrics (Reddy et al. 2008). Compared with kapok/sisal polyester composites, the properties of kapok fiber/polyester composites are more attractive (Reddy et al. 2009). For cotton–kapok fabric–polyester composites, with increasing the volume fraction of kapok fiber, the flexural strength and modulus are also increasing. This result implies that the cotton–kapok fabric–polyester composites will find promising industrial applications as design applications frequently involve a bending rather than tensile mode (Mwaikambo and Bisanda 1999; Mwaikambo et al. 2000). The addition of kapok fiber into the thermoplastic cassava starch (TPCS) can not only reduce the water absorption of the TPCS/kapok fiber composite, but also enhance its stress at maximum load and Young's modulus (Prachayawarakorn et al. 2013).

13.2.8 Pulping and Papermaking

Under the optimal dosage of sodium hydroxide, kapok fibers were firstly cooked and the resulting pulp was then refined with two passes using a disc refiner for further blending with commercial hardwood pulp and/or softwood pulp to make papers. The experimental results indicate that the incorporation of kapok pulp into the mixed pulps is beneficial for the improvement of tensile and burst strengths of the sheets, but unbeneficial for the tear resistance and elongation. Moreover, by mixing kapok pulp with the commercial pulps, the water repellency of the sheets is shown to improve. Therefore, it is concluded that kapok fiber will be a quality pulp source for papermaking, and will receive special attentions in packaging paper requiring strength and water repellency (Chaiarrekij et al. 2012).

13.2.9 Kapok-Derived Activated Carbon Fibers

In recent years, activated carbon fibers have attracted much attention as versatile materials having potential as a novel adsorbent, catalyst, and so on. Up to now, numerous research activities have further exploited the preparation of activated carbon fibers based on abundant natural plant fibers, such as kapok fiber. Some studies have been performed to obtain kapok-derived activated carbon fibers with or without an activation process. The experimental results demonstrate that with the assistance of activation process, the kapok-derived activated carbon fibers have a higher surface area and larger hollow pore volume (Chung et al. 2013; Wang et al. 2008).

These kapok-derived activated carbon fibers can be applied for the adsorption of methylene blue and phenol from an aqueous solution (Rong and Zhou 2009).

13.2.10 Kapok-Derived Biofuel

Recently, biofuels such as biodiesel and bioethanol have attracted the most attention for their potential renewable characteristics. However, the first-generation bioethanol is derived from edible sources that will result in food and fuel conflict from the viewpoint of food security. In this respect, bioethanol refined from lignocellulosic biomass such as agricultural residues offers a great option. This kind of bioethanol is recognized as the second-generation bioethanol, which is generally obtained by three main steps: (1) pretreatment, (2) enzymatic hydrolysis, and (3) ethanol fermentation.

Owing to its high glucose content, kapok fiber may be a potential resource for the production of second-generation bioethanol. Before a pretreatment, only 0.8 % of reducing sugar was obtained by enzymatic hydrolysis. After a pretreatment by water, acid, or alkaline, 39.1, 85.2, and >100 % of reducing sugar was produced. For the conversion of cellulose in kapok fiber into glucose, the maximum obstruction is believed to be the high hemicellulose and lignin contents. The acid treatment can remove only hemicellulose, while the alkaline pretreatment enables the removal of both hemicellulose and lignin. Therefore, alkaline pretreatment is more effective for the production of reducing sugar for that lower lignin content is more favorable for enzymatic hydrolysis as the presence of a large number of lignin will adsorb more enzymes to reduce their activity (Tye et al. 2012).

13.2.11 Other Applications

In recent years, renewable green resources are gaining more and more interests. As we have addressed, kapok fiber, as an abundant natural plant fiber, has been used widely for various industrial fields. However, kapok fiber is nonresistant to spark or flame. To remove the combustible compounds, the kapok fiber has been treated by using gamma ray. During this process, the functional groups as methoxyl group in kapok fiber can also be cleaved in addition to the removal of combustible compounds (Chung et al. 2009), by which kapok fiber has been converted into a flame-resistant fiber, but the fine hollow lumen is still present.

Due to the presence of a large proportion of lignin, ordinary cellulolytic bacteria are difficult to attack the kapok fiber. Therefore, kapok fiber can be used as a reference to investigate some properties of wood fibers as its chemical resemblance to wood fibers. Generally, it is time-consuming for preparing the wood sections for microscopic observation, whereas kapok fiber can be observed easily without sectioning. Therefore, it is possible using kapok fiber as a reference for enriching or purifying the wood-degrading bacteria (Nilsson and Björdal 2008).

13.3 Conclusions and Future Perspective

As an eco-friendly renewable material, kapok fiber has received increasing attention in recent years for its intrinsic superiorities, especially by combining its higher hollowness and hydrophobic–oleophilic characteristics. However, the difficulty in spinning of kapok fiber remains in limiting its fabrication for broader applications, especially as the oil-absorbing materials, an overwhelming product for kapok fiber. The development of novel technologies or methods based on kapok fiber will in future promote the further utilization of this natural fiber. Moreover, the unique structure of kapok fiber can direct to design and construct more materials for application in different fields.

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Chapter 14
Nanofibrillated Cellulose: Sustainable Nanofiller with Broad Potentials Use

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Contents

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Abstract This chapter reviews some of the recent advances in the realm of the extraction of nanofibrillated cellulose from lignocellulosic fibers and some aspects of their potential uses in different fields of applications. The production of nano-sized fibrils from cellulose fibers undoubtedly represents one of the most breakthroughs in cellulose-based materials during the two last decades and one of the most studied topics in the literature today. This is due to the attributes of nanocellulosics which include renewability, broad availability, and low cost of the raw material. Other features concerned its large surface-to-volume ratio, high strength and stiffness, low thermal expansion coefficient, low density, biodegradability, and high aspect ratio. Fields of use of nanocellulose include reinforcement of nanocomposite materials, thickening agents, tissue engineering scaffolds, dry-strength additive for paper, filtration media, adsorbents, etc.

Keywords Lignocellulosic fibers • Nanofibrillated cellulose • Nanocomposites • Properties

14.1 Introduction

Cellulose, the most abundant component of plant biomass, is found in nature almost exclusively in plant cell walls, although it is produced by some animals (e.g., tunicates) and a few bacteria. Cellulose constitutes the main structural component of the primary cell wall of green plants (Belgacem and Gandini 2008). The main functions of cellulose during plant life are to protect the cell membrane and to keep stems, stalks, and trunks rigid. Cellulose is a semicrystalline polysaccharide appearing in nature in the form of fibers with width ranging from 5 up to 20 μm and length in the range of 0.5 up to several mm. In its native form, cellulose fibers are embedded in a matrix of other structural biopolymers, primarily hemicelluloses and lignin, which comprise 20–35 and 5–30 % of plant dry weight. Cellulose fibers exhibit a particular structural hierarchy derived from their biological synthesis. At the molecular level (~Å), cellulose is composed of ß-1,4 linked glucopyranose units with about 10 Å long. The cellulose chains self-assemble in a sheet of ordered cellulose chains, stacking in a multiple parallel layer to form the elementary fibrils. Each elementary fibrils with square section 3–5 nm in size and length, which are linked together in repeating lengths along their chains alterned with amorphous domains (Fig. 14.1). In the ordered regions, cellulose chains are tightly packed together and are stabilized by a strong intra- and intermolecular hydrogen-bond network. These elementary fibrils further self-assemble into larger bundles to form the cellulose microfibrils which are embedded into hemicellulose matrix and enclosed by lignin.

At the macrostructural level, the cellulose fiber is organized in a cellular hierarchical structure and can be described as an association of concentric layers surrounding the lumen. The outermost layer is the primary wall (P), followed by the outer layer of the secondary wall (S1), the middle layer of the secondary wall

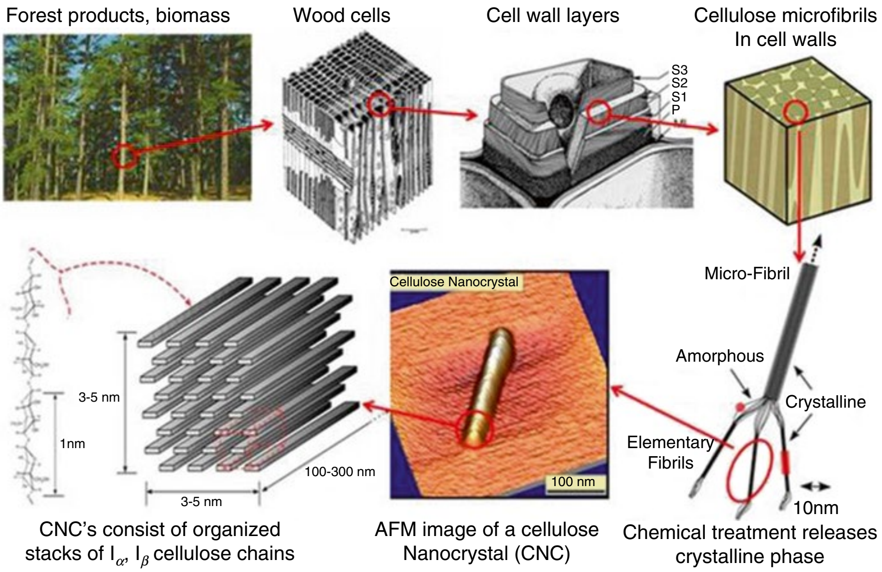


Fig. 14.1 Hierarchical morphology of cellulose from macroscopic to nanoscopic level (https://engineering.purdue.edu/nanotrees/)

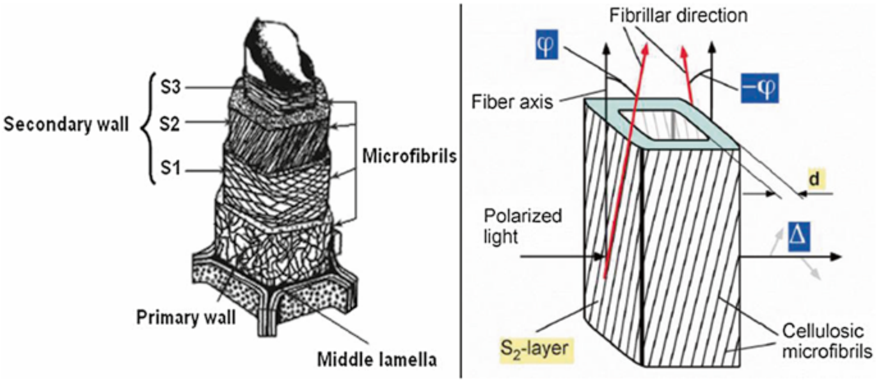


Fig. 14.2 Typical morphology of cellulose fiber (**a**) and representation of the MFA in the S2 layer

(S2), and the inner layer of the secondary wall (S3), as shown in Fig. 14.2. The cellulose microfibrils are associated in a helical pattern within the cell wall and oriented at different microfibril angles within the different layers to form the cellulose fibers. The microfibril angle, which is the angular deviation of the microfibrils from the longitudinal fiber axis differ depending on the cell wall layer and according to the plant type. In primary cell walls, the orientation of cellulose micro-

Table 14.1 Microfibril angle and tensile properties of different plant fibers from Madsen (2004)

Plant fiber	Microfibril angle (°)	Stiffness (GPa)	Ultimate stress (MPa)
Hemp	6	30–60	300–800
Flax	6–100	50–70	500–900
Jute	8	20–55	200–500
Sisal	10–25	9–22	100–800
Cotton	–	6–10	300–600
Softwood	3–50	10–50	100–170

fibrils is often random. In the secondary cell walls of xylem cells; the microfibrils are transversely oriented in the outer S1 layer, fairly parallel aligned in a helical pattern in the thick S2 layer and in the inner S3 layer they are transversely oriented in a S-Z-S helical organization (Fig. 14.2b). The orientation of the microfibrils in the S2 layer has strongly affected the mechanical properties, namely its stiffness and strength (Barnett and Bonham 2004; Cave and Walker 1994) (Table 14.1).

14.2 Nanocellulose Particle Types

Nanosized cellulose particles emerged as one of the most promising reinforcement nanofillers in the realm of sustainable materials. The number of publications on the topic of nanomaterials based on cellulose nanoparticles has increased at an almost constant rate since the early 1990s, reaching about 3,500 in the year 2012, referring to ISI Web of Knowledge database.

Unlike the synthetic nanoparticles, nanocellulose is completely renewable, is lightweight material with density around 1.5 g cm^{-3}, is less expensive to produce, and is safer to handle compared with synthetic nanoparticles. Among these nanosized fibrils, cellulose nanocrystals (CNC), and nanofibrillated cellulose (NFC) arose the major interest. The former are extracted from fibers after a complete dissolution of the amorphous fractions, while the latter results from the mechanical disintegration of the cell wall, yielding highly interconnected fibrils 10–100 nm in width and length within micronic scale.

14.2.1 Cellulose Nanocrystals

CNCs named also nanowhiskers, nanocrystals, are rod-like shaped cellulose nanoparticles with stiff structure and devoid of chain folding (Fig. 14.3). CNC correspond to the ordered crystalline components that can be extracted from various cellulosic materials. The isolation of crystalline zones from its natural occurring material call for a chemical treatment to destroy the less ordered region and release the crystalline domains as aqueous suspensions (Fig. 14.4). This process has been

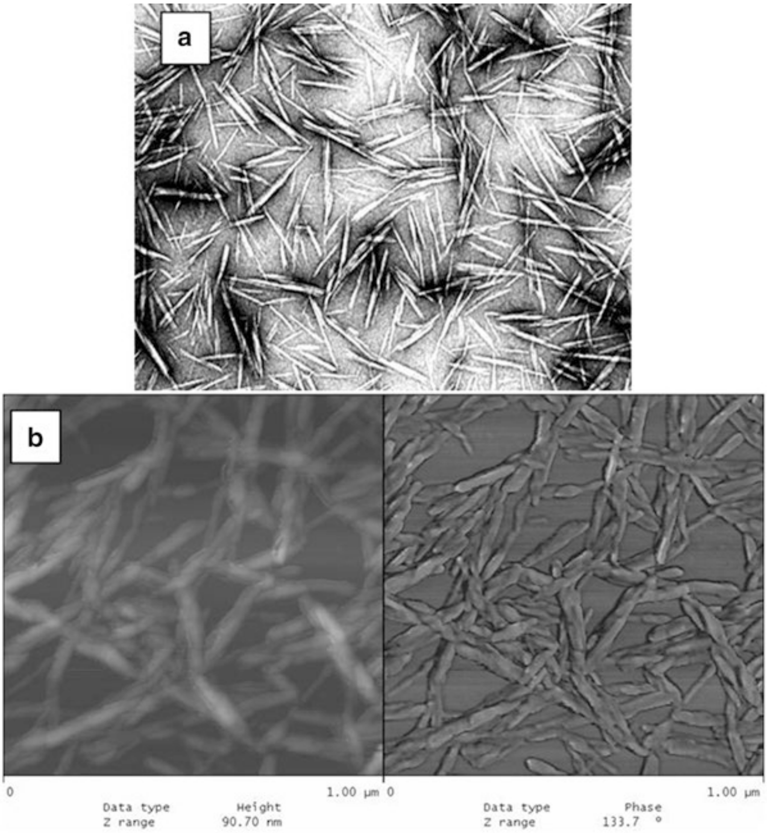


Fig. 14.3 (**a**) Transmission electron micrograph of ramie cellulose nanocrystals (CNC), and (**b**) AFM observation of Alfa CNC (*Stipa tenacissima*)

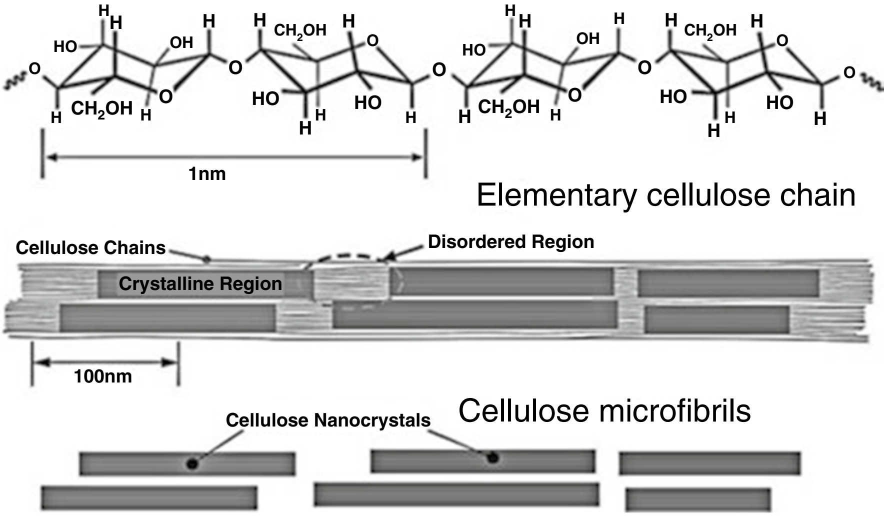


Fig. 14.4 CNC organization from the elementary cellulose chain to the microfibrils

described nearly 60 years ago by Ranby et al. to isolate cellulose microcrystals (Ranby 1951). Under controlled conditions, the amorphous regions of cellulose which are more accessible to acid attack compared to crystalline regions will be hydrolysed leaving CNC in suspension. The conditions of hydrolysis during the extraction process (such as the type of acid, acid concentration, temperature, and duration) affect the morphology of the ensuing nanocrystals (Dong et al. 1998). The morphological features of CNCs, in terms of length, *L*, and width *l*, are found to vary widely, depending on the source of the cellulosic material and the conditions under which the hydrolysis is performed. Several interesting reviews provide and update overview of the properties of CNC (Azizi Samir et al. 2004; Habibi et al. 2010; Siqueira et al. 2010).

CNC exhibited a high elastic moduli 100–150 GPa (10, 11) (depending on the source), and aspect ratio (10–100), with diameters ranging from 4 to 20 nm (3). The main breakthrough of CNC was found in their huge reinforcing potential when incorporated in a polymer matrix at a relatively low loading viz, lower than 10 wt%. The unusual mechanical enhancement observed in these materials was associated with the formation of a percolating fibrils network in the polymer matrix, in which stress transfer among the nanoparticles is driven by hydrogen bonding.

The properties of the dimensional characteristics with their respective sources, description of isolation processes, hydrolysis conditions, and techniques of determination and performance of this material in suspension and in polymeric matrices were gathered in several recent interesting reviews.

14.2.2 Microbial Cellulose

Microbial cellulose or bacterial cellulose (BC) is another form of nanosized cellulose that is produced by bacteria belonging to the genera of Acetobacter, Rhizobium, Agrobacterium, and Sarcina. This non-photosynthetic organism is capable of producing cellulose from a variety of inexpensive carbon substrates, which include glucose, sucrose, and fructose.

BC has an identical chemical structure as the Cellulose I found in plants. Cellulose chains are assembled together in the form of elementary fibrils, which then are linked together by hydrogen bonds to form microfibrils. Finally the microfibrils are assembled together into a ribbon, as shown in the figure below (Fig. 14.5). By controlling the substrates, cultivation conditions, additives type, and the bacterial strain, it is possible to control the molar mass, the length, and the supramolecular structure (Retegi et al. 2010). BC is composed of ribbon-shaped microfibrils having a width of 20–50 nm and length in the micronic scale. The bacterial cellulose is produced as flock or suspended matter in a form of sheet, dispersion, grain or the like by static culture or aeration agitation culture which effects entangling of fibers.

The cellulose obtained from bacteria is known to have unique properties over plant cellulose such as:

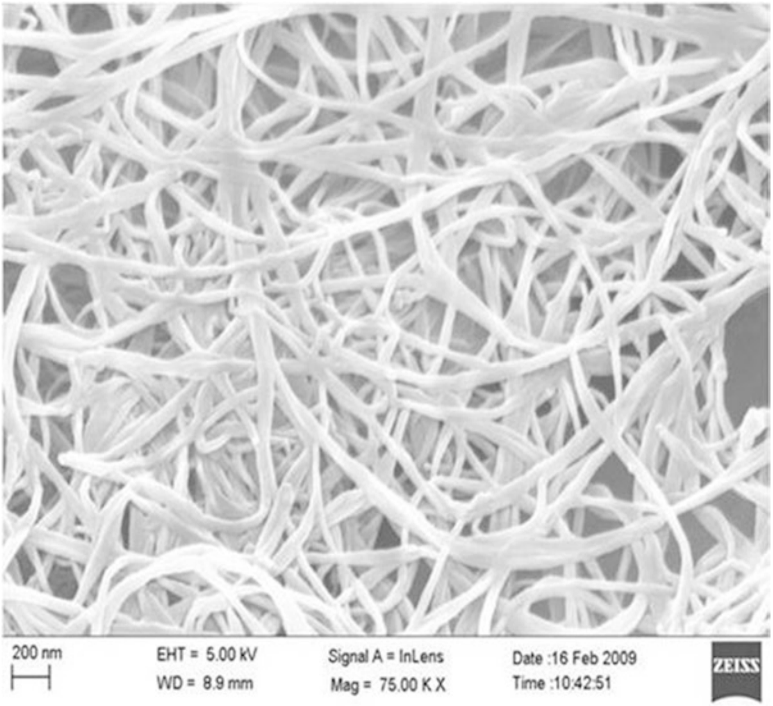


Fig. 14.5 Scanning electron micrograph of bacterial cellulose nanofibres

1. Absence of lignin and hemicelluloses, making it a highly pure source of cellulose.
2. High degree of polymerization combined with crystallinity (60–70 %), leading to high Young's modulus at room and elevated temperatures: The typical Young's modulus of BC is found to be in the range 15–35 GPa, with the tensile strength in the range 200–300 MPa.
3. Extremely high water-holding capacity, up to 100 times its self-weight.
4. Excellent biodegradability and biological affinity.

Because of these unique properties of BC, several applications based on advanced technologies have been reported, namely in the field of biomedical application for tissue engineering applications and wounds dressing material (artificial skin) (Czaja et al. 2007), artificial cardiovascular tissues, blood vessels (Klemm et al. 2001), skin and meniscus replacements (Aase et al. 2000). Furthermore; thanks to its high modulus and nanoscale dimension dense with high aptitude to set-up a dense entangled network structure, BC has gained interest in recent years in advanced technologies as a reinforcement nanofiller in nanocomposite material, nanopaper, and conducting paper (Satish and Thiruvengadam 2012; Wan et al.

2006; Ifuku et al. 2007). Despite their properties, BC use has not yet reached large-scale commercialization owing to its high price (about 100×more than plant cellulose), relatively low yields production.

14.2.3 Nanofibrillated Cellulose

Unlike CNCs, nanofibrillated cellulose (NFC) consists of long, flexible, and entangled cellulose nanofibers, encompassing alternating crystalline and amorphous domains, and is composed of elementary or bundles of cellulose microfibrils, with lateral dimensions in the order of 10–100 nm, and length within the micrometer scale. In the literature, the term NFC, or nanofibrilar cellulose, is also employed to designate the same material. The terminology microfibrillated/nanofibrillated or (NFC) was first used by Turbak et al. (Turbak et al. 1983a, b; Herrick et al. 1983). They were the first to report the extraction of NFC by high pressure homogenization (HPH) of dilute slurries of softwood cellulose fibers using a Manton Gaulin Homogenizer. As the slurry reached 80 °C at 500 MPa, the suspension turned into a translucent, high consistent gel that they called microfibrillated cellulose (MFC). Since that, MFC opens the way toward intense and promising research on nanocellulose-based material with expanding area of potential applications, including transparent materials (Abe et al. 2007a, b; Fukuzumi et al. 2009), packaging materials endowed with high mechanical properties, and low gas permeability (Syverud and St enius 2009; Rodionova et al. 2011; Spence et al. 2011a, b; Aulin et al. 2010a, b), biomedical applications (Czaja et al. 2007), nanopaper production, and strength additive for paper (Henriksson et al. 2009; Sukjoon and Jeffery 2010). NFC could also be used as a thickener additive in foods, cosmetics, paints, and pharmaceutical products (Turbak et al. 1983a, b). MFC/NFC has been also the subject of a number of several reviews focusing mainly on the method of preparation and on nanocomposite applications (Siró and Plackett 2010; Abdul Khalil et al. 2012; Hubbe et al. 2008; Moon et al. 2011).

In fact the term NFC should not be confused with cellulose microfibril which constitutes the smallest discernible building blocks of natural cellulose with lateral dimensions in the range of 5–20 nm depending on the cellulose origin (Donaldson 2007) and length generally in micrometer scale. Actually, the different process adopted to release NFC leads to a wide distribution in the width of the nanosized particles ranging from 5 up to 100 nm, depending on the energy input to disintegrate the cellulose fibers, and on the pretreatment used to facilitate the disintegration process (Fig. 14.6). It means that NFCs are nanofibrils composed of bundles of elementary fibrils separated by less ordered regions and have the ability to create entangled networks. Unlike CNC being composed of elementary monocrystals, CNC looks also as stiff rod-like fibrils, while NFCs are rather flexible and exhibited strong tendency to entanglement leading to a web-like structure as water is removed.

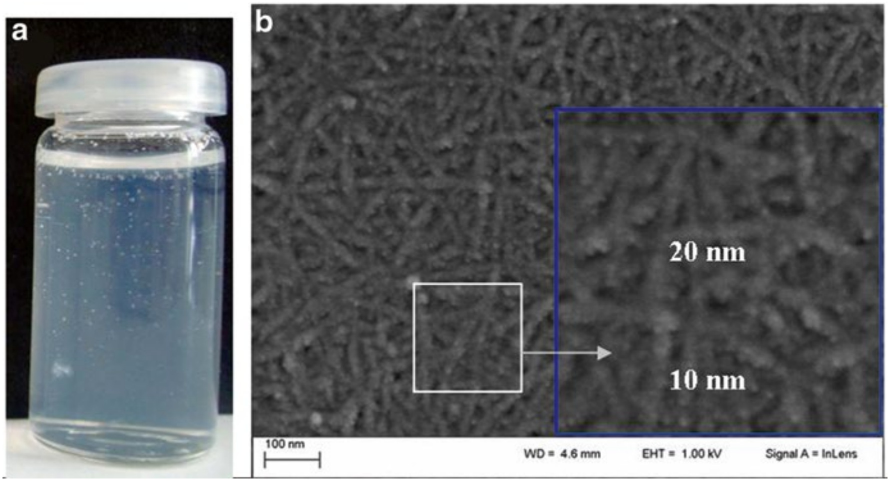


Fig. 14.6 (**a**) Appearance of the NFC gel at 1 wt%, and (**b**) field effect scanning electronic microscopy pictures of the NFC from eucalyptus

The promising potential of applications of NFC along with its sustainable character has attracted the attention of a number of companies and starts up to reach large-scale commercial production of NFC. In 2011, Innventia opened the world's first pilot plant for the production of nanocellulose with a capacity of 100 kg day^{-1}, which constitutes an important step towards the industrialization of the microfibrillar cellulose. Since that, other investments in NFC production were launched. In 2011 UPM has started pre-commercial production of fibril cellulose and is currently developing new fibril cellulose applications with industrial partners (http://www.upm.com/EN/PRODUCTS/biofibrils/Pages/default.aspx). In 2012 US Forest Products Laboratory opens the pilot plant to produce wood-derived renewable materials and Stora Enso (www.storaenso.com) makes a groundbreaking investment in nanotechnology at Imatra, Finland to produce and commercialize NFC. Moreover, according to Future Markets Inc., the production of nanocellulose is expected to grow by 1,000 % in 2014–2016, and will further grow by 500 % at least in 2017 (The global market for nanocellulose to 2017. 2012).

14.3 Cellulose Source Materials for Nanocellulose

Due to the diversity of cellulose, nanocelluloses can, in principle, be derived from a wide variety of sources. Although wood remained the main resource for cellulose fibers feedstock, any other available biomass resource containing cellulose might be used as a starting material for the production of nanocellulose. These include agriculture crops residues, annual plants, grasses, and other plant substances.

14.3.1 Wood

Wood is the most important source for the production of cellulose material and constitutes the main starting material for the production of NFC. However, before being used as a raw material for the production of NFC, the non-cellulosic material in wood, mainly lignin, should be removed using a chemical process.

14.3.2 Annual Plan and Agriculture Residues

Owing to their availability all over the word, their renewable character and their sustainability, agricultural crop residues represent an important source of cellulose fibers. This class of biomass has received increasing attention in recent years as an alternative resource for the extraction of cellulose fibers. Comparatively to the wood, non-woody plants have generally lower lignin contents (Marques et al. 2010), and offer several advantages, including short growth cycles with moderate irrigation requirements, they do not compete with wood supply and have lower lignin content, making easier the delignification process. The morphology of the NFC from the annual plants depends from their origin. An example of NFC from several annual plants is shown in Fig. 14.7. However, despite the abundance of non-woody plants, their use as a raw material for chemical pulping is still limited because of the high labor cost of collection of non-woody plants, namely in developed countries, and to the high silica content, namely for cereal straw, making the pulping process more difficult than woody fibers. The high silica content hamper to use the classical soda pulping technology, as the recycling of black liquor with a recovery boiler is harder to implement.

A wide range of non-woody plants have been used for the production of NFC, including cotton (Elazzouzi-Hafraoui et al. 2008), ramie (Habibi and Dufresne 2008), sisal (Rodriguez et al. 2006), flax (Cao et al. 2007), abaca (Alila et al. 2013) wheat straw (Helbert et al. 1996; Alemdar and Sain 2008), potato tubers (Dufresne et al. 2000) sugar beet pulp (Leitner et al. 2007; Dufresne et al. 1997; Habibi and Vignon 2008), banana rachis (Zuluaga et al. 2007), bagasse (Bhattacharya et al. 2008), palm tree (Bendahou et al. 2010), and alfa fibers (Ben Mabrouk et al. 2012) (Fig. 14.7).

14.4 Safety Aspects

The reduction in size to nanoscale has been widely recognized as a source of increased toxicity of nanoparticles. A large number of nontoxic bulk materials become poisonous when their size is reduced to nanoscale, as is the case for Carbon black which is nontoxic; while carbon nanotubes and fullerene are highly toxic when inhaled into the lungs (Carrero-Sanchez et al. 2006). Although, the number of publications on the topic of nanocellulose has increased at a steady rate, the total

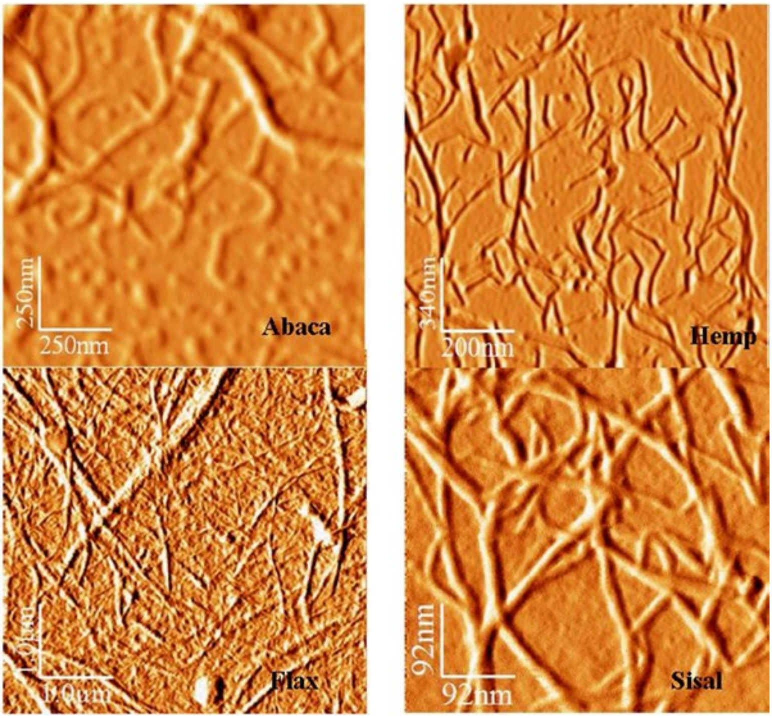


Fig. 14.7 AFM images of the NFC from several annual plants, namely; abaca, hemp, flax, and sisal (Alila et al. 2013)

number of papers on safety aspects and environmental aspects of nanocellulose-based nanoparticles remained low. Referring to ISI Web of Knowledge database, only several papers were devoted to this aspect (Foster et al. 2011; Vartiainen et al. 2011; Ni et al. 2012). In aqueous solution manipulating nanocellulose does not cause any risk of exposure to fine particles. No evidence of inflammatory effects or cytotoxicity on mouse or human macrophages has been reported after exposure to nanocellulose. The results of toxicity studies suggest that nanocellulose is not cytotoxic and does not cause any effects on inflammatory system in macrophages.

14.5 NFC Isolation

NFC is produced by delaminating cellulosic fibers under an intense high mechanical shearing action in order to release the NFC and to overcome interfibrillar hydrogen bonds into both crystalline and amorphous domains. Although HPH and microfluidization are the main methods currently used, other approaches were reported in the literature as schematically presented in Fig. 14.8.

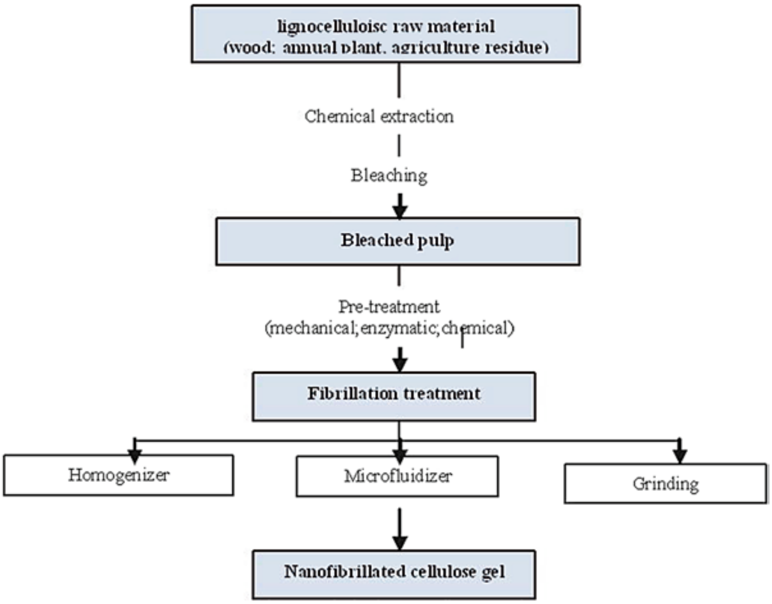


Fig. 14.8 Schematic overview of the main approach adopted for the extraction of microfibrillated cellulose

14.5.1 High Pressure Homogenization

This is the widely used method for large-scale operations as well as lab-scale production of NFC. High pressure homogenization (HPH) technique was introduced in early 1980s to produce fine emulsion based on the availability of devices able to generate high pressure in liquids as high as 500–1000 MPa. The process has been extensively used by the dairy and food industry, mainly to stabilize food emulsion and to disrupt lipid globules in liquid food. Different manufactures of HPH exist producing lab-scale or industrial equipment such as Microfluidics (http://www.microfluidicscorp.com), Avestin (http://www.avestin.com/company.html), Niro Soavi (www.nirosoavi.com/) and Stanted fluid power (http://www.stanstedfluid-power.com).

Homogenization involves the forcing of the suspension by a piston under pressure through a very narrow channel or orifice under pressure operating between 100 up to 2,000 MPa, typically 500 to 1,000 bar (Fig. 14.9). The width of the homogenization gap ranged from 5 to 20 μm, depending on the viscosity of the suspension and the exerted pressure. As the suspension leaves the gap of the homogenizer, the abrupt drop in the pressure led to the formation of gas bubbles that collapse immediately and implode resulting in the generation of cavitation and shockwaves that contributed to the disruption of the cellulose wall (Muller et al. 2001; Save et al. 1994). The size reduction of cellulose fibers is also promoted by the large pressure

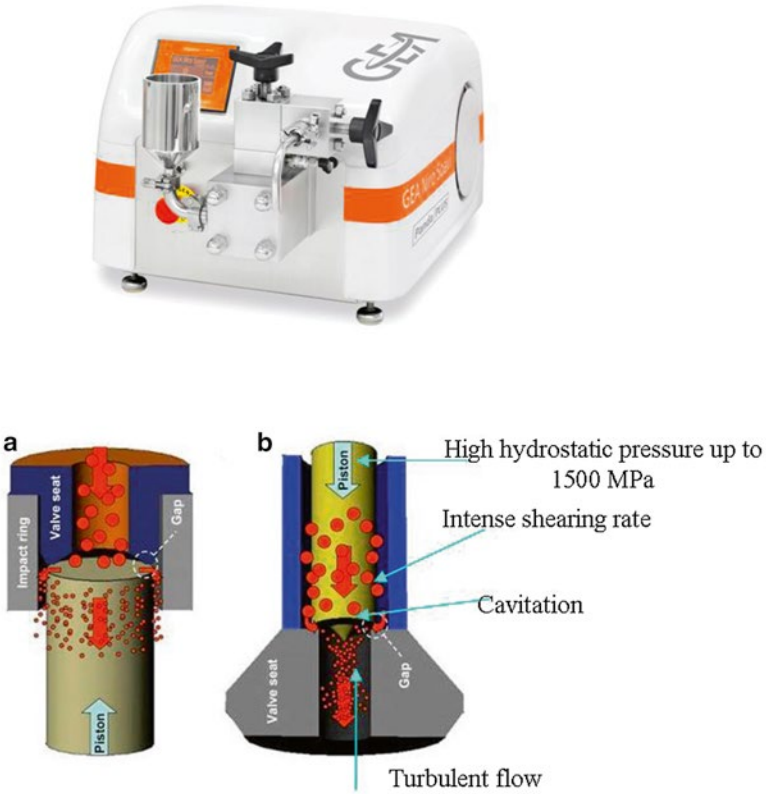


Fig. 14.9 (**a**, **b**) Scheme illustration of the principle of homogenization, and © Example of lab-scale homogenizer (GEA niro-soavi)

drop, the high shear forces, the turbulent flow, and the collision of the particles against each other. The extent of the cellulose fibrillation depends on the number of homogenization cycles and on the applied pressure. The higher the pressure, the higher is the efficiency of disruption per pass through the machine.

Based on the literature data, HPH is the most widely used method for the preparation of NFC (Bhatnagar and Sain 2005).

14.5.2 Microfluidization

Microfluidizer system is currently used in technology for miniaturization from macro to micro/nano structure dimensions (Il Park et al. 2010). This technology has been traditionally used in the pharmaceutical industry to make liposomal products and pharmaceutical emulsions, by the dairy and food industry to produce homogenized

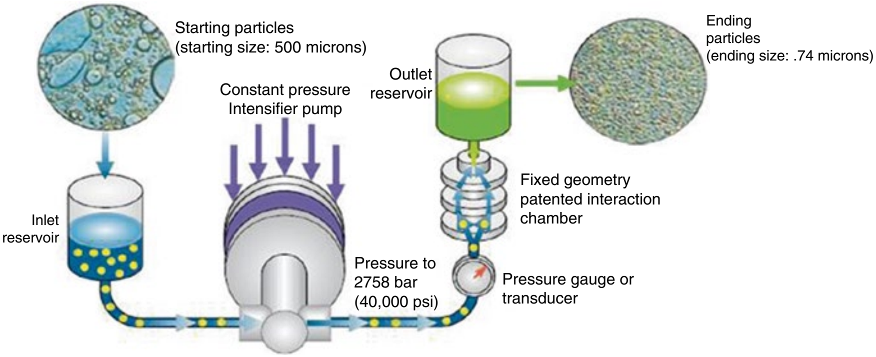


Fig. 14.10 Basic concept of the single pump microfluidizer functioning

milk and flavor emulsions. In the microfluidizer, the suspension is forced through a defined fixed geometry narrow channel being either Y-type or Z-type under high pressures as (150–210 MPa) (Fig. 14.10). As a result the product stream accelerate to high velocity, creating shear rate within the product exceeding 10^6 s^{-1} with intense particle collision and cavitation forces that bring about the disintegration of the cellulose fibers in its elementary building blocks. Unlike in the homogenizer which operates at a constant processing volume, the microfluidizer operates at a constant shear rate, which reduces the likelihood of clogs. Furthermore, the fixed geometry of the interaction chamber ensures reproducibility, especially when samples are processed multiple times. Furthermore, for efficient size reduction, it is necessary to multiply the number of passes until reaching the desired degree of fibrillation. Like HPH, the microfluidization processes have been widely used for the production of NFC (Aulin et al. 2010a, b; Ahola et al. 2008; Zimmermann et al. 2010).

14.5.3 Grinding

In micro-grinding, Dilute slurries of cellulosic fibers (consistency of ~2 %) are forced through a gap between two specially modified grooved disks—one static, the other revolving at about 1,500 rpm (Fig. 14.11). The disks are fitted with bursts and grooves to promote the fibers disintegration and the cell wall break-up (Abe et al. 2007a, b, 2009; Abe and Yano 2009). The repeated cyclic stresses and the friction of the fibers against the grooves result in the defibrillation of the fibers. To alter flow patterns during processing, different grit classes and different groove configurations are used. The extent of fibrillation is dependent upon the distance between the disks, the morphology of the disk channels, and the number of passes through the grinder. Like with a homogenizer, many passes are necessary (anywhere from three to ten passes) are required to generate adequate liberation of fibrillated cellulosic structures though refining pretreatment is not necessary. However, due to wearing action

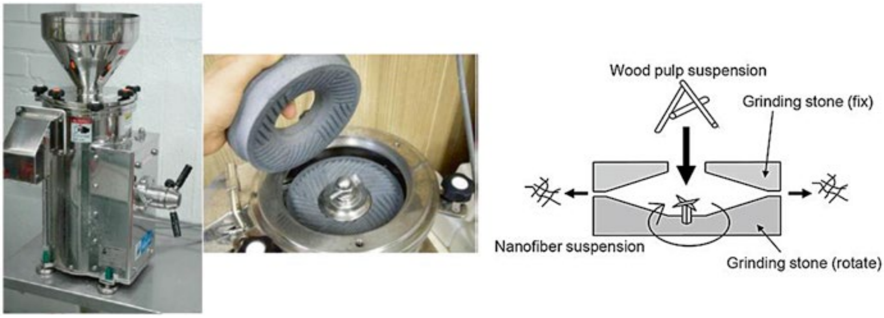


Fig. 14.11 MKCA 6-2 from Masuko Sangyo Ltd

of the fibers on the grooves and grits, disk maintenance and replacement is necessary which can constitute a drawback of this processing route.

14.5.4 Ultrasound Assisted Fibrillation

Sonication (ultrasonication) is the application of sound energy to physical and chemical systems. In liquids, sonication produces bubbles that grows and implodes hot spots that cause acoustic cavitations, formation, growth, and implosive collapse of bubbles to produce hot spots (Flint and Suslick 1991). The energy provided by cavitation during ultrasound irradiation might be controlled to be within 10–100 kJ mol^{-1}, which is within the hydrogen-bond energy scale. Thus, the ultrasonic impact can gradually disintegrate the micron-sized cellulose fibers into nanofibers. Although the basic technology of ultrasonication was developed over 50 years ago and its use in size reduction at the nanoscale level is widely adopted, only. Very little application of this technique to the production of nanocellulose was reported in the literature. Cheng et al. (2010) used high-intensity ultrasonication with a batch process to isolate fibrils from several cellulose sources. The results showed that a mixture of microscale and nanoscale fibrils was obtained with diameters ranging from about 30 nm to several micrometers. However, because of the complicated multilayered structure of plant fibers and the interfibrillar hydrogen bonds, the fibers obtained by these methods are aggregated nanofibers with a wide distribution in width (Wang and Cheng 2009).

Recently, the use of ultrasound irradiation as an alternative to mechanical disintegration for the release of cellulose microfibrils was the subject of numerous papers. Combining Cellulose nanofibers chemical pretreatment and high-intensity ultrasonication, improves the yield of nanofibrillated fraction cellulose nanofibers, and results and NFC with 5–20 nm in width and several microns in length (Chen et al. 2011a, b; Johnson et al. 2009; Tonoli et al. 2012; Mishra et al. 2012).

Table 14.2 Summary of the different technologies used to extract microfibrillated cellulose

Technology	Advantage	Disadvantage
High pressure homogenization	– It is a mechanical process that is quick and effective – It is a continuous process – The results obtained in laboratory are perfectly reproducible in industrial scale – You can vary pressure in order to find the right degree of cell delimitation – Ease of scale-up	– High number of homogenization cycle – High energy consumption – Increase in temperature of the suspension during processing.
Microfluidization	– Less risk of colloguing – Uniform particle size reduction – Fewer repeat passes to ensure optimum sample processing	– Unsuitable for industrial scale
Ultrasonication	– High energy transfer. – Quite rapid	– Heat generated by the ultrasound process must be dissipated. – High noise levels (most systems require hearing protection and sonic enclosures) – Useful only to a lab-scale level.
Micro-grinding	– Less energy consumption – Fewer passes are needed to obtain NFC	– Reduction in the crystalline degree of NFC

The main advantages and disadvantages of each preparation method were collected in Table 14.2.

14.6 Fibers Pretreatment to Facilitate the Release of NFC

Two problems were often encountered when manufacturing NFC from pulp; namely (1) the clogging of the pulp, when the pulp is pumped through high pressure fluidizers/homogenizers, and (2) the high energy consumptions associated with the fiber delamination involving multiples passes through the homogenizer until efficient delamination of the cell wall is observed. This high energy inputs is necessary in order to release the NFC and to overcome interfibrillar hydrogen bonds into both crystalline and amorphous domains. Values ranging from 20 up to 50 MWh/ton have been reported (Eriksen et al. 2008). Therefore, one of the most important challenges to produce NFCs on an industrial scale is to decrease the energy demand and facilitate the process of production. Pretreatments are sometimes used to address this problem. Examples of such pretreatments are mechanical, enzymatic, or chemical pretreatment were shown to heavily decrease the energy demand.

14.6.1 Mechanical Treatments Refining

Mechanical refining pretreatment is widely used prior to homogenization process in order to facilitate to defibrillation and reduce the energy input (Pääkkö et al. 2008; Hassan et al. 2012; Spence et al. 2011a, b; Stelte and Sanadi 2009). Disk refiners, PFI mills, and Valley beaters, were reported prior to the production of NFC (Andresen et al. 2006; Iwamoto et al. 2005; Nakagaito and Yano 2005). During this process, the dilute fiber suspension is forced through a gap between rotor and stator disks. These disks have surfaces fitted with bars and grooves against which the fibers are subjected to repeated cyclic stresses. This mechanical treatment brings about irreversible changes in the fibers morphology and size (Clark 1954). Actually, under the effect of the intense mechanical shearing action in the disk refiner, the cellulose fibers are subjected to repeated loading action of the refiner bars, leading to a progressive peeling off of the external cell wall layers, namely the primary (P) and first secondary (S1), making the subjacent thicker secondary cell wall layers (Hamad 1997) more exposed to fibrillation during the homogenization process. However, a damage of the microfibril structure along with a reduction in the molar mass and crystalline degree is likely to take place during the mechanical refining brings (Henriksson and Berglund 2007).

14.6.2 TEMPO-Mediated Oxidation Pretreatment

Another more promising route towards making easier the extraction of NFC relies on chemical treatments involving the addition of negatively charged entities at the microfibrils surface. Saito et al., were the first to report that 2,2,6,6-tetramethylpiperidine-1-oxyl (*TEMPO*)-mediated oxidation of cellulose fibers, facilitated the release of NFC and allowed for low energy mechanical disintegration of the oxidized fibers in aqueous suspensions (Saito et al. 2006, 2007, 2009; Isogai et al. 2011a, b; Iwamoto et al. 2010). TEMPO is a highly stable nitroxyl radical which is used extensively in the selective oxidation of primary alcohols to corresponding aldehydes and carboxylic acids. In aqueous environments, TEMPO catalyzes the conversion of carbohydrate primary alcohols to carboxylate (COO–) functionalities in the presence of a primary oxidizing agent e.g., sodium hypochlorite (NaOCl) (Bragd et al. 2004) (Fig. 14.12). The TEMPO-mediated oxidation could be carried at basic condition with pH around 11 and low temperature (≈4 °C) or under acid condition with pH

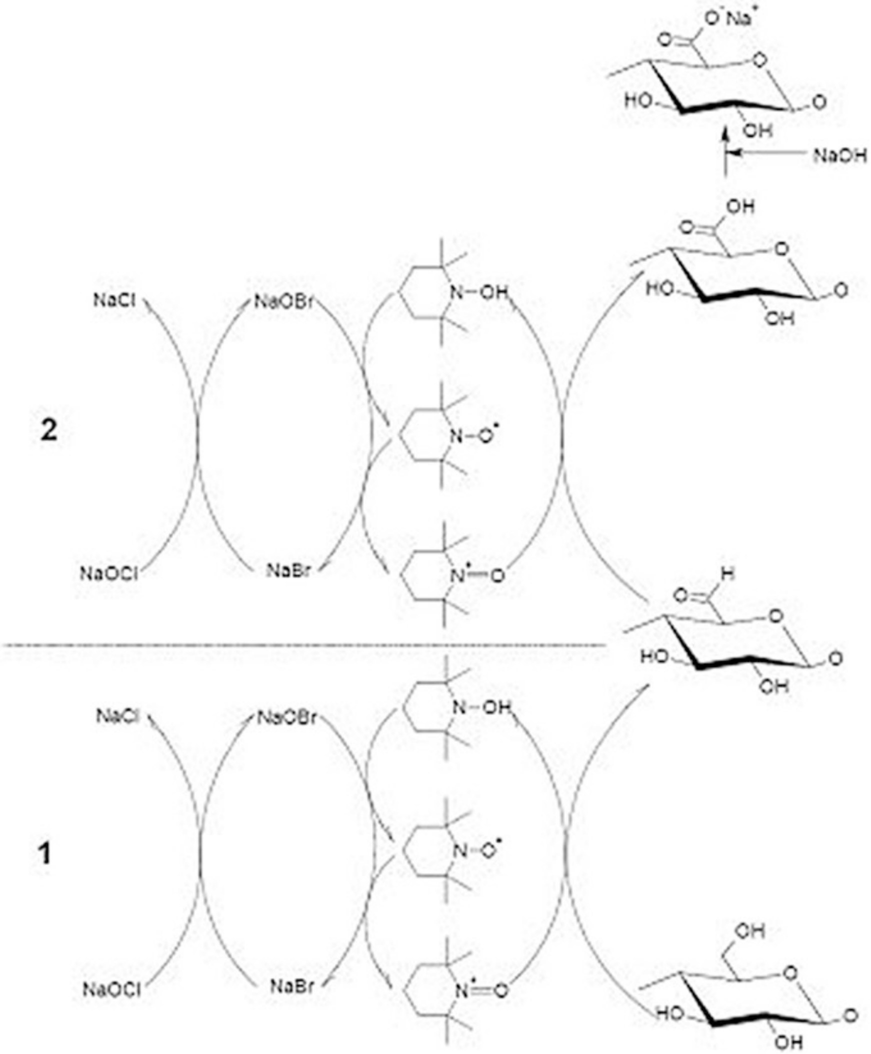


Fig. 14.12 Proposed mechanism for the oxidation of anhydroglucose to 6-carboxycellulose moieties via TEMPO/NaOCl/NaBr system in alkaline media. Numbers represent two levels of oxidation: (1) $-CH_2OH \rightarrow -CHO$ and (2) $-CHO \rightarrow -CO_2H$. (Adapted from Shibata and Isogai (2003))

around 4.5–5 and temperature 50–60 °C. The former condition leaves a fraction of the aldehyde groups (<0.08 mmol g^{-1}) in the oxidized cellulose, while no residual aldehyde groups is likely to remain in the oxidized fibers and the extent depolymerization side reactions or discoloration of the fibers were reduced (Isogai et al. 2011a, b).

Compared to the energy consumption using high pressure homogenizer, TEMPO-mediated oxidation pretreatment was shown to dramatically decrease the consumption by a factor more than 100 (Isogai et al. 2011a, b). Several hypothesis were postulated to account for this huge change in the delamination process; namely (1) the repulsion forces brought by the charged carboxylic groups contributed to loosen the microfibrils cohesion held by hydrogen bonding; (2) the presence of the carboxylic groups enhance the hydration of the fibers making the inner microfibrils more accessible; (3) the oxidation renders the S1 and S2 layers more accessible and more ready to fibrillation during the homogenization process; (4) and finally, the oxidation inevitably led to a chain scission in the amorphous zone that facilitated the detachment of the microfibrils.

In our study, we have shown that the level of oxidation is critical in reducing the energy input and improved the yield of nanofibrillation as well as the transparency degree of the NFC suspension (Fig. 14.13a). It was shown that a carboxyl content of about 300 μmol g^{-1} is necessary to observe a worthy change in the number of passes necessary to release the NFC and to prevent the risk of the clogging of the homogenizer jet. Furthermore, over a carboxyl content of 500 μmol g^{-1}, non meanfully change in the ease of nanofibrillation could be observed (Besbes et al. 2011a, b) (Fig. 14.14). However, the higher the carboxyl content the better is the optical transparency of the ensuing NFC suspension (Fig. 14.13b).

14.6.3 Enzyme Pretreatment

Enzyme pretreatment is an environmentally friendly alternative to chemical pretreatment was also reported to reduce the processing cost by lowering the number of passes through the homogenizer. Although, limited papers investigated the effect of the enzyme pretreatment on the ease of the release of NFC (Hayashi et al. 2005; Henriksson et al. 2007; Paakko et al. 2007; Janardhnan and Sain 2006; Zhu et al. 2011). A recent patent revealed an energy efficient process to produce microfibrillated cellulose (NFC) based on alternating enzymatic treatment with mechanical treatments, followed by a high shear mechanical defibrillation, such as homogenization, grinding, or microfluidization. The most widely used enzyme is commercial cellulase that catalyzes the hydrolysis of 1,4-β-D-glucosidic bonds of the cellulose chain. The enzyme comprises three groups of enzyme endoglucanases, cellobiohydrolases or exoglucanases, and glucosidases as illustrated in Fig. 14.15. These enzymes can act alone on the cellulose chain or together. Endocellulase breaks internal bonds to disrupt the crystalline structure of cellulose and exposes individual cellulose polysaccharide chains. Exoglucanases cleave 2–4 units such as cellobiose from the ends of the exposed chains produced by endocellulase. Glucosidases hydrolyze the exocellulase product into individual monosaccharides. When these groups acted together, a synergistic phenomenon is often generated, resulting in an efficient breakdown of the cellulose structure. The cell walls become softened by the enzymatic breakages of the cellulose networks prior to the mechanical disintegration, thus promoting the cell wall delamination and the release of the NFC.

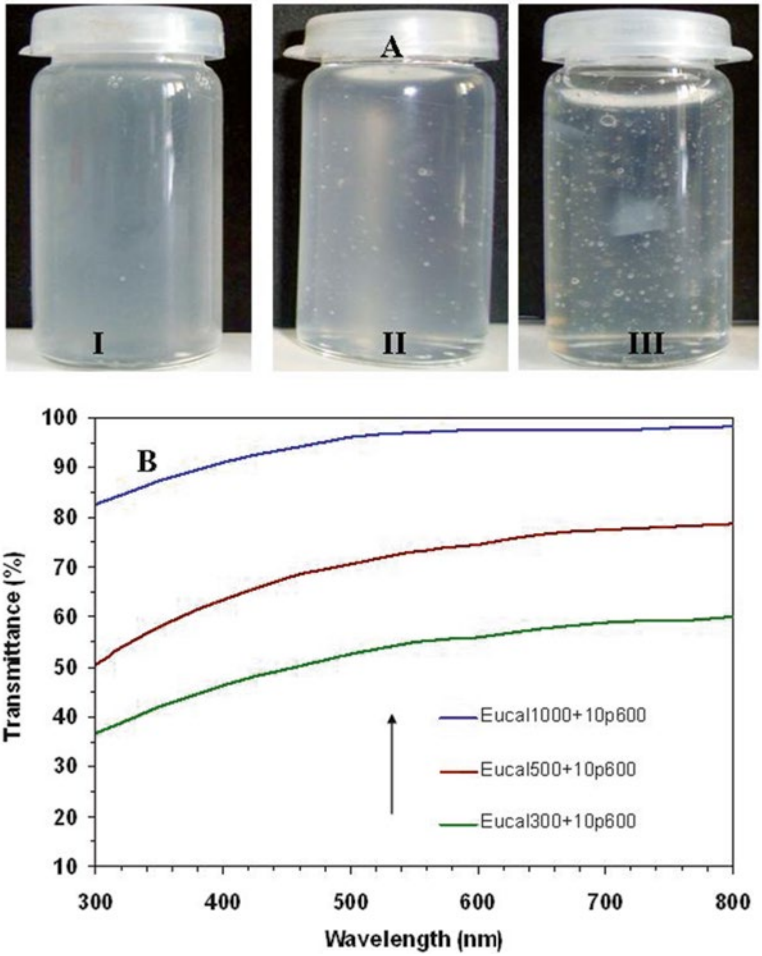


Fig. 14.13 (**a**) Appearance of NFC gel at 1.5 wt% from TEMPO-mediated oxidation of eucalyptus fibers after ten passes at 600 bar, at different carboxyl content, and (**b**) their corresponding transmittance behavior; (I) 300 μmol g^{-1}, (II) 500 μmol g^{-1} and (III) 1,000 μmol g^{-1}

14.6.4 Steam Explosion

The steam explosion process is based on short time vapor phase cooking at temperatures in the range of 180–210 °C, followed by explosive decompression, followed by sudden release of pressure, during which the flash evaporation of water exerts a thermo mechanical force causing the material to rupture. This effect results in a substantial breakdown of the lignocellulosic structure, the hydrolysis of a fraction of hemicellulose, the breakdown of the lignin, and partial defibrillation (Cristobal

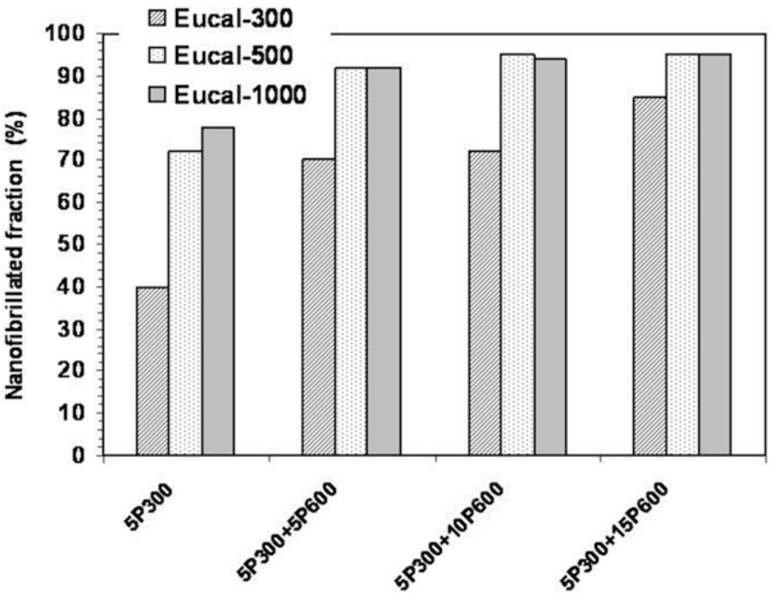


Fig. 14.14 Yield of nanofibrillated fraction according to the carboxylic content, the number of passes, and the fibrillation pressure: *5P300 + 5P600 means, five passes at 300 bar followed by five passes at 600 bar *Eucal-x: x design the carboxyl content of the oxidized fibers

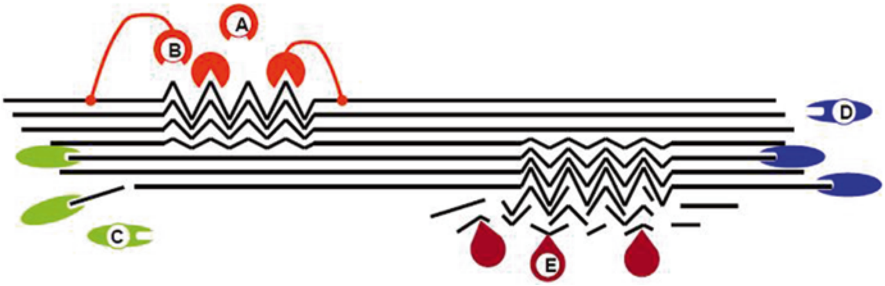


Fig. 14.15 Types of cellulases: (**a**) endoglucanases without cellulose-binding domain; (**b**) endoglucanases with cellulose-binding domain; (**c**, **d**) cellobiohydrolases, and (**e**) glucosidases. From Viviana (2008)

et al. 2008). To date, steam exploded fiber has been used mainly as a pulping process for the extraction of cellulose fibers from biomass. However, this approach was successfully extended to the extraction of cellulose nanofibrils from biomass (Deep et al. 2011; Cherian et al. 2008). The process was used either alone or in combination with high pressure.

The advantages of steam explosion include a significantly lower environmental impact, low energy consumption, lower capital investment, and less hazardous process chemicals. However, as is the case for the other fibrillation method the process should be repeated several times until efficient release of the cellulose microfibrils takes place (Cherian et al. 2010).

14.6.5 Delignification Using $NaClO_2$/Acetic Acid

When the delignification process was carried out using $NaClO_2$/acetic acid pulping process, higher yield in nanofibrillated fraction was obtained, compared to the conventional kraft or NaOH pulping process. This improvement was explained by the difference in the chemical composition of the delignified fibers, specifically the hemicellulose content. The correlation between the hemicellulose content and the nanofibrillation efficiency was confirmed by the work of Iwamoto et al. (2008) and Boufi and colleagues (Chaker et al. 2013). It was showed that higher the hemicellulose content in the fibers better is the yield of the nanofibrillated material. This correlation between the extent of fibrillation and the hemicellulose content was explained by considering the molecular organization of cellulose microfibrils and hemicellulose within the cell wall. Referring to the lamella model, hemicellulose is believed to be tightly bounded to the cellulose microfibrils via multiple hydrogen bonds and physically span the gap between them. Given its structural properties, namely amorphous character, macromolecular ramification and high hydrophilicity, hemicellulose will act as a physical barrier to keep the cellulose microfibrils apart from each other, consequently preventing their aggregation.

All of the above cited fibers treatment carried out prior to the disintegration process were reported to facilitate the delamination of the cell wall and the liberation of the cellulose microfibrils. This means that lower energy demand is needed to achieve high extent of cellulose nanofibrillation. However, the question to what extent these pretreatment affects the energy consumption still a matter of debate. To our knowledge the quantitative correlation between the carboxyl content or the mode of disintegration was tackled only by two publications (Spence et al. 2011b; Besbes et al. 2012).

14.7 Applications of Nanofibrillated Cellulose

14.7.1 Nanofibrillated Cellulose-Based Nanocomposite Materials

The most important potential application of nanocellulose is their use as a reinforcing agent in polymer-based nanocomposite materials. The outstanding mechanical reinforcing effect of nanocellulose is ascribed to the formation of a continuous network formed by the cellulosic nanofibrils (Favier et al. 1995a, b).

The formation of this rigid network, resulting from strong interactions between nanofibrils results from the set-up of percolated and entangled network held through hydrogen bonding. Given the high aspect ratio of NFC, the set-up of the entangled network occurs at a low critical threshold (lower than 1 wt%). Furthermore, the high stiffness of the elementary cellulose fibrils contributed to further enhance the reinforcing effect.

Another advantage of using NFC lies in the possibility of preserving the transparency of the polymeric matrix as long as an amorphous polymer is used. However, no study has been reported correlating the size of the reinforcing nanocellulosic phase with the optical properties of the nanocomposite.

Since NFC are produced in the form of a diluted aqueous suspensions and owing to the spontaneous aggregation of the cellulose fibrils during the drying process, most investigations regarding the use of NFC as nanofiller have dealt with polymer matrices in the form of a latex or water-soluble polymers. The dispersion of NFC in nonaqueous media or melt-processing route is not possible unless the NFCs were treated with a high concentration of surfactants or after proceeding with a surface grafting. Nanocellulose-based nanofiller possesses a reactive surface covered with hydroxyl groups, providing the possibility of extensive chemical modification. Even though this strategy proved to be successful in improving the good dispersion of the nanofiller within the polymer matrix during melt processing, the impossibility of the cellulose nanofiller to build up interaction through hydrogen bonding led to a huge decrease in the mechanical performances of the nanocomposite.

When nanocomposite processing was implemented by casting, the NFC suspensions were mixed with the latex in order to obtain nanocomposite dispersion with cellulose content ranging from 0 to 15 wt%. Then, after stirring, the mixture was cast or coated in a thin film and let at room temperature until complete evaporation of water and film formation complete through coalescence of polymer particles, giving rise to a transparent to translucent film, depending on the nanofiller content.

Dynamic Mechanical Analysis (DMA) is the most appropriate and useful technique to probe and investigate the reinforcing potential of nanocellulose. DMA is concerned with the measurement of the mechanical properties (mechanical modulus or stiffness and damping) of a specimen as a function of temperature. DMA is a sensitive probe of molecular mobility within materials and is most commonly used to measure the glass transition temperature and other transitions in macromolecules, or to follow changes in mechanical properties brought about by chemical reactions.

Examples of the change in the storage modulus E' versus the temperature for nanocomposite films prepared by casting a mixture of the aqueous suspension of NFC and a commercial latex polymer is shown in Fig. 14.16. The effect of the inclusion of NFC into the polymer matrix is different depending on the temperature domain. A huge enhancement in the modulus is observed above the glass transition (Tg) when the polymer matrix is in the rubbery state, while the increment in modulus is much more modest below the Tg. This behavior is typical to nanocomposite materials based on nanosized cellulose. In the glassy domain, the low difference between the modulus of the glassy matrix (around 3 GPa) and that of the NFC network (around 10–15 GPa) may be the reason for the ineffective reinforcing effect observed below glass transition. On the other hand, the huge reinforcement effect

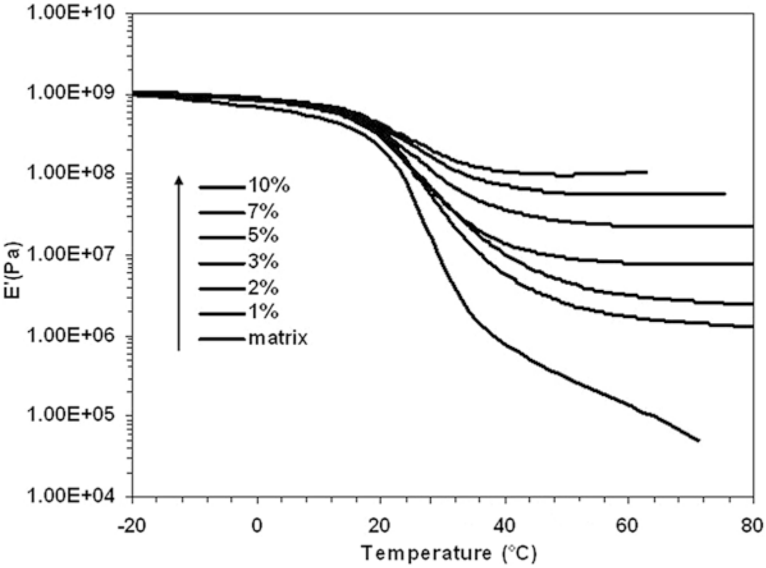


Fig. 14.16 Evolution of the storage tensile modulus, *E*′, loss modulus, versus temperature at 1 Hz for nanocomposites based on NFC extracted from abaca fibers and an acrylic latex matrix

above Tg is explained by the formation of a rigid network resulting from the fibrils entanglement and from the nanofibrils' bonded area interacting through strong hydrogen bonds. Nevertheless, a good dispersion of the nanofibrils within the polymer matrix is a prerequisite condition for the setting up of this network. In this context, the processing mode to prepare the nanocomposite should be carefully selected in order to prevent the nanofibrils aggregation.

To further highlight the stiffening effect imparted by the NFC introduction, the change in the storage modulus *E*′ in the rubbery domain is plotted in Fig. 14.17. A steady increase in the storage modulus is observed overt the whole NFC content. For instance, at 70 °C, nanocomposite containing 5 wt% NFC from sisal exhibits a storage modulus around 60 MPa, which represents a 450-fold enhancement over that of the neat matrix (0.133 MPa).

The setting up of interconnected networks has been proposed as a plausible mechanism to account for the huge increase in the modulus, exceeding those modeled by mean-field results e.g., Halpin-Kardos (Halpin and Kardos 1976). The concept of percolation in CNC-based nanocomposite has been adopted to account for the huge reinforcing potential of CNC in rubbery-like polymer. The concept of percolation was also successfully adopted to explain the strong reinforcing potential of NFC-based cellulose nanofiller. According to this model, the elastic tensile modulus E_c of the composite can be expressed by the following equation:

$$E_c = \frac{\left(1-2\psi+\psi\phi\right)E_s E_r + \left(1-\phi\right)\psi E_r^2}{\left(1-\phi\right)E_r + \left(\phi-\psi\right)E_s} \tag{14.1}$$

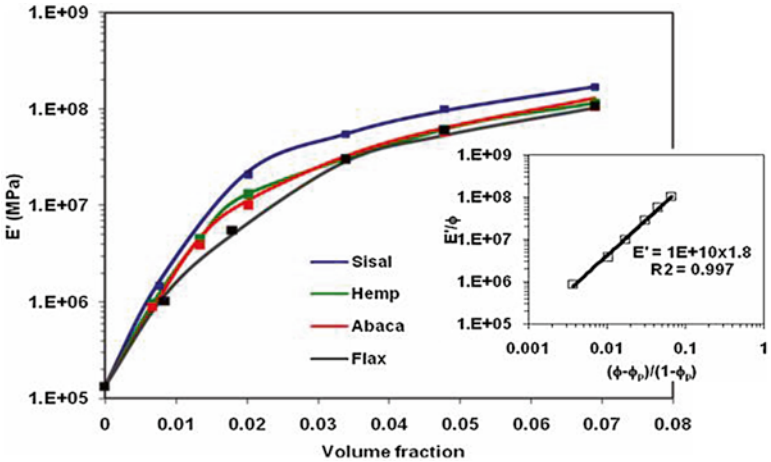


Fig. 14.17 Evolution of the storage modulus versus NFC content at 70 °C for nanocomposite films prepared from NFC obtained from the different plant and acrylic latex: comparison between the experimental data (*filled*), and predicted data according to the Percolation model (—)

Table 14.3 The critical exponent, the percolation threshold and the modulus of the cellulose network

Plant	b	ϕ_p (vol.%)	$R2$	E_r
Abaca	1.8	0.3	0.996	17
Sisal	1.62	0.4	0.995	9.4
Flax	1.78	0.25	0.997	9.3
Hemp	1.65	0.25	0.997	9

where ψ can be written as:

$$\psi = 0 \quad \text{For } \phi < \phi_p \tag{14.2}$$

$$\psi = \phi.\left(\frac{\phi - \phi_p}{1 - \phi_p}\right)^b \quad \text{For } \phi \geq \phi_p \tag{14.3}$$

ψ, ϕ, and b are the volume fractions of percolated network, the total volume fraction of the nanofiller and the critical exponent, respectively. E_s and E_r are the modulus of the cellulose network and the matrix, respectively. The modulus of the cellulose network E_r is different than that of individual nanofibrils. It could be determined from DMA using thin sheet films nanopaper prepared from NFC suspension. The E_r values for the different NFC are reported in Table 14.3, from which one can note a higher value for abaca NFC. A possible reason of the stiffer network for abaca NFC might be due to the higher hemicellulose content in the starting fibers used to produce the NFC. The key role of hemicelluloses in paper strength was pointed by numerous publications (Molin and Teder 2002).

The percolation volume threshold (ϕ_p) can be determined by applying a power law function to the E' versus NFC loading using Eq. (14.4), as predicted from the percolation theory (Favier et al. 1995a, b; Ouali et al. 1991).

$$\frac{E'}{\phi} \propto \left(\frac{\phi - \phi_p}{1 - \phi_p}\right)^b \quad \text{For } \phi > \phi_p \tag{14.4}$$

Applying this concept to the NFC of different origins, the percolation threshold ϕ_p was adjusted to the value giving the best linear regression for E'/ϕ versus $\left(\frac{\phi - \phi_p}{1 - \phi_p}\right)$ on a log–log scale (Fig. 14.17: see inset). This model provides a good linear fitting and led to a value of ϕ_p comprised between 0.25 and 0.4 depending on the NFC origin (Table 14.3). Moreover, the critical exponent coefficient was also assessed and found to be within the range of 1.6–1.8, which is in agreement with the predicted value of 1.6–2 for a 3D percolated network (Lin et al. 2010).

The percolation threshold for NFC was found to be within the range of 0.25–0.4 vol.% which was lower than that commonly observed for CNCs being higher than 1 vol.%. This difference is likely the consequence of the higher aspect ratio of NFCs compared to CNCs. Indeed, the percolation threshold is known to be inversely proportional to the aspect ratio of the dispersed objects (Nan 1993).

14.7.1.1 Tensile Properties of Nanocomposite Films

The nonlinear tensile mechanical properties of the nanocomposites film is another technique to highlight the strong reinforcing effect, namely in terms of the mechanical strength imparted by the inclusion of NFC in a polymer matrix. An example of tensile with different content of NFC is shown in Fig. 14.18. It can be observed that both of the tensile modulus and the tensile strength dramatically increased with the inclusion of the NFC. For instance, with 10 wt% NFC from abaca, tensile strength went from 0.36 to 9 MPa which is more than 25-fold higher than that of the neat matrix. Even a loading as low as 1 wt%, which is only 0.6 % by volume, brought about sevenfold enhancements in the tensile strength over that of the neat matrix (Fig. 14.19).

However, it can be seen that the reinforcing effect of the NFC depends on their origin and the mode of preparation. If we refer to the example reported in the work of Chaker et al. (2013), then it was noted that NFC from flax gives rise to the highest level of tensile strength (NFC yield about 70 %). On the other hand, NFC from sisal brings about the lowest level of strength, regardless of the NFC content. For jute and abaca, the strength is roughly the same being at a level intermediate between flax and sisal. This behavior seems unexpected if we consider that the high reinforcing aptitude of NFC arises from their nanosized scale. This difference in the reinforcing capacity was explained by the difference in the nanofibrils morphology.

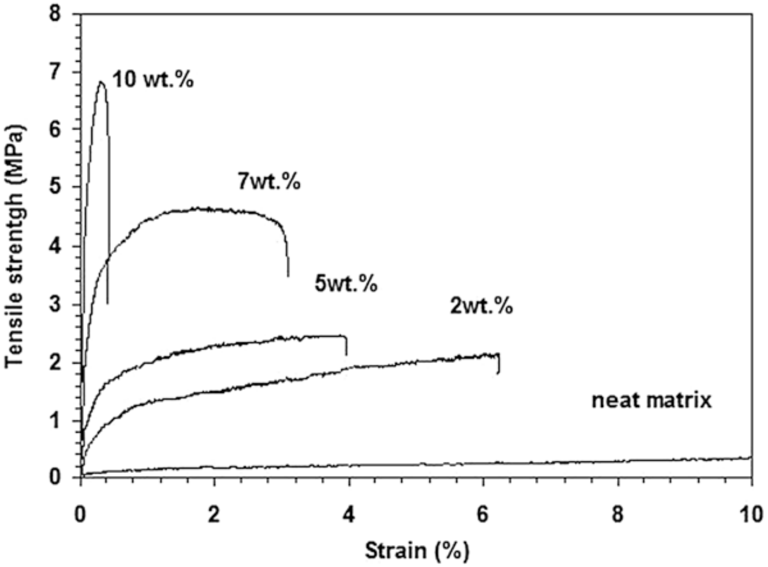


Fig. 14.18 Typical stress-strain curve for nanocomposite films, prepared via casting, based on NFC extracted from sisal fibers and a polyacrylate matrix

14.7.1.2 Optical Properties of the Nanocomposite Films

Generally, besides the mechanical reinforcing effect imparted by the addition of nanocellulose in a polymer matrix, preserving the optical transparency of the polymeric matrix is also highly desired. In general, the reduction in the transparency degree for nanocomposite materials is the result of light scattering brought by the inclusion of the nanoparticles.

According to Rayleigh's Law the light intensity loss by scattering is given by the following equation:

$$\frac{I}{I_o} = \exp - \left[\frac{3\phi l D^3}{4\lambda^4} \left(\frac{n_r}{n_s} - 1 \right) \right] \tag{14.5}$$

where I and I_o are the intensity of the transmitted and incident light, respectively, l is the optical path length, λ is the wavelength of light, φ is the volume fraction of the particles, D is the diameter of the particles and n_r and n_s are the refractive indexes of the particle and matrix, respectively.

According to Eq. (14.5), light scattering is a function of the relative refractive index of the dispersed phase and steeply increased with particle size and in general, 40 nm is the upper limit for nanoparticle diameter to avoid loss of transmitted light

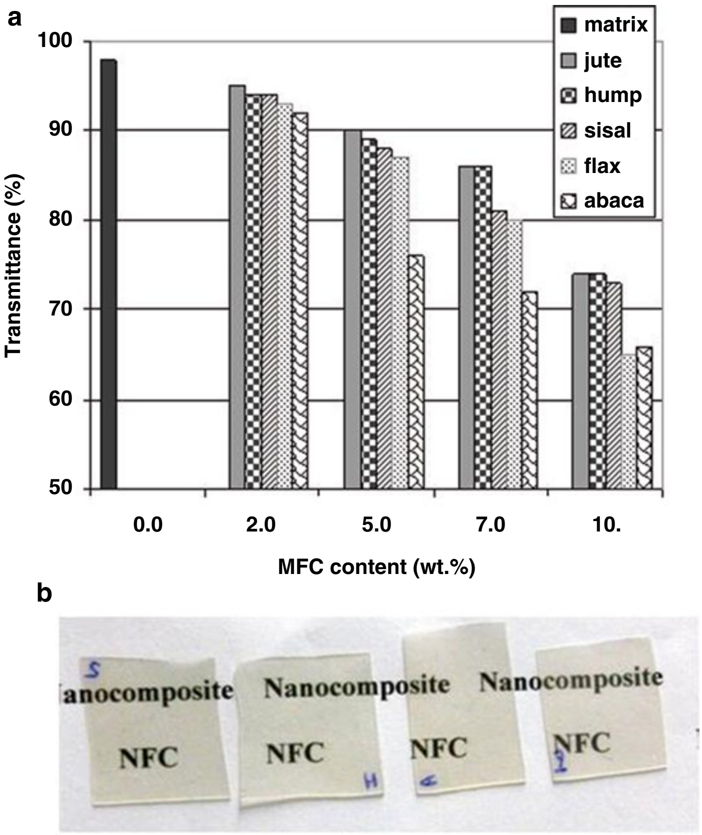


Fig. 14.19 Evolution of the (**a**) tensile modulus and (**b**) tensile strength of the nanocomposite film with the NFC content

via scattering. Given the mismatch in the refractive index (RI) of cellulose (1.58) and the host matrix (1.48), the key parameter governing the transparency of nanocellulose-based nanocomposites is the effective cross-sectional area of a scattering and its dispersion level within the host polymer matrix.

One simple method to assess the optical transparency of the nanocomposites consisted to measure the transmittance at 700 nm. Example of the transmittance value in nanocomposite prepared with different content of NFC from several non-woody plants is shown in Fig. 14.19a. A digital photo of nanocomposite film prepared from NFC is shown in Fig. 14.19b.

From Fig. 14.19 transmittance values exceeding 70 % were reported for nanoparticle contents lower than 7 wt%, which is indicative of a good transparency and dispersion of the nanofiller within the nanocomposite film. However, the scattering effect imparted by the NFC depends on their origin, the mode of preparation, and the processing route of the nanocomposite. The most transparent nanocomposite films were obtained when polymer in the form of latex dispersion was used and the nanocomposite was prepared via casting.

14.7.2 Biomedical Applications

In recent years, cellulosic nanofibers were successfully used by many researchers for biomedical applications. Valo et al. (2011) have studied the application of cellulosic nanofibers in drug delivery. Hydrophobin coupled with two cellulose-binding domains was used in order to facilitate drug nanoparticle binding to nanofibrillar cellulose. Cellulose fibrils matrix provides protection for the nanoparticles during the formulation, process, and storage.

NFC composite hydrogel was developed for the replacement of the nucleus pulposus. It was reported that composite hydrogels reinforced with cellulosic nanofibers may be viable as nucleus pulposus implants due to their adequate swelling ratio, which may restore the annulus fibrosus loading, and their increased mechanical properties, which could possibly restore the height of the intervertebral discs (Borges et al. 2011). Biocomposite hydrogels with carboxymethylated, NFC powder were also prepared by UV polymerization of *N*-vinyl-2-pyrrolidone with Tween 20 trimethacrylate as a cross-linking agent for replacement of the native, human nucleus pulposus in intervertebral disks. NFC powder was prepared after solvent exchange and centrifugation by drying the suspension at 60 °C and ambient pressure under subsequent stirring with a glass bar (Eyholzer et al. 2011). Cellulosic nanofibers were used as a material for the development of nanocomposite scaffolds for use in artificial ligaments or tendon substitutes. Nanocomposites were prepared with mechanical properties similar or better than the natural ligaments and tendons. The nanocomposites were found to exhibit excellent cytocompatibility required for biomedical applications. Collagen-based implantable scaffolds reinforced with the cellulosic nanofibers were also prepared. Cellulosic nanofibers reinforcement resulted in better mechanical performance and dimensional stability without affecting the biocompatibility and nontoxicity of collagen (Mathew et al. 2012).

Cellulosic nanofibers were prepared from native cellulose by TEMPO-mediated oxidation and individually dispersed in water by mechanical disintegration. These cellulosic nanofibers were found to exhibit characteristic biological activities when administered to mice and may have potential applications to biomedical fields for human health. TEMPO-oxidized cellulosic nanofibers were orally administered with glucose and glyceryl trioleate to mice and blood levels of metabolic variables were followed over time. Blood glucose, insulin, glucose-dependent insulinotropic polypeptide, and triglycerides were significantly decreased, especially 10 min after the administration of cellulosic nanofibers (Shimotoyodome et al. 2011). Cellulose nanocomposites reinforced with NFC isolated from pineapple leaf fibers were also proposed as prosthetic heart valves as well as vascular grafts (Cherian et al. 2011).

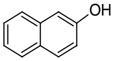
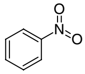
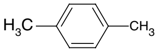
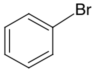
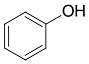
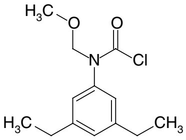
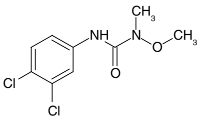
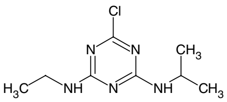
14.7.3 Nanofibrillated Cellulose as Adsorbent for Removal of Heavy Metal Ions

Given the high surface area of the NFC, adsorbent based on modified NFC might afford an interesting alternative to conventional adsorbent-like activated carbon, ion exchange resins or zeolite. This new area of potential use of NFC in the field of water treatment was explored by several recent publications that showed the possibility to prepare adsorbent based on modified NFC for removing heavy metal ions but also organic pollutants. The possibility to implement wide possibility of surface modification on the cellulose surface opens the way toward the insertion of specific groups, such as carboxyl, amine, ammonium, and thiol likely to interact with metallic cations or organic compound. Adsorption is the most effective and versatile method for the removal of heavy metals as other methods have high operating cost and generates solid waste which poses disposal challenges (Sang et al. 2008; Belhalfaoui et al. 2009). Stephen et al. (2011) used oxolane-2,5-dione modified cellulose nanofibers for adsorption of cadmium and lead ions from model wastewater samples for the first time. They studied adsorption kinetics using different concentrations for lead and cadmium: 20, 50, 100, 150 and 200 mg L^{-1} at an adsorbent concentration of 2 g L^{-1}. The order in the adsorption efficiency was Cd > Pb which was explained by the chelation and entrapment of cadmium on the surface of functionalized cellulose. The maximum adsorption ($Q_{\max}$) demonstrates the higher capacity of cellulose-g-oxolane-2,5-dionenanofibers for Pb and Cd removal as compared with oxolane-2,5-dione functionalized raw cellulose fibers. The adsorption capacities for functionalized cellulose nanofibers were 1.0 and 2.91 mmol g^{-1} for Pb and Cd, respectively in comparison to 0.002 mmol g^{-1} of raw cellulose.

14.7.4 NFC as an Adsorbent for Dissolved Organic Compounds

Cellulose-based hydrogel prepared from highly porous cellulose aerogels were made from NFC suspension and were used as an adsorbent for a wide range of organic pollutants including aromatic compounds; herbicides, and pesticides were investigated by Matter et al. (2013). It was shown that by functionalizing the cellulose nanofibrils of the aerogel with long hydrocarbon chains, the adsorption capacity is significantly enhanced, making possible to use the modified aerogel as an adsorbent for organic compounds (Table 14.4). Adsorption capacity ranging from 50 up to 500 μmol g^{-1} was reached for the modified NFC aerogel. The mechanism of adsorption was shown to involve the diffusion of the organic solute inside the grafted hydrocarbon chains and the accumulation of the organic solute within hydrocarbon layer acting as a reservoir. Once exhausted, the adsorbent could be regenerated easily by a simple washing treatment and might be reused for multiple adsorption cycles without any loss of the adsorption capacity.

Table 14.4 Physical characteristics of the different solutes and their maximum adsorbed amount on both the unmodified and modified nanofibrillated aerogel

Chemical structure	Molar volume (cm^3)	Water solubility (mmol L^{-1})	Q_{max}[a] unmodified (μmol g^{-1})	Q_{max}[b] modified (μmol g^{-1})
Aromatic organic solutes				
 2-naphthol	121.9	5	15	455
 Nitrobenzene	101.2	16.9	13	210
 Xylene	121.9	1	10	52
 Bromobenzene	105.6	2.86	10	80
 Phenol	87.8	1,041	12	165
Herbicides				
 Alachlor	224.4	240	ND	70
 Linuron	176.5	81	Undetected	47
 Atrazine	169.8	28	Undetected	25

[a] Maximum adsorption capacity on the unmodified cellulose aerogel
[b] Maximum adsorption capacity on the modified cellulose aerogel

14.7.5 NFC as a Strength Additive for Paper and Paperboard

The use of NFC as a reinforcing additive to improve physical and mechanical properties of paper has recently aroused much interest and promising potential in the field of paper technology and packaging is expected in the near future (Gonzalez et al. 2012; Hii et al. 2012; Taipale et al. 2010). In fact, owing to the large specific surface area and high aspect ratio NFC and their strong affinity with cellulosic pulp, along with their ability to form a 3D network constitute so many benefits for the improvement of paper strength when NFC was added to the pulp slurry. Taipale et al. (2010) showed that the addition of NFC decreased the drainage rate of pulp suspension and increased the strength of paper, especially if a cationic polyelectrolyte is used as a retention aid. However by optimum selection of materials and process conditions, an enhancement of the strength properties could be achieved without simultaneously deteriorating the drainage. The effect of the NFC addition on the paper strength was also confirmed by Gonzalez et al. (2013) who had undertaken a deep investigation on how the NFC addition might improve the mechanical strength of paper and reduce the energy demand during the refining process.

In a recent work carried out by González et al. (2013), it was showed that combination of the enzymatic treatment of the pulp (biobeating) and NFC addition can be considered as a promising alternative to traditional beating as a way of improving mechanical properties of the final paper without simultaneously reducing drainage rate at undesirable levels. The addition of NFC to the enzyme-treated pulp significantly increased mechanical properties of paper; porosity was reduced, whereas opacity remained unmodified. The hypothesis of NFC acting as an adhesion promoter of cellulose fibers was clearly confirmed by FE-SEM observation (Fig. 14.20). A schematic illustration of the strengthening mechanism of NFC for paper was also proposed (Fig. 14.21). It was found that enzymatic treatment improved the mechanical properties of fibers without modifying drainability. After biobeating, NFC was added to the enzyme-treated pulps. Mechanical properties were enhanced, obtaining length at break values similar to those observed in commercial printing/writing paper. Opacity remained constant, whereas porosity was gradually reduced as more amount of NFC was added. The presence of NFC also reduced drainability, although it remained at suitable levels for the papermaking industry. The results suggest that the combination of biobeating and NFC addition can be considered as an alternative to mechanical beating.

14.8 Conclusions

This chapter summarizes some of the recent advances in the realm of the extraction of NFC from lignocellulosic fibers and some aspects of their potential uses in different fields of applications.

The extraction of nanosized fibers from cellulose fibers undoubtedly represents one of the main breakthroughs in cellulose-based materials during the last several

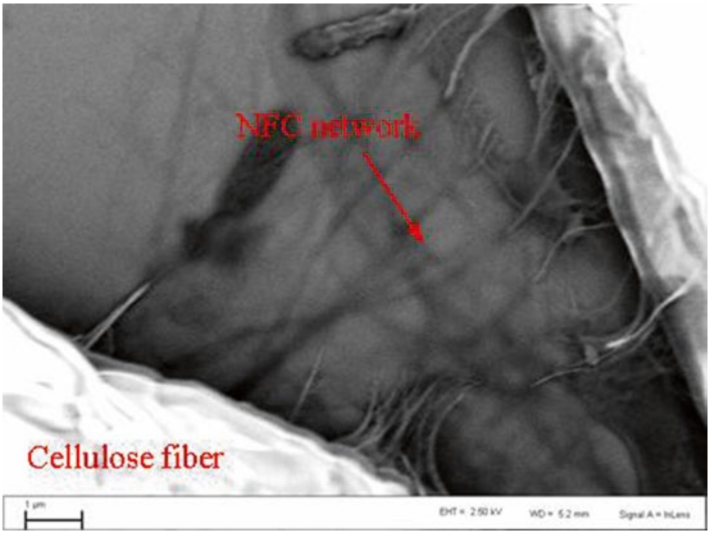


Fig. 14.20 FE-SEM of ultra-thin layer of paper prepared in presence of added NFC

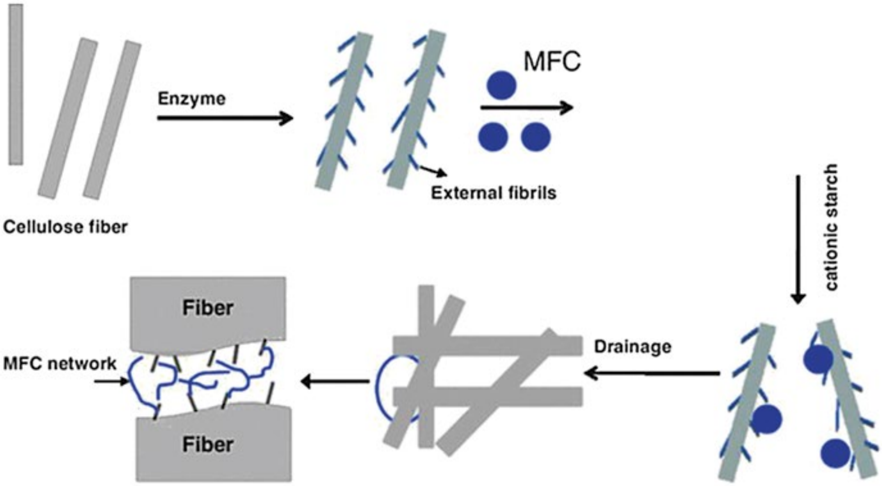


Fig. 14.21 Schematic illustration of the mechanism of paper strengthening in presence of added NFC

years and one of the most studied topics in the literature today. This is due to a number of desirable characteristics of nanocellulosics which include renewability, abundance, and low cost of the raw material (cellulose), as well as a large surface-to-volume ratio, high strength, and stiffness, very low coefficient of thermal expansion, low weight, low density, high aspect ratio, and biodegradability. Applications of nanocellulosics include reinforcement for nanocomposite materials, moisturing masks for cosmetic applications, tissue engineering scaffolds, filtration media, rheology modifiers, adsorbents, paper reinforcement, etc.

Due to the improved properties, in applications NFC-composites are being developed for use in engineering and medical fields. Transparent nanocomposite material with enhanced stiffness and strength could be obtained with the incorporation of NFC in a polymer matrix. Water-soluble harmful organic pollutants can be removed with the help of nanofibrillated membranes, and paper and paperboard with improved strength and reduced energy consumption can be produced by the addition of NFC to the pulp. However, the scale-up of commercial production of NFC is still tributary on the energy requirement for the disintegration process, and how efficient will be the fibers pretreatment to make easier the cell wall break-up.

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Chapter 15
Unlocking the Destructive Powers of Wood-Eating Termites: From Pest to Biopolymer Derivatives Extractor

Kit-Ling Chin, Paik-San H'ng, and M.T. Paridah

Contents

Abstract Termites are social insects that live in colonies and its incredible digestive system may provide a breakthrough in efficient biopolymer derivatives production. Termite has the ability to digest a kind of food that few other living organisms are able to; the woody material. It has mouthparts that chew up wood into pieces. But the secret is that it carries special microorganisms that can digest the lignocellulosic material. By being the host to these special microorganisms, termites are able to do something that most living organisms are unable to; the ability

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to digest lignocellulosic materials. Termites have been considered nothing more than nuisance pest which destroy woody materials. The termite is found chewing on frames, furniture, and flooring made out of wood. But new research shows how the termite digest lignocellulose could hold a key to the production of numerous biopolymer derivatives from lignocellulosic material. Annoying as they may be, termites are amazingly efficient at converting wood into sugars, and that ability is very useful for making numerous biochemicals and biofuels. Researchers are studying the termite's digestion process in order to synthetically copy the process so that lignocellulosic materials can be used as the source to derive numerous biochemicals. For decades, much effort was made to increase the utility of lignocellulosic materials. In consideration of the ever-growing demand for traditional usage such as fiber products, novel markets for lignocellulosic materials have been identified in recent years, in replacement of petrochemicals. The scientists believe that information learned from the termite could increase the efficiency of wood derivation, making these biopolymer derivatives even more cost-effective and utilizing lignocellulosic biomass as a sustainable source of chemicals and fuels by replacing fossil fuel. This chapter comprises information on recent conversion methods of biochemicals from lignocellulosic biomass for application enablement and commercialization, laying special emphasis on termite lignocellulolytic system.

Keywords Termites • Lignocellulosic material • Biopolymer derivatives • Biochemical • Lignocellulolytic digestion

15.1 Overview

The global demand of the chemicals and fuel satiated with derived forms of the fossil fuel (more than 80 %) has highlighted the importance of this finite resource. The continuous depletion of the fossil fuel reserves and the emission of greenhouse gases had resulted in an increased focus on production of biochemicals and biofuel by replacing fossil fuel. Wood derivatives had been seen as alternative chemical sources and its future use as fuel will be seen greatly increased due to the ever-rising cost of fossil fuel (current price USD 100 per barrel). Furthermore, wood derivatives are a primary target in many countries to help reduce greenhouse gas emissions, water pollution, and soil degradation. As reported by Puhan et al. (2005), there is a growing trend in developed countries, toward the application of modern technologies and efficient conversion involving a range of microorganism and insects, with their target to make the wood derivatives as competitive with fossil fuel derivatives as possible, in terms of costs.

Wood or biopolymer derivatives from lignocellulosic biomass had been studied intensively in recent years. There are many researches done previously to improve the production of biochemicals derived from lignocellulosic materials with different new methods and enzymes to produce cheap and plentiful, ecologically sound biochemicals. Chin et al. (2010) found that bioethanol can be produced from lignocellulosic materials at conversion factor of 26 % over the dry weight of lignocellulosic biomass. Although the research result provided the novel knowledge about the amount of bioethanol that can be produced from lignocellulosic biomass, the problem with wood-derived chemicals is that it takes a lot of resources and energy to convert the lignocellulose into sugars using current technology. During ethanol production, the complex organic compounds of cellulosic materials need to be converted first into much simpler soluble compounds like sugars before reacting in further stages to produce bioethanol or other biochemicals. Nevertheless, the hard part is that the carbohydrate polymers of lignocellulosic materials form extremely dense, resilient bonds. Lignin molecules that deposited around the sugar molecules act as a barrier preventing the microorganisms from penetrating. Additional pretreatment steps such as heat, steam, or caustic acids and bases treatments are required to be used to break it down. Such steps cause the process to be more costly, and in often cases, generate hazardous waste. Ragauskas et al. (2006) stated that currently, the inability to efficiently derive simple, utilizable sugars from lignocellulosic material through depolymerization reactions is a significant limiting factor for this biochemical industry.

Therefore, continuous study is needed in finding a quick, efficient means of extracting wood derivatives from lignocellulosic materials to improve the production of biochemical with lower cost and energy consumption. Ohkuma (2003) reported that the ability of insects to convert recalcitrant lignocellulosic material into a usable or intermediate chemical source has attracted much interest recently due to the numerous potential applications in biofuel and biochemical production. The latest research on conversion of biochemicals using enzymes shifted their intention on using enzymes extracted from wood eating insects such as termites.

Termites are one of the most pervasive and destructive insects that efficiently digest lignocellulosic material and nurture on this apparently nutritionally poor diet. Wherever termite invasion happens, the termites cause tremendous damage to woody constructions and trees (Osbrink and Lax 2003). As mentioned earlier, the problematic part in producing wood-derived chemical is obtaining the metabolic intermediates from the lignocellulose but then has never been a problem to termites. Interpretation of digestive mechanisms underlying the termite's ability to hydrolyze the lignocellulose is a potential target for the development of effective bio-termiticides (Zhou et al. 2008) and also the hydrolyzing enzymes can be utilized for the conversion of wood cellulose into simple sugars for biochemical production (Warnecke et al. 2007; Scharf and Tartar 2008; Rubin 2008). Bacteria that help termites digest wood could be key to derive biochemical cheaply from nonfood crops such as wood and grass. This chapter comprises information on recent conversion methods of biochemicals from lignocellulosic biomass for application enablement and commercialization, laying special emphasis on termite lignocellulolytic system.

15.2 Lignocellulosic Material: Chemical Composition, Enzymatic Degradation and Depolymerization, and Biopolmer Derivatives

15.2.1 Chemical Composition

Chemical composition directly affects the efficacy of biomass energy conversion. Lignocellulosic biomass mainly contains a mixture of carbohydrate polymers (cellulose and hemicellulose), lignin, extractives, and ashes (Van-Dyne et al. 1999; Kamm and Kamm 2004). The composition of these constituents varies from one plant species to another. The ease of energy conversion of biomass reflects lignocellulosic structure and composition. Cost-effective conversion of potential feedstocks to fuels and products needs appropriate levels of cellulose, hemicellulose, extractive, and lignin. Understanding the effect of chemical composition on pretreatment chemistry and ultimately feedstock reactivity is the key in achieving the robust conversion processes in handling variety of feedstocks and biomass.

As cellulose is the main structural constituent in plant cell walls, it is often found in a fibrous structure of an organized manner (Sjostrom 1993). Cellulose molecules are completely linear without branching and intra- and intermolecular hydrogen bonds are easily formed. Cellulose molecules are thus aggregated to microfibrils in bundles which form either highly ordered (crystalline) regions or less ordered (amorphous) regions. The susceptibility of cellulose to enzymatic degradation is higher in its amorphous form. Fibrils are built up by microfibrils and, finally, the formation of cellulose fibers (Sjostrom 1993). Cellulose chains are converted into microfibrils which constitute the basic framework of the cell, delivering a great deal of resistance to the presence of tensile forces (Jarvis 1984). Cellulose is a homopolysaccharide composed of D-glucose subunits linked to each other by β-1,4-glycosidic linkages (Swati et al. 2013). While, β-1,4-glycosidic is the chemical repeating unit, the structural repeat unit of the cellulose chain is cellobiose constituent of wood, comprising approximately 40–45 % of dry wood (Fengel and Wegener 1983). Cellulose chains are packed into microfibrils that linked together by hydrogen bonds and Van der Waals forces (Hermans 1949).

Hemicellulose is covalently bound to lignin and bound to cellulose through hydrogen bonds (Sjostrom 1993). Hemicellulose is lower in molecular weight than cellulose and has branches with lateral and short chains that consist of various sugars. It is a heteropolymers of D-glucose, D-xyloses, D-mannose D-galactoses, and, L-arabinoses and various other sugars that is low in molecular weight. Hemicellulose is more susceptible to hydrolysis than to the rigid structure of cellulose because it has a low degree of crystallinity and microfibrils and with more amorphous regions. Its composition differs among wood. Hardwood hemicellulose mainly consists of xylose, but in softwood mannose and glucose are the dominating building blocks of carbohydrates (Sjostrom 1993). In comparison to cellulose, the polymers present in hemicelluloses can be hydrolyzed easily. Even when such polymers co-crystallize with cellulose chains, it do not aggregate.

Lignin is a complex polymer of aromatic alcohols known as monolignols. It is highly resistant to microbial attack due to its chemical complexity, insolubility, and lack of hydrolysable linkages (Taherzadeh 1999). In nature, cellulose and hemicellulose comprise the major energy source in lignocellulosic biomass and are encrusted with lignin and create an ability to protect against enzymatic attack in lignocellulosic materials. Lignin composes around 25 % of lignocelluloses and is an aromatic cross-linked polymer synthesized from phenylpropanoid precursors. Differing in the substituents of the phenylpropanoid skeleton, lignins are categorized into two classes, the guaiacyl lignins and guaiacyl-syringyl lignins, respectively. Guaiacyl lignins have a methoxy-group in the 3-carbon position, whereas syringyl-lignins have a methoxy-group in both the 3-carbon and 5-carbon positions (Galbe and Zacchi 2002). The lignin component of lignocellulosic biomass is responsible as a protective sheath around the cellulose microfibrils (Palmqvist and Hahn-Hagerdal 2000). The composition of lignin varies depending on the source of raw material. Softwood contains a higher amount of lignin (about 30 %) than hardwood (about 20 %).

15.2.2 Enzymatic Degradation and Depolymerization

15.2.2.1 Lignin Biodegradation

The enzymatic degradation and depolymerization of lignocellulosic material into fermentable sugars is an intricate process that involves an extensive collection of enzymes. For first step in the process, it is of great importance to facilitate the degradation of cellulose and hemicellulose which involves depolymerization of hydrophobic lignin polymers (Scharf and Tartar 2008). Lignin is problematic substrate during biodegradation due to its insolubility behavior and high molecular weight. Theoretically, carbohydrolases such as hemicellulases and cellulases should have no significant effect in lignin degradation and depolymerization, as lignin is not a carbohydrate. The initial steps of lignin depolymerization can be catalyzed by extracellular, oxidative, and unspecific enzymes that are able to liberate highly unstable products which further undergo different oxidative reactions. Two major groups of enzymes that are involved in ligninolysis include laccases and peroxidases (Arora and Sharma 2010). Laccases are blue multicopper oxidases and with the presence of mediators it catalyze the oxidation of phenolic and non-phenolic compounds (Thurston 1994). The phenolic nucleus is by the removal of one electron, oxidized, creating a phenoxy-free radical which leads to polymer cleavage of the polymer. One-electron subtraction from phenolic hydroxyl group of lignin is catalyzed by laccase to provide phenoxy radicals which basically undergo polymerization through radical coupling along with partial depolymerization of propyl side chains via alkyl-aryl cleavage. It has been revealed that lignin biodegradation with laccase is mostly polymerized, but some parts are subject to depolymerization (Arora and Sharma 2010).

There are two groups of peroxidases function in delivering effective hydrolysis of the lignin polymer, lignin peroxidases, and manganese-dependent peroxidases. Lignin peroxidase is a glycoprotein which contains a heme as a group in its active center. Lignin peroxidase cannot enter the plant cell due to the size of this protein, thus lignin degradation occurs at the exposed regions of the lumen (Perez et al. 2002). Manganese-dependent peroxidases are molecularly very similar to lignin peroxidases; a glycosylated protein containing a heme group. Manganese-dependent peroxidase generates phenoxy radicals which further undergo various reactions, resulting in depolymerization (Gold et al. 2000). Manganese peroxidase oxidizes Mn^{2+} into Mn^{3+} by hydrolysis of hydrogen peroxide (Kirk and Cullen 1998). Mn^{3+} is a powerful oxidant that degrades lignin.

In addition, reductive enzymes including sugar oxidase and alcohol oxidase are a diverse group of enzymes that play major roles in ligninolysis (Eriksson et al. 1986; Nishida and Eriksson 1987; Kersten and Krik 1987; Kersten 1990). These enzymes are involved in the production of H_2O_2 which is vital in ligninase activity (Sarikaya and Ladisch 1997). In conventional processes, physicochemical treatments such as thermal treatment and chemical treatment are used to release fermentable sugars from raw material with high lignin content. However, extensive research to replace the physicochemical treatment with enzymatic treatments has been done. The main benefits of biological delignification include higher product yields, mild reaction conditions, less energy demand, and fewer side reactions.

15.2.2.2 Hemicellulose Biodegradation

Hemicellulose degradation is the second stage in the overall lignocellulose biodegradation process. This process is crucial to make the cellulose accessible for depolymerization. Enzymes required for efficient hemicellulose biodegradation include xylan esterases, p-coumaric and ferulic esterases, methyl glucuronosidases, and α-arabinofuranosidases (Subramaniyan and Prema 2002; Shallom and Shoham 2003). Compared to cellulose, more enzymes are required for total degradation and depolymerization due to the heterogeneity of hemicellulose. Hemicelluloses can be biodegraded to acetic acid and monomeric sugars. Xylan, the principle carbohydrate in hemicellulose, requires the combined activity of xylan 1,4-β-xylosidase and endo-1,4 β-xylanase during biodegradation process. The specific conversions achieved by each of these enzymes are as follows: (1) endo-xylanases hydrolyze the β-1,4-xylose linkages in the xylan backbone; (2) exo-xylanases hydrolyze reduced β-1,4 xylan linkages releasing xylobiose; (3) β-xylosidases act on xylobiose to liberate xylose and other short chain oligosaccharides; (4) α-arabinofuranosidases hydrolyze terminal non-reducing α-arabinofuranose from arabinoxylans; (5) α-uronidases release α-glucuronic, α-mannuronic, and α-galacturonic acids; and (6) esterases hydrolyze phenolic ester bonds (Collins et al. 2005). Xylanese is highly responsible to release the reducing sugars from xylan. For biodegradation of O-acetyl-4-O-methylglucuronxylan (one of the common hemicelluloses), four different enzymes are required for the degradation; endo-1,4-β-xylanase (endoxylanase), acetyl esterase, a-glucuronidase, and β-xylosidase. The degradation of O-acetylgalactoglucomanann is as follows: (1) endomannases rupture the polymer; (2) acetylglucomannan esterases remove acetyl groups; (3) α-galactosidases eliminate galactose residues; and (4) β-mannosidase and β-glycosidase break down the endomannases (Saha 2003).

15.2.2.3 Cellulose Biodegradation

After hemicellulose degradation, cellulose is exposed for enzymatic degradation. Cellulose depolymerization requires the action of two primary cellulases; endoglucanases and cellobiohydrolases. The β-1,4-glycosidic linkages of cellulose are hydrolyzed by cellulases. Endoglucanases (endo β-1,4-glucanases) releasing new terminal ends by hydrolyzing internal bonds, preferably the amorphous regions in cellulose. Cellobiohydrolases (exo β-1,4-glucanases) act preferentially on the endoglucanase-generated or existing chain ends. Although both enzymes are able to degrade amorphous cellulose, the only enzymes that are able to degrade crystalline cellulose efficiently are cellobiohydrolases. Cellobiohydrolases and endoglucanases release cellobiose molecules. A requirement for effective hydrolysis of cellulose also includes β-glucosidases, which hydrolyze cellobiose and render two glucose molecules. Endoglucanases, cellobiohydrolases, and β-glycosidases must be stable in the exocellular environment and may form a ternary complex with the substrate to function properly (Perez et al. 2002). For microorganisms living in the environment where cellulose is being degraded, the products of cellulose hydrolysis are available as sources for carbon and energy. As a matter of fact, such release of sugars from cellulose is the main basis for microbial interactions occurring in such environments (Leschine 1995).

15.2.3 Biopolymer Derivatives from Lignocellulosic Material

Lignocellulosic material can be converted to a multitude of products. A vast number of chemicals and pharmaceuticals might be produced through enzymatic degradation and depolymerization of lignocellulosic biomass. Chemists and chemical engineers can eventually produce nearly any chemical from lignocellulosic material if they are given unlimited time and money. Though most of the produced chemicals will not be economically viable, various chemicals are potentially produced from lignocellulosic material with many uses. Seven chemicals derivable from lignocellulosic material that appear to have potential for production are: (1) furfural, (2) lactic acid, (3) acetic acid, (4) succinic acid, (5) ethanol, (6) methanol, and (7) hydrogen (Wang and Wang 1984; Zhan et al. 2003; Neureiter et al. 2004; Okino et al. 2008; Wang et al. 2011; Martin and Ignacio 2011; Agirrezabal-Telleria et al. 2013). These listed chemicals are often cited in the scientific research as potential products, and some have the potential to be platform chemicals. Acetic acid and furfural are often used as chemical intermediate. These chemicals come from a range of technologies, many of which are still emerging technologies for biomass. The first four would more likely be created through low energy processes, while five, six, and seven through higher energy processes. Over the past two decades, gradual improvement has been made in the bioconversion of lignocellulosic material into chemicals and fuels, and the price of these products have dropped so much that nowadays biochemicals derived from lignocellulose can compete with petroleum derivatives. The conversion of lignocellulosic material into biochemical is accomplished in two main steps: (a) hydrolysis of the polymer, release the hemicellulose and cellulose from their composite with lignin through delignification, and depolymerization of carbohydrate polymer to produce fermentable sugars; and (b) fermentation using pentoses and hexoses obtained in the first step to produce biochemical. The main advantages of using biological process to derive chemical from lignocellulosic material include higher product yields, less energy demand, and fewer side reactions.

15.3 Nature-Inspired Technologies from Wood-Eating Termite

15.3.1 Lignocellulolytic Systems of Termite

Termites (order Isoptera), well-known pests to cause substantial economic damage to wood construction and landscape tree, are recently used as model for wood derivatives systems. The order Isoptera is separated into lower and higher level termites; characterized by the presence or the lack of symbiotic protists residing in hindgut (Ohkuma et al. 2007). Both higher and lower termites harbor a dense and diverse population of prokaryotic symbionts (Brune 2007). According to Scharf and Tartar (2008), the lignocellulolytic digestion model in termites is defined as group of host and symbiont genes in the termite gut that cooperate to achieve high efficiency of lignocellulose digestion. Besides as a host for numerous microorganism that assist the lignocellulose digestion, termites themselves contribute to the digestion by producing a series of cellulases, hemicellulases, and lignases (Scharf et al. 2010; Zhou et al. 2010).

Worker termites are the most numerous individuals in the colony and are majorly responsible on feeding and lignocellulose digestion. Three main body regions of a worker termite are the foregut, the midgut, and the hindgut (Wood and Johnson 1986). The foregut region which is responsible for mechanically grinding ingested wood fragments comprises of the esophagus, crop, and attached salivary glands. The termite produces and secretes numerous endogenous enzymes such as β-glucosidases, exoglucanases and endoglucanases by the salivary glands into the digestive tract. Apparently, the midgut is a location where some lignocellulose degradation and depolymerization happen. This slender tubular region continuously secretes peritrophic membrane, a protective lining secreted by the midgut that surrounds food and other ingested materials (Tokuda et al. 2004). The midgut of higher termites is known to secrete endoglucanases as well. Attached at the junction of midgut and hindgut are the malpighian tubules which participate in nitrogen recycling and waste excretion. In comparison, less microbiota is to be found in the foregut and midgut, while microbiota is found more abundantly in the hindgut (Hongoh 2011; Köhler et al. 2012). The hindgut, which originates ectodermally, is the largest organ. The hindgut is fermentation compartment that is generally anaerobic, but does possess a microoxic region around its periphery (Leadbetter et al. 1999). The hindgut hosts the majority of gut symbionts and is where most cellulose degradation happens, as well as fermentation occurs. Additionally, Ke et al. (2010) report that lignin modification mainly occurs within termite foregut and midgut sections, then the ingested materials further depolymerize by protozoa in the hindgut.

Termite gut consisting of diverse microorganisms from all three domains of life: Bacteria, Archaea, and Eukarya (protists). Most of these symbiotic microorganisms inhabiting the termite hindgut, including the protists in lower termites and the bacteria responsible for lignocellulose degradation in higher termites, are culture-independent and difficult to isolate for growth and identification by traditional culturing methods. In the hindgut of lower termites, wood particles are endocytosed by symbiotic protists and decomposed within their food vacuoles (Yamaoka 1979). Using PCR technology, scientists identified several diverse genes encoding protist cellulases of the glycosyl hydrolase families 5, 7, and 45 (GHF 5, 7, and 45) from the hindguts of two lower termites *Reticulitermes speratus* and *Coptotermes formosanus* (Ohtoko et al. 2000; Nakashima et al. 2002; Inoue et al. 2005). These studies demonstrate that the symbiotic protists in lower termites may be a rich source of novel cellulase genes.

In consideration of the significant activity of xylanase that was observed in the hindgut of termites, diverse glycosyl hydrolases also are expected to exist in symbiotic protists (Inoue et al. 1997). Symbiotic bacteria in the hindguts of wood-feeding termite species decompose lignocellulosic substrates efficiently despite the lack of gut protists. The demand for the identification of novel lignocellulosic degrading enzymes from these symbiotic bacteria, the need for heterologous protein production at higher efficiencies, and the exigency of reducing the costs of commercial cellulases have generated an interest in obtaining genomic sequences of these symbiotic bacteria.

15.3.2 Integrating Nature-Inspired Technologies from Wood-Eating Termite

The world is on the inclining growth in the production and use of biochemicals and biofuel. Alternative and renewable source to derive fuels and chemicals such as lignocellulosic material offers the chance to potentially reduce the dependence on fossil fuels and prevent further global warming. In fact, there is still a big gap in between the current state of lignocellulosic material conversion technology from being established for commercial application due to its efficiency and processing costs. Over the past 20 years, biochemical industrial technology has mostly laid its basis on the fermentation and biocatalysis technologies from fungal and bacterial lignocellulolytic enzymes, in tandem with discoveries in enzyme engineering, molecular genetics, and metabolic engineering. Hence, there is still improvement needed in developing the commercial techniques for converting lignocellulosic material to chemicals and fuels. As mentioned earlier, the hard part in deriving chemical and fuel from lignocellulosic material is obtaining the metabolic intermediates due to the complicated lignocellulosic biomass structure. To improve the wood-derived chemical and fuel technology, researchers explored and learned from the comprehensive digestive systems of wood-feeding termites in nature (Ohtoko et al. 2000; Nakashima et al. 2002; Inoue et al. 2005).

Termites possess a highly competent natural bioreactor, a specialized gut system that can efficiently process lignocellulosic material. The ability of termite to feed on lignocellulosic material has inspired extensive research into the termite digestion mechanisms of the structural and recalcitrant lignocellulose in their diet, which is potentially to advance current biochemical technologies and processing. The digestion of wood-feeding termites mainly comprises collaboration between two catalyst systems; catalysts from a variety of gut symbiotic microorganisms and termite endogenous catalyst systems, including lignocellulolytic bacteria and protozoa (Ohkuma 2003). The digestion efficiency of wood-eating termite is 65–87 % for hemicellulose and 74–99 % for cellulose (Prins and Kreulen 1991). Therefore, the critical goal development for efficient lignocellulose processing in the biochemical industry is dependent on the development of pretreatment methods that is suitable for vast diversity of lignocellulosic feedstock. Pretreatment procedures are important steps to improve cellulose dipolymerization where substrate that creates obstacles to cellulases is being removed. Researchers are now trying to see if we can use these same microorganisms in termite gut to ease the process for wood-derived chemicals. Current technologies to break down the cellulose in wood are nothing in comparison to termites. Termites are incredibly efficient at it and if we could somehow harness them to do the work for us, we may be able to make biochemicals in a cost-effective manner. One of the important goals behind the exploration of termite lignocellulolytic systems is to screen the genes or enzymes that are appropriate for biochemical industrial applications (Sun and Scharf 2010). Other than just shedding light upon the enigmas of the termite lignocellulolytic systems, researches have also been carried out on physiochemical microhabitats of termite gut systems which provide new information of the gut environments and the specific condition that may actually be essential for an efficient lignocellulolytic system. Hence, theoretically and practically speaking, such studies are important for understanding termite lignocellulolytic systems and evolving current biochemical and biofuel technology.

Zhang et al. (2010) defines two recombinant endogenous glycosyl hydrolases from a lower termite species that functionally convert cellulose to glucose.

This study provides better understanding to scientists in optimizing recombinant cellulolytic enzyme production and combinations for lignocellulose conversion. On the other hand, Ke et al. (2010) identified that all known termites possess a hindgut microbial community of high density and diversity, which is of aid in their digestion and is the source of lignocellulosic fermentation products like glucose, acetate, ethanol, and methane as they contain hydrolytic, acidogenic, acetogenic, and methanogenic bacteria. Methane and hydrogen emission from lower termites are reported to be by-products produced through termite gut lignocellulolytic and metabolic systems. These investigations suggest a distinctive mechanism for generating methane or hydrogen as a by-product during lignocellulose conversion (Cao et al. 2010).

A genomic study of the microbes that ultilizes the termite gut as their habitat has identified close to 1,000 possible enzymes that break down wood (Warnecke et al. 2007). This has proven that bacteria in termite guts encode a diversity of genes and enzymes that may play a role in wood degradation. The plethora of lignocellulolytic enzymes could explain the termite's well-known capacity of wood-eating and provides the suggestion of cheaper and more efficient ways for generating lignocellulosic-derived chemicals. Inspired by the termite gut system, simultaneous saccharification and fermentation is a compelling option to the two-step bioconversion, in which the presence of both hydrolytic enzymes and fermentative microorganism is in the same reactor. The great advantage of using simultaneous saccharification and fermentation is that hydrolysis and fermentation using the resulting sugar to desired biochemical happens at the same time, in the same reactor, thus, recovery of the products is easier. There are much efforts carried out by the laboratories throughout the world in order to obtain the production of biochemical or biofuel directly from lignocellulosic materials using a cocktail of microorganisms. The cocktail of symbiotic microbes and lignocellulolytic enzymes from the termite gut show promises for industrial use. The ability of termite to convert lignocellulose into fermentable sugars efficiently in a short time has made studying the insects a point of focus for number of scientists, to apply that capability to the large-scale generation of biochemical from lignocellulosic materials. From the evidence observed in laboratory bioassays, many of the enzymes isolated from termites could have a significant synergistic effect on wood degradation when mixed with other commercial enzyme preparations, e.g., >47 % more reducing sugar at 1:1 mixture than with pure commercial enzyme (Azuma et al. 1984). Therefore, the cellulases or other related hydrolases isolated from termite guts may act as unique catalysts and be an economically viable solution for the bioconversion of lignocelluloses. Besides, Nakashima et al. (2002) also stated that enzyme-producing genes from termite gut may be transferred to a creature that is more controllable, allowing cellulases to be mass produced to generate biofuels. Oftenly, this normally meant that the transfer of the genes would be done onto fungi or bacteria that are modified genetically, or into other bigger living organism, such as caterpillars, to industrially produce the enzymes. These diverse cellulase genes could potentially be cloned into *Escherichia coli* or other vector bacteria.

15.4 Conclusions and Future Perspective

Many researchers throughout the world are participating in the research on the various aspects of bioconversion of lignocellulosic material in hopes of a replacement for petrochemicals. Subsequently, practises that use microorganisms and enzymes are being industrialized to explore the possible applications to derive chemical and fuel from lignocellulosic material. This novel and evolving multidisciplinary area has emerged between entomology and bioengineering sciences; and thus, without a doubt, it will open the way for future discoveries and inventions in biotechnological application especially in the wood chemical industry. Through intensive studies, multiple genes discovered from the termite lignocellulolytic system and successful recombinant techniques with such enzyme genes have provided initial tools vital for further research. Notwithstanding the progress achieved so far, more effort is required for microorganisms and lignocellulolytic enzymes on the mechanism of crystalline microfibril depolymerization and lignin modifications/disruption on hemicellulose and cellulose digestion to obtain a significant industrial impact. Further understanding of the efficient lignocellulolytic system of termites by exploring the enzymes produced by termites and their symbiotic microorganisms will lead to the development of optimal enzyme cocktails with high efficiency of lignocellulose degradation, and in addition, provide novel approaches for biochemical and biofuel industrial applications.

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Chapter 16
Agricultural Residues from Crop Harvesting and Processing: A Renewable Source of Bio-Energy

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Abstract Agricultural residues are widely used as fuel for cooking and other industrial purposes. World population increases day by day; as a result there is an increased demand of food supply to mitigate poverty and nutrition. A huge amount of biomass is obtained as residues of agricultural crops and the production of residues increases as well. Agro-residues are a renewable source of energy as the combustion products (carbon dioxide) and the energy from residue renews within a very short period of time by consuming next growing season. Entire amount of field residues cannot be used and harvested as energy because a large share of residues should be left in the field for maintaining the health of soil. However, entire amount of crop-processed residues can be utilized as source of energy. There are several technologies for converting the residues to energy. The type of residues available at specific region is an influence to the use of technology in energy conversion. The research on technologies for energy conversion is under progress at satisfactory level. The processes of harvesting and conversion of agro-residues also generate green job in different sector in the society. The success of sustainability of renewable energy from agricultural residues depends on the development of efficient conversion technology.

Keywords Renewable energy • Agricultural residue • Processing • Burning • Densification • Biogas • Gasification

16.1 Introduction

The first civilization started with agriculture on earth. Till then people cultivate crops to meet up their daily needs and other recreations. Plant is the primary accumulator for storing energy from sun capturing carbon from environment. Biomass is an important resource of energy in the world since the beginning of civilization. Agricultural crops produce large amounts of biomass residues. A large share of the crop residues are left in the field during harvesting; some could be used to produce energy. The solar energy is captured as carbon in plant through photosynthesis process; in this process, carbon dioxide (CO_2) is transformed into organic compounds, and it is the first key step for the growth of plant. The photosynthesis process is illustrated as following:

$$\text{Carbon dioxide} + \text{Water} \frac{\text{Light}}{\text{Chlorophyl}} -> \text{Carbohydrate} + \text{Oxygen}.$$

The structural block of carbohydrate (CH_2O) is the primary product for growth of plant. To fix one gram mole of carbon in the carbohydrate about 470 kJ energy from sunlight is absorbed (Klass 2004). Then the concept of using ago-residues as a source of renewable energy consists of the capture of energy from sunlight and carbon from air (CO_2) in growing plant. This biomass is transformed into other usable forms of fuel or chemicals or chemical intermediates or it is used straightforwardly as a source of heat energy.

Agricultural biomass is the greater energy potential on earth (EEA 2006). By means of existing technologies, biomass from agricultural residues can satisfy the energy demands in a wider range. Expanding demand of energy and price hike of fossil fuel and awareness on the climate change impacts are dictating an increasing demand for new types of biomass as a source of sustainable thermal energy production. Crop residues offer significant potential source of raw material to satisfy the increasing quantity. The main problem with the use of agro-residues is that they are not easy to burn due to their large dissimilarities of chemical and physical characteristics. However, progressive technical development in biomass processing and burning systems collective with further perceptiveness of strategies to get better biomass quality of herbaceous feedstock create the materialization of a potentially large new bio-energy sector.

16.2 Agricultural Residues as Potential Source Energy

Agricultural residues are indentified as a potential of biomass energy worldwide. As the residues from agricultural and forestry sources have the opportunities to be used more efficiently, several countries are giving emphasize on the development of biomass energy technology (Anonymous 1998; Li et al. 2005). Adaptation of new technologies for biomass energy conversion can reduce air pollution and net carbon dioxide emissions. Such technologies could be synthetic gas generation, liquid biofuel production, and carbon dioxide capture (Ragauskas et al. 2006). Several scenarios are to be evaluated for quantification of the potential biomass generated from agriculture. The evaluation processes include a choice of combinations of options as following (USDE 2005):

- Crop yields on active cropland.
- Ratios of grain-to-residue.
- Technological capabilities for collection of residue.
- Tillage practices for crop production.
- Crop rotation to accommodate perennial crops.
- Production of biofuels (ethanol, biodiesel, etc.).
- Residues from postharvest processing and others.

Yields of crop are of specifically important because they affect the amount of land used to meet the demand of food, feed, fiber, and other demands the amount of residue generated. Total crop production has increased significantly over last decades by two to fourfolds. Trends of major crops produced around the world are shown in Fig. 16.1. It reveals that amount of residues from agricultural produces increases as well. Oil palm fruit production is estimated to be 249.53 million tons worldwide. However, one third of oil palm fruit (93.85 million tons) was produced in Malaysia in 2012 (FAOSTAT 2014). Amount of residues not only depends on the

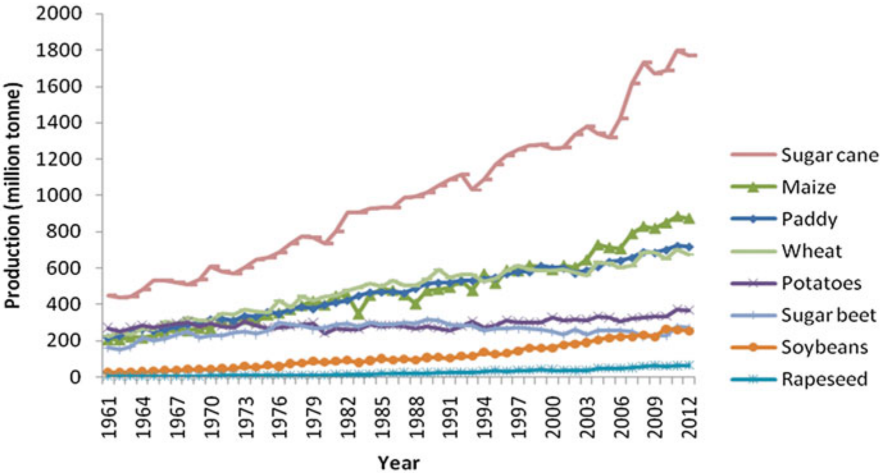

Fig. 16.1 Trends of world production of some selected crops (www.faostat.fao.org, FAOSTAT 2013)

production but also ratios of crops to residues are important factor. Ratio of crop to residues varies crop to crop (Table 16.1). A portion of entire amount of residue is recommended to leave in the field for maintaining the soil health. Moisture content of residues is another important factor that governs the actual and effective crop residue yield (Table 16.2).

16.3 Agricultural Residues from Crop Harvesting

Corn stover, cereal straw (wheat and rice straw, etc.), soybean stubble, potato stubble, and other residues are the sources of harvested residues from agriculture.

Residues from crop harvesting could potentially be converted to bio-energy, but there is a big debate regarding the harvesting rate of crop residues in a sustainable manner. Removal of residues decreases soil carbon at rate 40–90 kg carbon per hectare per year per ton of harvested residue. If the soil loss remains within allowable limits, even then the harvesting of residue arises a question of trade-offs in relation to the reduction of crop yield and reduction of nutrients of soil. The effects of the rate of residue harvesting are highly variable because it depends on local climate conditions and soil erodibility. Thus, it is problematic to recommend a single rate of residue harvest globally. In a flat land condition, a lion share of residue could be harvested sustainably for bio-energy under conservation management (Gregg and César Izaurralde 2010).

The rate of residue harvested sustainable could be decided based on a number of local conditions, for example, nutrient available in soil; organic matter exists in soil;

Table 16.1 Residue-crop ratio for different crops

Type of crops	Type of residues	Residues-crop ratio	Reference
Barley	Straw	2.25	(Kowoksing and Lapp 1975)
Cassava	Stalk	0.088	(Srisovanna 2004)
Coconut (*Cocos nucifera*)	Husk	0.419	(Koopmans 1998)
	Shell	0.12	(Koopmans 1998)
Cotton (*Gossypium hirsutum* L.)	Stalk	1.5	(Lal 1995)
		0.9175	(Allen and Musick 1972, Glover 1975)
Groundnut (*Arachis hypogaea* L.)	Straw	2.3	(Koopmans 1998)
	Straw	1.2	(Stanford Research 1976)
	Shell	0.477	(Koopmans 1998)
Jute (*Corchorus capsularis*)	Stalk	3.0	(Koopmans 1998)
Maize (*Zea mays* L.)	Stalks	2.0	(Koopmans 1998)
	Stalks	1.07	(Arnold 1975, Dugas 1973)
	Cob	0.273	(Koopmans 1998)
	Husk	0.2	(Koopmans 1998)
Oats	Straw	2.5	(Kowoksing and Lapp 1975)
Oil palm	Empty bunches	0.428	(Srisovanna 2004)
	Fiber	0.147	(Srisovanna 2004)
	Shell	0.049	(Srisovanna 2004)
	Frond	2.604	(Srisovanna 2004)
	Male bunches	0.233	(Srisovanna 2004)
Potato (*Solanum tuberosum*)	Straw	0.25	(Lal 1995)
Rice (*Oryza sativa* L.)	Straw (Local variety)	1.697	(Yokoyama et al. 2000)
	Straw	1.4	(Kowoksing and Lapp 1975)
	Straw (high yielding variety)	1.05	(BRRI 1996, 1997)
	Husk	0.20	(www.knowledgebank.irri.org)
	Bran	0.083	(Koopmans 1998)
Rapeseed (*Brassica napus*)	Stalk	1.5	(Lal 1995, Lal 2005)
Rye	Stalk	2.25	(Kowoksing and Lapp 1975)
Sesame(*Sesamum indicum*)	Stalk	1.5	(Ahiduzzaman 2011a)
Sorghum	Stover	1.07	(Allen and Musick 1972, Allen et al. 1975)
Soybean	Straw	0.85	(Stanford Research 1976)
Sugarcane (*Saccharum officinarum*)	Top	0.3	(Koopmans 1998)
	Bagasse	0.29	(Koopmans 1998)
Sunflower	Stover	5.0	(Stanford Research 1976)
Vegetables	Residues	0.4	(ICCEPT 2005)
Wheat (*Triticum aestivum*)	Straw	1.5	(Lal 1995)
		2.75	(Allen and Musick 1972, Allen et al. 1975)

Adapted from Ahiduzzaman (2011a)

Table 16.2 Moisture content of different agro residues

Agro residues	Moisture content percentage by mass	Reference
Rice straw	12.7	(Yokoyama et al. 2000)
Wheat straw	9.2	(Koopmans and Koppejan 1997)
Maize stalks	11.11	(Koopmans and Koppejan 1997)
Sugarcane top	50.0	(Koopmans and Koppejan 1997)
Jute stalk	9.5	(Ahiduzzaman 2011a)
Groundnut straw	12.1	(Koopmans and Koppejan 1997)
Rapeseed stalk	7.5	(Hossain and Badr 2007)
Sesame stalk	9.5	(Hossain and Badr 2007)
Cotton stalk	12.0	(Koopmans and Koppejan 1997)
Vegetables	20.0	(ICCEPT 2005, Hossain and Badr 2007)
Potato	12.0	(Ahiduzzaman 2011a)
Rice husk	10	(Ahiduzzaman 2011a)
Rice bran	14.9	(Qingci et al. 1999)
Maize cob	15	(Hossain and Badr 2007)
Maize husk	11.1	(Koopmans and Koppejan 1997)
Bagasse	49	(Yokoyama et al. 2000)
Groundnut shell	8.2	(Koopmans and Koppejan 1997)
Coconut husk	10.3	(Koopmans and Koppejan 1997)
Coconut shell	8.7	(Koopmans and Koppejan 1997)

effects of wind and runoff on soil erosion; moisture content of soil; crop yield; and the cost of harvesting. An estimate recommended that 2–3 tons/acre of residues after harvesting should be remained in the field for maintaining the good soil health (NebGuide 2012). Several studies examine the rate of residue removal considering different practices of management and soil conservation programs; soil coverage by the residues left in the field after harvest. McCool et al. (1995) showed that it is not linearly related that after 30 % of residue removal 70 % of land is covered, regardless whether the land coverage is measured. They measured that a 30 % removal of residue resulted in 93 % of soil coverage after harvest (Fig. 16.2). The relationship between land covered by the residue and the amount of residues removed will differ with respect to different crop and yield data. Therefore, it is recommended to determine the appropriate removal rate of residue for a particular crop at particular location (USDA 2006).

Soil organic matter content is important to allow proper nutrient supply and to maintain physical properties of soil that are essential for soil health, water infiltration rate, and soil water-holding capacity. Harvest efficiency of agro-residues depends on several aspects as following:

- Time of residues collection depends on grain harvesting period.
- Amount of traffic on crop residues during harvesting of grain.
- Water content in soil and standing water on soil surface and any natural calamity during the crop harvest and after the harvest as well.
- Type of harvesting machinery used.

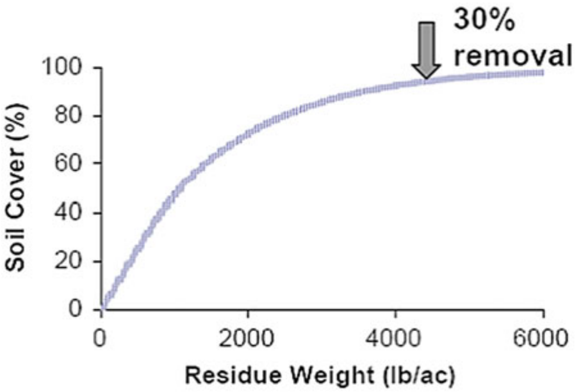

Fig. 16.2 The relationship between percent of soil covered by residues after harvest and residue weight per acre for common small grains and annual legumes in the non-irrigated U.S. Northwest (McCool et al. 1995)

16.4 Residues from Crop Processing

Residues from crop processing are generally all dry, uniform in quality. Types of residues from crop processing typically vary based on the available crop processed in certain location. In Canada, the main crop milling residues are wheat bran, oat hulls, corn cobs, barley hulls, and sunflower hulls being commercially developed for bio-heating. The quantity of residues obtained from grain processing in Canada was estimated at 1.5 million tons approximately (Samson et al. 2006). Presently, there is a rising competition for grain milling residues between the bio-fiber pellet fuel and feed industry for livestock. Rice husk is another milling by-product from rice-processing industries. Total potential production of residues from crop processing can be easily estimated from the total production data shown in Fig. 16.1 multiplied by the residues ratio shown in Table 16.1. For example, world rice husk production potential is approximately 132 million tons. Rice husk has very good properties as biomass fuel for producing steam and other process heat, e.g., crop drying as well. World bagasse production is estimated to be 531 million tons in 2012. In Malaysia, total production of empty fruit bunches and fruit shell of the oil palm was 40.17 and 4.60 million tons, respectively (FAOSTAT 2014).

16.5 Physical, Chemical, and Thermal Properties of Agricultural Residues

Moisture content of residues is another important factor that governs the actual and effective crop residue yield (Table 16.2). The moisture content of agro-residues varies widely from 8.2 to 49 % by mass. Calorific value of a biomass depends on percentage of cellulose, hemi-cellulose, and lignin. Higher amount of ash lower the calorific value of biomass. Net calorific value is also affected by inherent moisture content of residues. Calorific values of some typical residues are shown in Table 16.3.

Table 16.3 Calorific value of different agricultural residues

Type of crops	Calorific value (GJ/ton)	Reference
Barley straw	16.94	(Kowoksing and Lapp 1975, Green 1975)
Cassava stalk	18.42	(Srisovanna 2004)
Coconut husk	18.62	(Koopmans 1998)
Coconut shell	18.10	(Koopmans 1998)
Cotton stalk	12.38	(Koopmans 1998)
Cotton field trash	16.25	(McCaskill and Wesley 1976)
Groundnut shell	15.66	(Koopmans 1998)
Groundnut straw	17.58	(Koopmans and Koppejan 1997)
Jute stalk	16.91	(Hossain and Badr 2007)
Maize cob	16.23	(Koopmans 1998)
Maize husk	12.38	(Koopmans 1998)
Maize stalks	16.80	(Koopmans 1998)
Oats straw	17.40	(Kowoksing and Lapp 1975, Green 1975)
Oil Palm		
Empty bunches	17.86	(Srisovanna 2004)
Fiber	17.62	(Srisovanna 2004)
Shell	18.46	(Srisovanna 2004)
Frond	9.83	(Srisovanna 2004)
Male bunches	16.33	(Srisovanna 2004)
Potato	17.35	(Hossain and Badr 2007, ESTU 1999)
Rapeseed stalk	16.50	(Kordas and Bojanowska 2010)
Rice bran	13.97	(Koopmans 1998)
Rice husk	12.6–15.19	(Ahiduzzaman 2011a)
Rice straw	16.30	(Yokoyama et al. 2000)
Rye stalk	17.40	(Kowoksing and Lapp 1975, Stanford Research 1976)
Sesame stalk	15.92	(Cuiping et al. 2004)
Sorghum straw	13.93	(Green 1975)
Soybeans straw	16.25	(Stanford Research 1976)
Sugarcane bagasse	18.10	(Koopmans 1998)
Sugarcane top	15.81	(Koopmans 1998)
Sunflower stalk	18.57	(Stanford Research 1976)
Vegetables	13.00	(ICCEPT 2005, Hossain and Badr 2007)
Wheat straw	15.90	(Koopmans and Koppejan 1997)

16.6 Conversion of Agricultural Residues to Energy

Most common way of conversion of agro-residues is burning process. The heat energy is generally used directly for cooking, parboiling process, heating buildings, drying of crops, and processes heat in the industry. It could be used as source energy for producing steam as well as generating electricity. Agricultural residues could be transformed into liquids or gases fuel. They are suitable for running electric generator or automobile transportation. Ethanol fuel is produced through typical fermentation and distillation process. Residues also can be transformed into a gas by pyrolysis process under low oxygen condition in a reactor.

Animal dung can be transformed into biogas through an anaerobic digestion process. The biogas is burned to produce heat, steam, or electricity. Extra pure methane gas can be obtained from biogas by removing carbon dioxide and sulfide gas. Technological innovation of advanced applications of biogas is still in development process. Direct combustion of biogas is very old fashion; however, it is a promising technology to run advanced gas turbine and produce electricity. The efficiency of this system is higher by twofold as direct combustion of raw biomass to generate electricity from steam. Biogas obtained from residues also can be converted into hydrogen fuel or liquid methanol, which also can be transformed through chemical process to electricity in an advanced and efficient fuel cell (USDE 2002).

16.6.1 Direct Burning of Agricultural Residues

Direct burning of biomass is traditional way of biomass conversion technology. Cook stove is used to burn biomass in rural household and small restaurant. The thermal efficiency of traditional stove is very low, sometimes less than 10 %. However, a lot of improved cook stove (ICS) programme has been implemented worldwide to reduce pollutions. In agro-processing industry, boiler is run by direct combustion of residues.

16.6.2 Densification of Agricultural Residues

A large quantity of agricultural residues are produced and used in inefficient manner in many developing countries causing contamination to the environment. The most common agricultural residues are straws of wheat and rice, rice husk, coffee husk, sugarcane bagasse, jute sticks, groundnut shells, mustard, and cotton stalks. Sawn waste, a milling residue of timber, is also available in a large quantity. Difficulties arise during the transportation, long time storage, and handling. The bulky residues also create problems during direct burning in conventional stoves or furnace in association with very low combustion efficiencies and air pollution. The energy conversion efficiencies of residues are as low as 20–40 % in association with incomplete combusted carbon in the form of carbon monoxide in excess of 10,000 ppm in flue gas and the particulate matter emissions in the flue gases in excess of 3,000 mg/Nm^3 (Grover and Mishra 1996; Ahiduzzaman et al. 2009). In addition, a large amount of unburnt carbonaceous ash needs to be disposed of. Biomass briquetting pelleting could solve these problems and could provide the important domestic and/or rural industrial energy. Densification/compaction of loose biomass is known as briquetting or pelleting of sawdust and any other agricultural residues. The technology for biomass briquetting is adapted and practically using for many years in several countries. The screw extrusion technology for biomass briquetting was first invented and developed in Japan in 1947. There are some other densification processes such as the “Prest-o-log” technology developed in the United States, the “Compress” method in West Germany, and the “Glomera” method in Switzerland.

Table 16.4 Properties of densified biofuel

Bulk density of raw material (husk), kg/m^3	117.0
Bulk density of densified fuel, kg/m^3	825.4
Apparent density of densified fuel, kg/m^3	1219.0
Bulk compaction ratio	7.01
Nominal length of fuel, cm	60–100
Nominal diameter, cm	5.6–6.0
Inner hole diameter, cm	1.8–2.4
Calorific value of raw rice husk, MJ/kg	13.50
Calorific value of rice husk briquette, MJ/kg	15.20

Source: Ahiduzzaman (2006), Ahiduzzaman (2011a)

The bulky and loose waste biomass materials are transformed into solid biomass fuel by compression process or commonly known as briquetting process. The most commonly used briquetting process in the developing countries is screw press briquetting or screw extrusion process. Compression ratio of biomass briquette ranges from 2.5: 1 to 8.25:1 or might be more (Moral and Rahman 1999; Ahiduzzaman 2007; UNEP 2009). For instance, some properties of briquette fuel from rice husk are shown in Table 16.4. The biomass briquette fuel has also a social impact in gender issues and employment generation. Time savings for cooking fuel collection by women in rural area is estimated to be 12 man-day per year if the briquette fuel is used. Another important issue is that green job creation by briquette process in rural area is estimated to be 3.73 man-day/ton of briquette production (Ahiduzzaman 2011b).

16.6.3 Biogas Production from Agricultural Residues

Biogas is a product produced in anaerobic digestion phenomenon by which organic matter is transformed into methane (CH4) in the absence of air (oxygen). Biogas is produced naturally from the anaerobic digestion of biomass in such situations as wet rice fields, ponds, or marshes. Methane released from microbial activity is estimated about 590–880 million tons into the atmosphere worldwide. About 90 % of the Methane emitted from biogenic sources contributes approximately 90 % of global methane emission. The rest is derived from fossil origin. Concentration of methane is estimated to be 1.65 ppm in troposphere of northern hemisphere. Global warming potential of methane is 21 times more than that of carbon dioxide (Uwe Rehling 2001). Trapping the biogenic methane by producing biogas is the solution of reducing global warming effect. The methane gas yield potential from various types of agro-residues is shown in Table 16.4. Using this factors biogas potential can be estimated for a certain region based on the amount and type of residues.

Biogas consist of a large number of complex microbe species involves in biogas production process those act in a different way, remarkable the methane-producing microbes. The whole process of biogas production is divided into three different footsteps: hydrolysis, acidification, and finally the methane production. Three types of species of bacteria are involved here.

Table 16.5 Methane yields of some selected agro residues in milliliter per gram volatile solid (VS) added

Source of agro residues	Particle size (mm)	Methane gas yield, mL/g VS_{added}	Reference
Barley straw	50–100	229	(Dinuccio et al. 2010)
Cotton stalks		145	(El-Shinnawi et al. 1989)
Maize stalks		229	(El-Shinnawi et al. 1989)
Oats	<20	250–260	(Kaparaju et al. 2002)
Potato		390	(Buffière et al. 2006)
Rapeseed straw		240	(Lehtomäki et al. 2008)
Rice straw	50–100	195	(Dinuccio et al. 2010)
Rye straw	<2	360	(Petersson et al. 2007)
Sorghum whole plant	20–40	362	(Bauer et al. 2010)
Sugarcane residue	1	177	(Nzila et al. 2010)
Sunflower whole plant	20–40	345	(Bauer et al. 2010)
Wheat straw	10	299–331	(Hashimoto 1989)

Firstly, in the fermentation process, bacteria break the longer chains of the complex molecules of carbohydrate, protein, and lipid into smaller molecules. For instance, polysaccharides are transformed into monosaccharide. Proteins are broken into amino acids and peptides.

Secondly, bacteria are responsible for acid production and convert the intermediate products obtained from fermentation step into acetic acid (CH_3COOH), carbon dioxide (CO_2), and hydrogen (H_2). These bacteria involved in acidification are facultatively anaerobic and have the ability to grow in acidic conditions. They consume carbon and oxygen to generate acetic acid. In this process, they consume the dissolved oxygen in the solution or the oxygen bounded in other molecule. Hereby, the bacteria involved acid production to ensure an anaerobic environment which is necessary for the microorganisms involved in methane production. Moreover, in this process the compounds are reduced with a lower molecular weight into organic acids, carbon dioxide, alcohols, hydrogen sulphide, amino acids, and traces of methane.

Finally, methanogenic bacteria decompose the compounds with a lower molecular weight. In the last step, the microbes utilize acetic acid, carbon dioxide, and hydrogen to generate methane and carbon dioxide. Under natural conditions, methanogenic bacteria occur under natural condition to the point that anaerobic situations are provided, such as under water (e.g., wet paddy field, marine sediments, etc.), in ruminant stomach, and in marshes. The yield potentials of methane gas from some typical biomass residues are furnished in Table 16.5.

16.6.4 Biomass Gasification

Biomass gasification means incomplete combustion of biomass resulting in production of combustible gases consisting of carbon monoxide (CO), hydrogen (H_2), and traces of methane (CH_4). This mixture is called producer gas. Producer gas can be used to run internal combustion engines (both compression and spark ignition), can be used as substitute for furnace oil in direct heat applications, and can be used to produce, in an economically viable way, methanol—an extremely attractive chemical which is useful both as fuel for heat engines as well as chemical feedstock for industries. Since any biomass material can undergo gasification, this process is much more attractive than ethanol production or biogas where only selected biomass materials can produce the fuel.

16.7 Conclusion

Wide varieties of agricultural residues are produced worldwide. Production of agro-residues increases over time due to the intensive increased food production to mitigate poverty and nutrition. Agro-residues are a renewable source of energy. Entire amount of residues cannot be used as energy because a large share of residues should be left in the field for maintaining the health of soil. Maximum 35 % of field residues can be harvested for energy purposes depending on the local condition. However, entire amount of agro-processed and agro industrial resides can be used as energy. Physical, chemical, and thermal properties are different for different source of resides. There are several technologies for converting the residues to energy. The technological aspects could be varied based upon the type of residues available at certain locality. Advanced and modern technologies are under development and the progress is satisfactory. Therefore, more usable energy could be harvested from conversion process of agro residues which ensures the sustainability of renewable sources of energy from agro residues in future.

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Chapter 17
Application of Micro- or Small-Scale Biomass-Derived Fuel System for Power Generation

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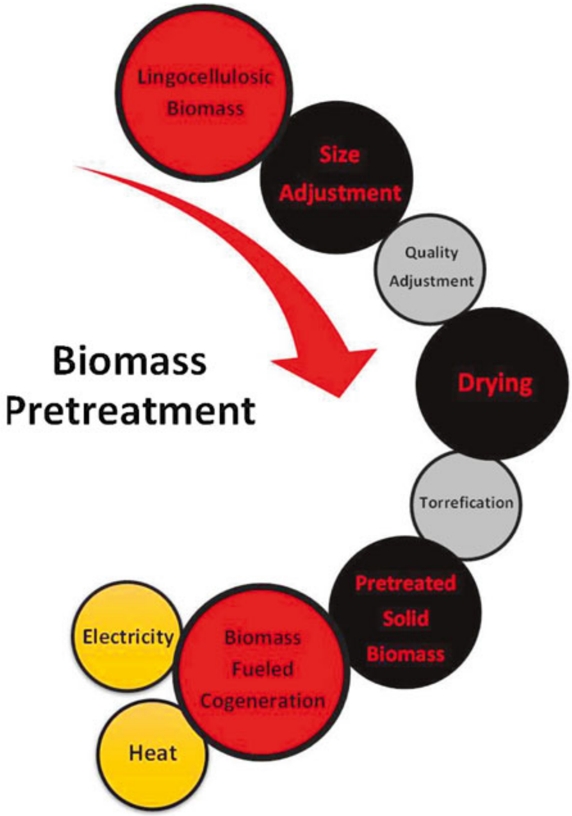
Abstract Biomass being world's largest renewable fuel source is now considered as the best alternate for fossil fuels owing to the CO_2 saving nature as well as more economical as compared to fossil fuels. Although, some pretreatment process is required in order to utilize the raw biomass for power generation. There are various systems to generate power but combined heat and power (CHP) generation has proved to be the most beneficial method to generate electricity as well as heat by recovering the surplus heat to make an overall efficiency of up to 90 %. Various types of CHP systems have been discussed and compared for their working and efficiency along with their applications in different dwellings depending upon their power capacities. Moreover, biomass CHP systems have been thoroughly overviewed for their economic, energy, and environmental aspects.

Keywords Biomass • Pretreatment • Power generation • CHP system • Fuel

17.1 Introduction

Utilization of fossil fuels for power generation is becoming a burning issue from past few decades due to the threat of its depletion in near future and increasing environmental pollution in terms of CO_2 addition to the atmosphere. Various alternatives to these fossil fuels, especially renewable energy sources, have attracted the attention of researchers in recent years because of having reduced CO_2 emissions and environmental friendly nature. Because of this, scientists are looking towards natural sources, especially biomass, which is a renewable energy source (Wang et al. 2013; Zhang et al. 2013). Biomass is actually, a biologically produced matter based on carbon, hydrogen, and oxygen. Biomass is also categorized as lignocellulosic biomass as it is largely composed of lignin, cellulose, and hemicellulose (Agbor et al. 2011). The total biomass production of the world is about 146 billion tons a year, consisting of mostly wild plant growth (Liu et al. 2010). The reason why scientists are more attracted towards biomass is its CO_2 neutral nature that is if grown and utilized properly the net CO_2 emissions will be zero. It can also reduce the amount of acid rains by lowering sulphur dioxide pollutants in the atmosphere. Besides this, biomass is not very challenging to store as well as not location dependent. Therefore, it could be an auspicious choice to replace fossil fuels and reduce greenhouse gases (Demirbas 2011; Huang et al. 2013a, b). Moreover, being an indigenous fuel it can support economy by offering local employment opportunities (Abnisa et al. 2013; Demirbas 2011; Van Dael et al. 2013). Briefly, lignocellulosic biomass is one of the promising renewable solid fuel sources, but requires some pretreatments before its use as a solid fuel. Pretreatment process makes biomass suitable enough to be used directly for power generation, which results in efficient production of heat and electricity. The ratio of heat to electricity can be varied as per requirement of the area under consideration. Figure 17.1 shows a simple flow chart for power generation from biomass.

Fig. 17.1 Simple flow chart for biomass to power generation



17.2 Biomass Pretreatment

Lignocellulosic biomass available in our environment is more vulnerable to biodegradation because of its high moisture content which make it unfavorable to be used directly for power generation. Therefore, biomass pretreatment is obligatory to make it an ideal choice for power generation. The pretreatment process is divided mainly into two categories: one is size adjustments such as briquetting, chipping, grinding, and pelletizing, and the other is consisted of moisture and quality adjustments such as drying and torrefaction. It is important to have an idea on the general properties of lignocellulosic biomass, such as chemical analysis (cellulose, hemicellulose, and lignin contents), proximate analysis, and elementary analysis before proceeding to these pretreatments.

Table 17.1 shows cellulose, hemicellulose, and lignin contents of the representative lignocellulosic biomass. This data is not required to evaluate energy density and combustion behavior, but crucial for estimating pelletization behavior. It is known that lignin works as a thermoplastic binder for pelletization. In other words, lignin

Table 17.1 Chemical composition of lignocellulosic biomass [wt%]

	EFB	Mesocarp fiber	Kernel shell	Fronds	Trunk	Rice husk	Rice straw	Bagasse	Hard wood	Soft wood
Ref	Goh et al. (2010); Yong et al. (2007)								Liu et al. (2010)	
Cellulose	54.4	20.8	20.8	62.3	41.2	35.1	35	50	40–44	40–44
	38.3	33.9	20.8	30.4	34.5					
	39	21	6	42	59					
Hemicellulose	28	38.8	22.7	24.2	34.4	20.6	21	25	15–34	20–32
	35.3	26.1	22.7	40.4	31.8					
	22	16	36	21	10					
Lignin	17.6	28.5	50.7	14.8	17.1	17.6	6	25	18–25	25–35
	22.1	27.7	50.7	21.7	25.7					
	29	43	36	23	11					
Extractives	2.8	6.3	4.8	1.8	2.8	NA	NA	NA	NA	NA
	2.7	6.9	4.8	1.7	3.7					
Ash	3.8	5.6	1	NA	3.4	12.1	16	2.4	0.2–0.5	0.2–0.5
	1.6	3.5	1	5.8	4.3					

plays an important role as a glue to maintain the shape of pellets. Since most of the woody biomass can be pelletized by using ordinary pelletizing machines, lignocellulosic biomass having similar lignin contents as woody biomass is likely to be pelletized. Table 17.2 shows the values of proximate analysis of the representative lignocellulosic biomass. Higher volatile contents result in a longer time period of flame combustion. On the other hand, higher fixed carbon contents result in a shorter time period of flame combustion. Table 17.3 shows the values of elementary analysis. In this table, the carbon content has the most significant meaning since the content is the major variable to determine the energy density or the calorific value of the biomass. The higher the carbon content, the larger will be the calorific value and vice versa.

17.2.1 Size Adjustment

The size requirement for solid fuel is depending on the burner type, in specific the residence time. If the residence time is in a short range of a few second, the size should be submillimeter. On the other hand, if the residence time is in a rather longer range of several minutes, the size can be more than several millimeters. In the case of pelletization, the relevant size ranges from 1 to 3 mm (Liu et al. 2010; Mahlia et al. 2001). It is worthwhile to mention that the moisture content is also a significant variable for pelletizing biomass smoothly since the moisture content determines the temperature of the pelletizer dice under steady state operation (Goh et al. 2010; Yong et al. 2007). In other words, lignocellulosic biomass can be pelletized at the relevant dice temperature range and moisture content.

17.2.2 Quality Adjustment

Lignocellulosic biomass is required to undergo quality adjustment after its size has been adjusted. This pretreatment is performed in two main steps: drying and torrefaction that makes the biomass suitable to be utilized for power generation.

17.2.2.1 Drying

Lignocellulosic biomass just after harvesting or generation from industrial processes contains rather high moisture; core of broad-leaved trees, 35–60 wt%; annulus of broad-leaved trees, 30–55 wt%; core of conifer, 25–35 wt%; annulus of conifer, 60–70 wt%; agricultural residues, 20–70 wt%. This wider range for the moisture content of agricultural residues is attributed to a variety of the processes for the residues (Aljuboori 2013; Diep et al. 2012; Prakobboon and Vahdati 2013; Wu et al. 2013; Yee et al. 2000). Anyway most of the lignocellulosic biomass contains too high moisture content to be utilized as a solid fuel.

Table 17.2 Proximate analysis of lignocellulosic biomass [wt%]

	EFB	Mesocarp fiber	Kernel shell	Fronds	Trunk	Rice husk	Rice straw	Sugarcane bagasse	Eucalyptus (hard)	Spruce (soft)
Ref	Idris et al. (2012)			Idris et al. (2012)	Van Dael et al. (2013)	Parikh and Ghosal (2007)				
Moisture	NA 8.65	NA	NA	Dry basis	5.89	Dry basis				
Volatile matter	70.5 75.09	68.8	69.2	85.1	76.84	69.3	72.7	73.78	82.62	70.2
Fixed carbon	15.4 12.34	15.2	16	11.5	11.42	14.9	11.8	14.95	16.15	28.3
Ash	4.5 3.92	10.2	10.5	3.4	5.85	15.8	15.5	11.27	1.23	1.5

Table 17.3 Ultimate (elementary) analysis of lignocellulosic biomass [wt%]

	EFB	Mesocarp fiber	Kernel shell	Fronds	Trunk	Rice husk	Rice straw	Sugarcane bagasse	Eucalyptus (hard)	Spruce (soft)
Ref	Aljuboori (2013), Uemura et al. (2011), Idris et al. (2012) Mahlia et al. (2001)			Parikh and Ghosal (2007)	Van Dael et al. (2013)	Parikh and Ghosal (2007)				
C	40.93	43.19	41.33	46	40.64	38.92	35.97	44.8	47.1	51.9
	48.8	48.7, 47.2	52.8, 52.4							
	45.53	46.92	46.68							
H	5.42	5.24	4.57	6	5.09	5.1	5.28	5.35	6	6.1
	6.3	6.3, 6.0	5.7, 6.3							
	5.46	5.89	5.86							
O	51.78	49.79	53.02	44	53.12	37.89	43.08	39.55	45.43	40.9
	36.7	44.4, 36.7	41.3, 37.3							
	43.4	42.66	42							
N	1.56	1.59	0.99	NA	2.15	NA	NA	NA	NA	NA
	0.2	0.6, 1.4	0.1, 0.6							
	0.45	1.12	1.01							
S	0.31	0.19	0.09	NA	NA	NA	NA	NA	NA	NA
	0.2	0.3	0.2							
	0.044	0.089	0.06							
Ash	7.3	8.4	3.2	3.4 [f]	5.85	15.8	15.5	11.27	1.23	1.5
	5.12	3.32	4.38							

Drying of lignocellulosic biomass is done either under ambient atmosphere or at higher temperatures. Lignocellulosic biomass contains the cell water and free water. The cell water content varies between 0 and 25 wt% depending on the temperature and humidity of the atmosphere (Parikh and Ghosal 2007). If the moisture content is higher than 25 wt%, it is likely that free water contribution cannot be negligible. If biomass is dried under ambient atmosphere, the final moisture content will be between 0 and 25 wt% depending on the temperature and humidity of the atmosphere. If the moisture is required to be below the level, then the biomass need to be dried by using a drier at higher temperatures.

17.2.2.2 Torrefaction

Torrefaction is a thermochemical process, in which lignocellulosic material undergoes lower temperature (200–300 °C) treatment under inert atmosphere (Uemura et al. 2011). During this process, hemicellulose decomposes mainly water, carbon dioxide, and minor amounts of organics, such as acetic acid (Prins et al. 2006; Van Dael et al. 2013). Small portions of cellulose and lignin also decompose. As a result, torrefied biomass gains higher carbon contents, higher calorific values, better grindability, and higher resistance to biodegradation than the raw material.

17.3 Biomass to Power Generation

The efficiency of power generation systems largely depends on the properties of the biomass like moisture content, calorific values, grindability, and resistance towards biodegradation. The pretreatment of biomass make it suitable enough to be utilized as solid renewable fuel in power generation system by enhancing the abovementioned features. Biomass can be used for the production of clean energy (such as biodiesel, bio-methane, producer gas, and ethanol) because of having reduced CO_2 emissions and environmental friendly behavior and helping to reduce the consumption of fossil fuels. One of the major applications of biomass in clean energy production is through electricity generation, which is gaining more and more considerations worldwide. Biomass co-firing with coal in conventional power plants and combined heat and power (CHP) systems would be a better option for clean energy production as it can produce up to 90 % lesser emissions as compared to electricity generated by fossil fuels through conventional means (Bianchi et al. 2013; Sadrul Islam and Ahiduzzaman 2012). CHP generation system is considered now-a-days as a major alternative to traditional energy systems in terms of lower CO_2 emissions as well as energy saving (Liu et al. 2011). In CHP generation heat is always produced along with power generation (Dong et al. 2009). Much attention is diverted towards the consumption of small buildings and houses where electricity requirement is only less than 100 kW, for this reason they are called “small-scale CHP.” Small-scale CHP with electrical capacity less than 15 kW are often termed as “micro-scale CHP.”

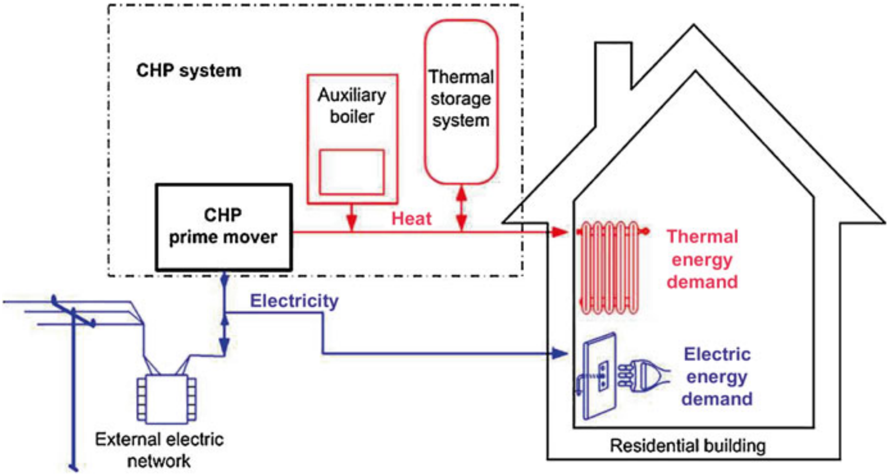


Fig. 17.2 Simple layout of a CHP system (Bianchi et al. 2013)

Micro/small-scale CHP systems are suitable to be installed in small commercial buildings, hospitals, schools, and domestic buildings. Small-scale and micro-scale CHP are also advantageous in terms of reduction of greenhouse gas emissions and economical by omitting the electricity transmission and distribution network. Moreover, in some countries they have been integrated into pre-installed power networks saving operational cost as well (Compernolle et al. 2011; Rong et al. 2009; Thomas et al. 2013; Touš et al. 2011). Usually individual residential CHP systems are also interconnected with each other to exchange energy as and when needed. A simple layout of CHP system is represented in Fig. 17.2 using prime mover to satisfy the thermal and electrical needs of a residential building utilizing preinstalled conventional grid system. In the case where the production is higher than the demand, the excess energy can be sent to external electric network. Contrarily, if the demand is higher than the CHP production, the external electric network can fulfill this energy shortage. Therefore, CHP system connected with external electric network works as an infinite capacity system that can serve in either case. The application of a certain CHP system largely depends upon the type of prime mover technology being used.

17.4 Types of CHP Systems

There are several distinct prime mover technologies which are under development for CHP systems such as internal combustion engines (ICE), micro gas turbine (MGT), organic Rankine cycle (ORC), thermophotovoltaic generators (TPVG), Stirling engines (SE), and fuel cells (Dong et al. 2009; Maghanki et al. 2013). These technologies can work with different fuels giving out different amounts of electrical and thermal outputs.

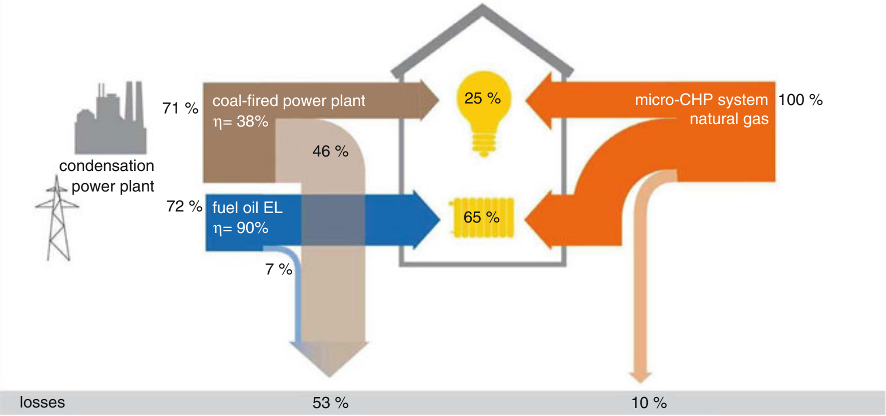


Fig. 17.3 Comparison of efficiency between conventional generation and micro CHP generation (Sommer 2011)

The main difference between these technologies is the ratio of heat and electricity produced by the systems ranging from 5 (Stirling engine) to 0.8 (high temperature Fuel cell). Also different CHP systems determine the type of dwelling in which there are to be installed. Additionally, the efficiency of the CHP system is not only influenced by the type of fuel source being used but also by the type of prime mover technology. However, whichever technology is utilized the efficiency of CHP system is always higher than the conventional or separated heat and power systems. As shown in Fig. 17.3, a conventional on-site coal-fired power plant along with gas boiler is compared with an on-site CHP system which represents energy saving of up to 30 % by CHP system (Nascimento et al. 2013). Energy efficiency of 100 % can be attained with micro-cogeneration. Furthermore, distributed CHP system reduces the primary energy consumption and increase the site energy consumption. It is reported in the literature that all the available CHP technologies give CHP efficiency not less than 75 %, increasing energy reliability for the user. Besides this, CHP technologies are well known due to their efficient CO_2 saving as compared to conventional grid electrical network. Different CHP prime mover technologies offer different range of CO_2 saving capabilities ranges from 0.50 to 0.85 tons per annum (t/a) as shown in Table 17.4.

17.4.1 Internal Combustion Engines

ICE works with the input energy in the form of fuel and air (as oxidizer) for the combustion process to proceed in combustion chamber of ICE, giving out the change in temperature and pressure of the working gas (mixture of fuel and air) which act upon the piston of the engine to produce useful work as shown in Fig. 17.4. ICE has electrical output of 1 kW while thermal output is around 2.5 kW. ICE has the total efficiency up to 92 % and the electric efficiency ranges from 20 to 26 % (Bianchi et al. 2013; Sommer 2011). Caresana et al. (2011) investigated a 28 kW_e

Table 17.4 Main characteristics of prime mover technologies

Type of CHP system	Capacity kW	Electrical output (kW_e)	Thermal output (kW_t)	Electrical efficiency (%)	Thermal efficiency (%)	CO_2 saving (ratio)
ICE	1–100	1–13	3–29	20–26	60–70	0.8
MGT	30–250	30	–	33	60	0.5
ORC	100–200	1–10	8–44	6–20	70–80	0.5
TPVG	–	1.5	12.2	<15	75	0.7
SE	50–250	1–9	5–25	13–28	60–80	0.65
FC	5–200	1–4.6	0.521–2	52	30–40	0.85

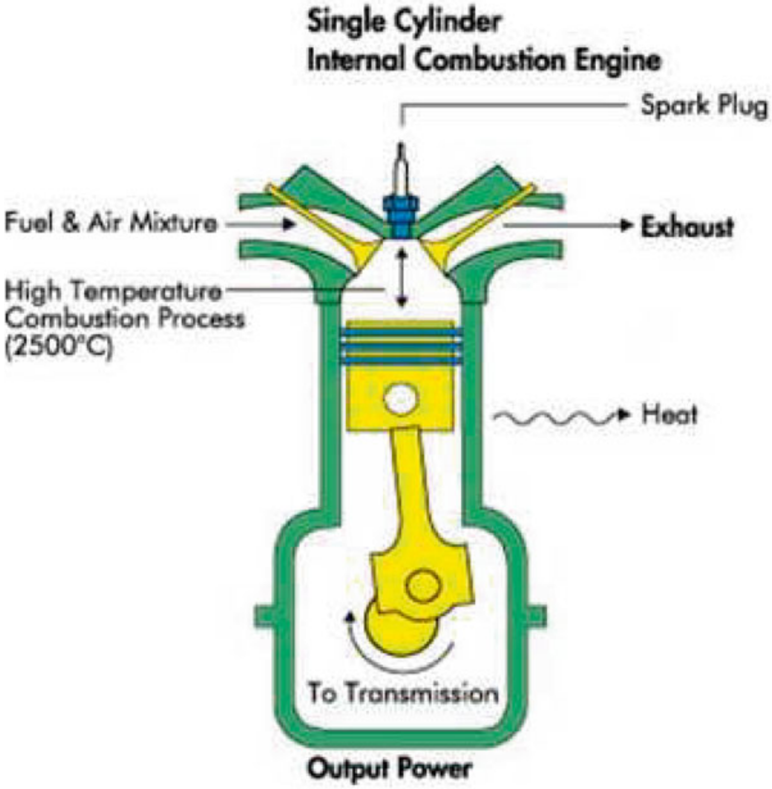


Fig. 17.4 Diagram of internal combustion engine

variable speed ICE based micro CHP system for its energy and economic analysis for the application of ten-flat residential building, an office, and a hotel. It was found that ICE performance is quite satisfactory with high electrical efficiency as compared to conventional power generation systems for both residential and hotel applications. For commercial applications the variable speed ICE based CHP systems pose higher initial investments and longer payback period.

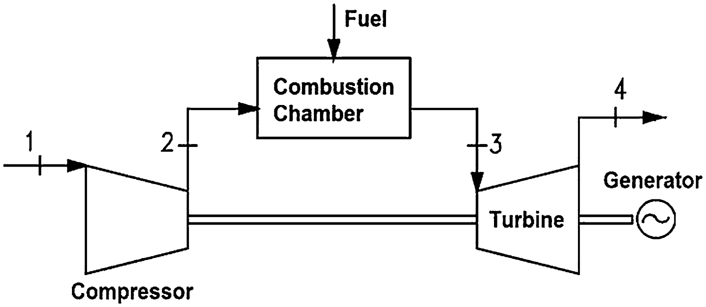


Fig. 17.5 A simple schematic diagram of micro gas turbine (Nascimento et al. 2013)

17.4.2 Micro Gas Turbine

MGTs work on the principle of open cycle gas turbine. Generally, a typical MGT include a compressor, combustion unit, turbine, and a generator giving out electricity as shown in Fig. 17.5. Firstly, air is pumped into the compressor where it is compressed and then passed in combustion chamber. The temperature of the air (working gas) is increased by gaining energy from the fuel burning in combustion chamber and is then directed towards the turbine. Hot working gas expands to run the turbine and transfer its power to the compressor and electric generator. MGTs have high working efficiency as the exhaust heat is recovered and reused to heat the working gas before it enters the combustion chamber. This process increases the system efficiency up to 30 %. MGT range in their energy capacity from 15 to 300 kW but they work well with micro CHP systems having electrical outputs higher than 30 kW (Bang-Møller et al. 2011; Bianchi et al. 2012). MGT can possibly work with electric efficiency of up to 33 %. They are more popular for their high speed, low maintenance, compact size, and low emissions. The major problem with MGTs is that they can perform well only with high demands and are noisier. Efforts have been made by many researchers to improve the electrical efficiency of a few kW MGT (Maghanki et al. 2013).

17.4.3 Organic Rankine Cycle

In ORC an organic working liquid is used to transfer the energy between the contents of the cogeneration system. ORC basically works with two cycles where one is water cycle while the other is Rankine cycle (Fig. 17.6). It mainly consists of a pump, biomass boiler, evaporator, turbine, and condenser. The heat from the combustion of biomass work to heat the water in the water cycle through the heat exchanger of the boiler. While at the same time the pump supplies organic liquid to the evaporator and the hot water act as a source of heat for the Rankine cycle heating

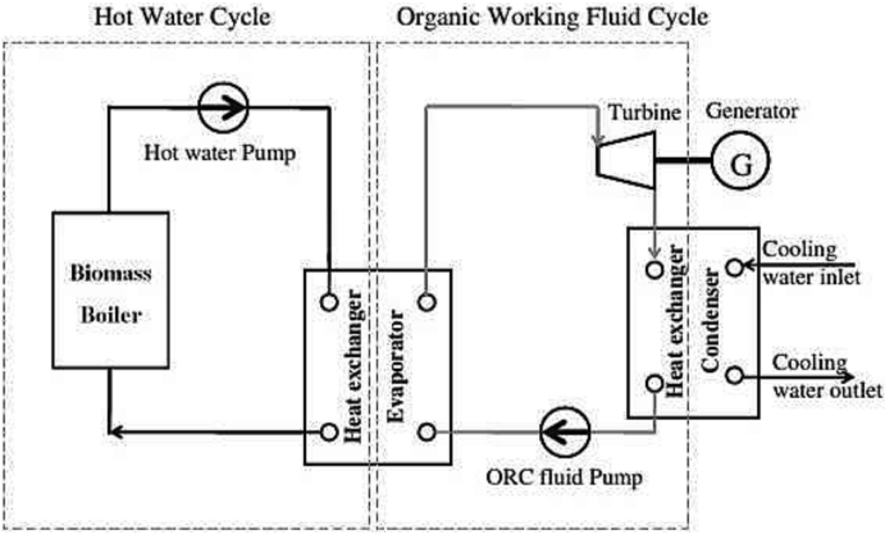


Fig. 17.6 Schematic diagram of biomass fueled ORC based micro CHP (Dong et al. 2009)

the organic working liquid through heat exchanger of the evaporator. Evaporator works to heat up the working liquid and convert it into vapors. After being vaporized it is then moved to turbine to be expanded to a certain condensing pressure to generate electrical current and at last it is condensed again in condenser into a saturated liquid and pumped again to start a new cycle (Dong et al. 2009; Tchanche et al. 2011). The surplus heat produced during expansion is recovered by an internal heat exchanger that can be utilized again to heat the compressing liquid before it enters the evaporator. As a result, the efficiency of the system is improved (Algieri and Morrone 2013; Liu et al. 2011). The best thing about ORC based CHP systems is that they can work even with very low temperature heat sources for power generation (Nguyen et al. 2001). The nature of organic working liquid largely affects the ORC based system performance. Working liquid must has appropriate thermodynamic properties like boiling point, low critical points (temperature, pressure, and volume), latent heat, viscosity and surface tension, high thermal conductivity, non-corrosive, nontoxic, slope of the saturation vapor temperature-entropy (T-s) line, maximum stability temperature compatible with turbine material, and environmentally friendly (Maizza and Maizza 2001; Qiu 2012). The slope of saturation vapor T-s line is an important factor of the working fluid for the better operation and efficiency of the ORC system as it represents all the energy inputs and outputs of the system in terms of temperature changes (Qiu et al. 2011). T-s diagram for an ideal system is shown in Fig. 17.7. The line from point 2 to point 3 represents the heat gain of the working liquid while from point 4 to point 1 depicts the heat rejected from the working liquid and it shows a constant pressure process. Point 3 to point 4 represents the overall work done by the working liquid by running the turbine through adiabatic expansion process. Point 1 to point 2 is an adiabatic compression

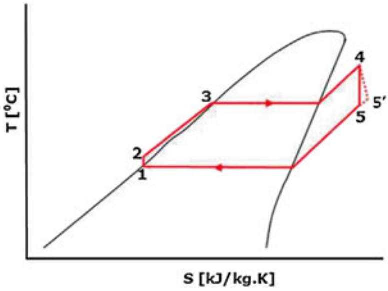


Fig. 17.7 A typical T-s diagram of ORC (Qiu et al. 2012)

process representing the utilization of power by the pump. The total work done by the working liquid is always equal to total energy output minus the total energy consumption of the pump. The thermal efficiency (η_{TH}) of the system can be calculated as:

$$\eta_{\mathrm{TH}} = \frac{W_{\mathrm{output}}}{q_{\mathrm{input}}}$$

where W_{output} is the total work done and q_{input} is the total amount of input energy in the form of heat and is represented as:

$$W_{\mathrm{output}} = W_{3-4} - W_{1-2} = (h_3 - h_4) - (h_1 - h_2)$$

$$q_{\mathrm{input}} = h_3 - h_2$$

W_{3-4} is the work done in adiabatic expansion from point 3 to 4 in T-s diagram while W_{1-2} represents the adiabatic compression from point 1 to 2 in T-s diagram. h_1, h_2, h_3, and h_4 are the specific enthalpies of the working liquids. Electrical efficiency (η_{EL}) of the system can be calculated as:

$$\eta_{\mathrm{EL}} = \frac{W_{\mathrm{EL}}}{Q_{\mathrm{input}}}$$

$$\eta_{\mathrm{Net}} = \eta_{\mathrm{TH}} + \eta_{\mathrm{EL}}$$

W_{EL} is evaluated by the electrical load while η_{Net} is the overall efficiency of the system and is always equal to the sum of η_{TH} and η_{EL} (Liu et al. 2011; Qiu et al. 2012; Taljan et al. 2012). Organic working liquid can be classified into three basic types depending on the slope of its saturation vapor curve in T-s diagram as dry, wet, and isentropic (Fig. 17.8). A dry organic liquid (e.g., n-pentane) has a positive slope while a wet liquid (e.g., water) has a negative slope and an isentropic liquid (e.g., R123) has an infinitely large slope (Liu et al. 2004). ORC also offer several other

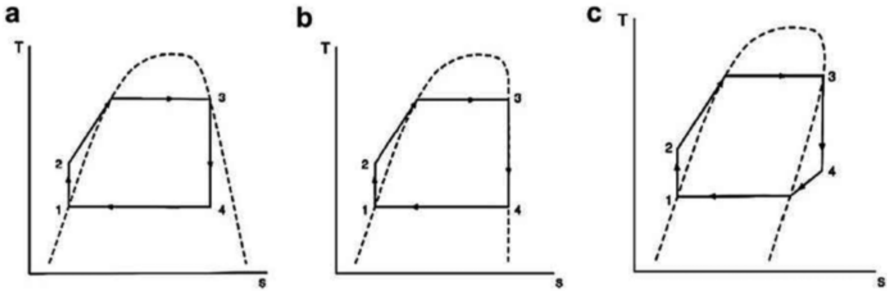


Fig. 17.8 Comparison of three types of organic working liquids, (**a**) wet, (**b**) isentropic, and (**c**) dry (Qui 2012)

advantages including lower maintenance requirements, faster operation, greater flexibility, and safety as compared to conventional systems. The typical CHP efficiency is about 90 % with electrical power output of 1 to 10 kW and thermal output ranging from 8 to 44 kW (Qiu et al. 2011, 2012; Qiu and Hayden 2009). ORC based micro CHP systems have an energy capacity of 200 kW_e to 1.5 MW_e with electrical efficiency of 6–20 % (Liu et al. 2011). Biomass based ORC is the most developed technology in the recent time but still it is not appropriate for the systems with capacity smaller than 100 kW_e because of low electrical efficiency and high operation costs.

17.4.4 Thermophotovoltaic Generators

TPV generators originated in early 1960s but their development started in recent years (Coutts 2001). TPV generators can be easily obtained by modification of appropriately designed combustion boilers but the electrical efficiency is always less than 15 %, while the overall CHP efficiency is still higher than 90 %. A TPV generator consists of heat source or burner, photovoltaic cells, an emitter, and a filter. In TPV generator, photovoltaic cell is kept in front of surface radiant burner in a combustion chamber (Bianchi et al. 2012; Coutts 2001). The heat source emits energy in the form of radiation (E_{RAD}) and passed through an optical filter which absorbs some energy (E_{Abs}) and allows passing specific energy known as E_{GAP} which when passed through photovoltaic cell convert this amount of energy into thermal (E_{TH}) and electrical energy (E_{EL}). The surplus heat that is not converted to electricity is recovered in the form of thermal energy which as a result increases the overall efficiency of the system. Although the main advantages of TPV include silent operation, portability, low maintenance cost as well as versatility in fuel sources and high energy density, they are still not widely accepted throughout the world (Coutts 2001) (Fig. 17.9).

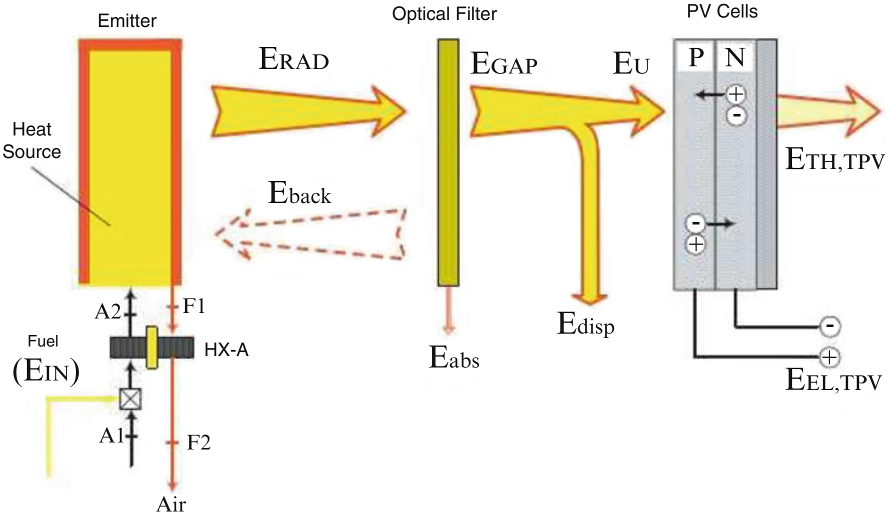


Fig. 17.9 A schematic diagram of TPV generator, an emitter (EM), a filter (F) and a photovoltaic cells (PV) (Coutts 2001)

17.4.5 Stirling Engines

These are high efficiency CHP systems (up to 98 %). SE can work well for old and new house as well, along with two family houses. Stirling engines are advantageous because they can work with any type of energy source (Ulloa et al. 2013). Also they require less maintenance and are much quieter. But they have the disadvantage of high operation cost as well as more heavy and bulky. SE has an electric power size of 1–9 kW and thermal power size of 5–25 kW with electric efficiency that ranges from 13 to 28 % (Caresana et al. 2011). The Stirling engine works on the principle of Stirling cycle. It consists of two pistons, one cold and hot end, power cylinder, and a displacer cap. The displacer piston acts to move the working gas from the hot to the cold area. Resultantly, hot and cold working gas expands and contacts to produce pressure waves. These waves act to move the working piston which as a result produces electricity running the generator, connected linearly with working piston (Sommer 2011) (Fig. 17.10).

17.4.6 Fuel Cells

These are electrochemical systems in which chemical energy is converted into electrical energy without combustion. Fuel cells utilize electrolyte materials for the transfer of electrons and ions towards respective electrodes and then flow within the outer circuit. It uses hydrogen and oxygen at anode and cathode, respectively, to produce water by an electrochemical reaction. The main advantages of fuel cells are

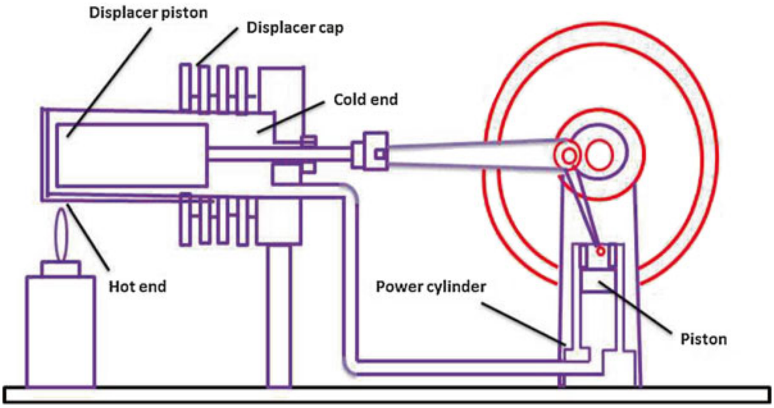
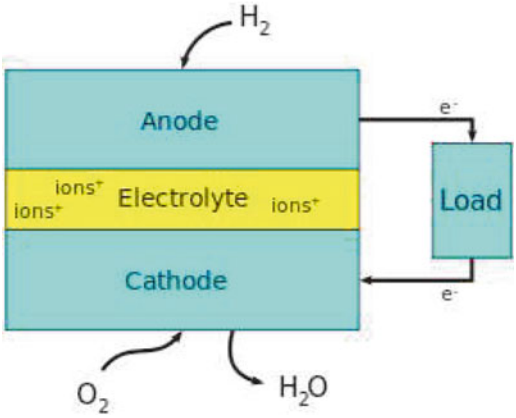


Fig. 17.10 Diagram of Stirling engine

Fig. 17.11 Block diagram of fuel cell



their low level of emissions, ease of use, lower level of noise, and high efficiency as compared to other CHP systems but the only reason for their less popularity in being commercially available is their high operation cost and short life-span. Fuel cells are available in several different types, including alkaline (AFC), phosphoric acid (PAFC), molten carbonate (MCFC), solid oxide (SOFC), and proton exchange membrane fuel cells (PEMFC). Among all these fuel cells only SOFC and PEMFC are the most developed and efficient for power generation. Solid oxide fuel cells (SOFC) work at high temperature around 800–1,000 °C and PEMFC work at 80 °C (PEMFC). It is reported that SOFC based on 2 kW CHP system can generate electric power of 1.005 kW and thermal energy of 0.521 kW with the electric efficiency of 52.1 % and overall efficiency of 79.2 %. It is found that the inlet temperature greatly influence the efficiency of fuel cell based CHP systems (Vincenzo et al. 2013; Xu et al. 2012). Table 17.4 shows a simple comparison of electrical and thermal efficiencies of different CHP technologies. Highest electrical efficiency is exhibited by fuel cells whilst thermal efficiency is maximum for ORC and ICEs (Fig. 17.11).

17.5 Applications of Micro CHP Systems

Biomass fueled micro CHP systems are considered to have possible applications in small community house systems, especially in the areas where heat demand is higher. Micro-cogeneration (less than 15 kW_e) is also reported to work best for domestic as well as low-scale commercial applications due to their ability to change heat-to-power ratio as and when needed (Ahrenfeldt et al. 2013; Arsalis et al. 2011, 2013; Barelli et al. 2012; Shaneb and Taylor 2009). Huang et al. (2013b) reported that biomass fueled ORC based CHP systems can work best for micro-scale building systems if their heat-to-power ratio is in the range of 4.5–6.7. Therefore, conventional heating system and complex electrical networks can be replaced by using isolated CHP units with efficient greenhouse gas savings (Dentice d'Accadia et al. 2003; Vanneste et al. 2011; Veldman et al. 2011). Several countries in Europe have already implemented biomass as a source of power generation due to its numerous benefits as well as higher energy efficiency. Likewise in Austria and Sweden, the utilization of biomass for power generation has increased up to six- and eightfolds, respectively, within the last decade (Bernotat and Sandberg 2004; Thek and Obernberger 2004; Veringa and Alderliesten 2006). While in France and Finland, direct wood combustion for electricity production has reached up to 5 % and 18 % of total electricity production, respectively, and is planned to attain a figure of 23 % by 2025 (Sipilä et al. 1993). It is reported in the literature that the estimated production of electricity using different biomass sources has increased up to a considerable extent until 2010, such as electricity production for energy crops is 27,395 GWh, forestry residues 38,309 GWh, municipal solid waste 12,789 GWh, agriculture residues 40,942 GWh, and others 23,873 GWh (including industrial organic waste and sewage sludge) (Skytte et al. 2006). Huang et al. (2013b) performed a techno-economic analysis of biomass fueled ORC tri-generation system using three different biomasses including willow chips, straw, and rice husk. It is reported that all these biomass sources are technically feasible to utilize as fuel for tri-generation system but only a slight difference in overall efficiency is noted, that is the system fueled with willow chips showed lower efficiency than others due to its higher moisture content. In another study Huang et al. (2013a) compared willow chips and miscanthus as fuels for ORC based CHP systems and found similar results. The heat recovery by willow chips fueled CHP system is less as compared to miscanthus fueled, possibly due to higher moisture content of willow chips. Chiew and Shimada (2013) performed a case study in Malaysia, comparing seven different technologies (methane recovery, CHP plant, ethanol production, briquette production, composting, medium density fiberboard (MDF) production, and pulp and paper production) utilizing Malaysia's largest biomass source, empty fruit bunches (EFB) of oil palm industry. It was reported that electricity generation potential of raw EFB is 968 MJ/t when used as a fuel in CHP system along with electrical efficiency of 22 %. While the electrical generation potential can be increased up to 1,715 MJ/t if the methane gas produced is recovered by methane recovery. Francois et al. (2013) utilized wood chips as biomass source for CHP plant and obtain a net CHP efficiency of 66 % with electrical efficiency of 27 % (Fig. 17.12).

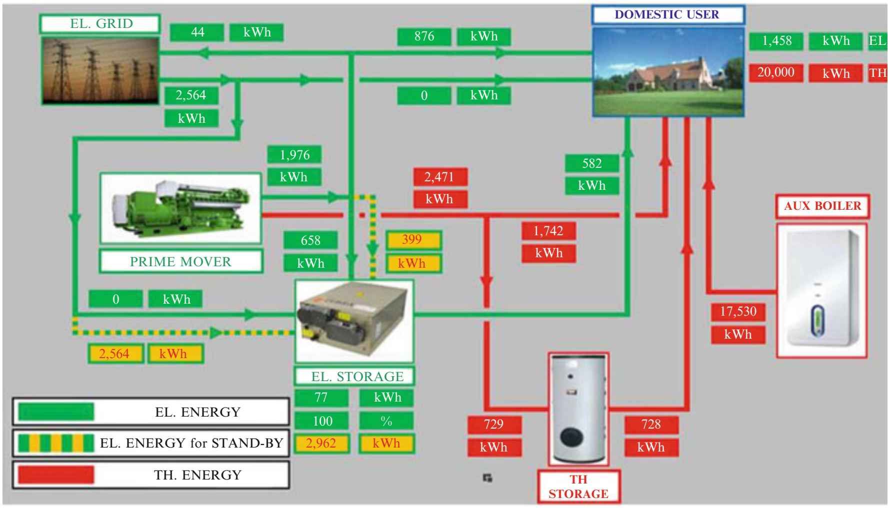


Fig. 17.12 Power flow for micro CHP system (Bianchi et al. 2013)

Residential energy consumption covers almost 15–25 % of the total energy consumption of most of the countries, including heating and cooling systems, lighting and other household appliances (Dong et al. 2009). Micro CHP systems can work best with these energy demands along with appropriate safety, lower emissions and lower the cost by omitting the use of electrical transmission and distribution systems (Hawkes and Leach 2007; Wood and Rowley 2011; Wright 2008). Presently, micro-scale CHP systems are under prompt development and most of the countries are trying to implement these systems as their major energy output systems. The heat produced in cogeneration systems is utilized for heating houses and water whilst the electricity can be fed into grid or directly use for electric appliances. It is reported that the conventional power generation systems convert only 30 % of the total energy of the fuel to electrical energy while the rest is exhausted in atmosphere as waste heat. CHP systems can boost this efficiency from 30 to 90 % by reducing the amount of waste heat. After comparing different CHP systems with different prime mover technologies, the logical step would be to choose the right technology for the right application. ICE is the most suitable technology for small- and micro-scale CHP systems for domestic applications due to its high electric and CHP efficiency, low investment and operation cost as compared to other technologies and more reliability due to mature technological aspect (De Paepe et al. 2006; Onovwiona et al. 2007) but with the disadvantage of producing relatively higher emissions and noise (Maghanki et al. 2013). Ren and Gao (2010) investigated and compared two different types of CHP systems (micro gas engine and fuel cells) for the cost of operation and greenhouse gas emissions for a residential building and found that fuel cells showed better results than gas engines in terms of both economic and environmental aspects and can save energy cost up to 26 % per annum. Recently, a new term, fuel energy saving ratio (FESR) has been introduced by Li and co-workers.

It has been observed that systems producing more electrical power have higher FESR values, therefore having higher energy saving potential (Li et al. 2006). Bellomare and Rokni (2013) studied SOFC and gas turbine (GT) with municipal solid waste as biomass fuel and reported the thermodynamic efficiency of up to 52 %. The gasification plant incorporated with SOFC and GT uses municipal solid waste to produce syngas which in turn is utilized by fuel cell to produce electricity while the exhausted gases from SOFC are combusted again and sent to GT for producing more electricity. This setup is not only beneficial for generating cheaper electricity but also help in reducing the storage of waste in landfills. Iora and Silva (2013) introduced a new CHP solution based on double shaft intercooled externally fired gas turbine cycle (EFGT cycle). It is shown that a 50 kW biomass EFGT system can reach up to 21 % of electric efficiency which is higher than other available technologies of the same size. Prasara et al. (2012) compared the performance of three different technologies (combustion-steam based CHP, gasification based CHP, and pyrolysis based CHP systems) for rice husk fuelled CHP system. It is found that pyrolysis based CHP is considered as the best technology among others as it has the most distinct advantage that the pyrolysis oil produced from rice husk biomass can be easily stored and transported to the sites for power generation. These technologies also pose some other benefits, including it can be utilized in current power generation plants with fewer emissions and lesser operation cost. Ahmadi et al. (2013) proposed a multi-generation system based on ORC, biomass combustor, proton exchange membrane electrolyzer, and an absorption chiller that can produce cooling, heating of air, hot water, hydrogen, and electricity generation at once. It is concluded that multi-generation systems are more economical and environmental friendly as compared to conventional power generation systems and CHPs. Moreover, results depicted that the change in some specific parameters like temperature and pressure of the system can largely influence heating and cooling load as well as hydrogen production rates.

17.5.1 CHP Overview (Economic, Energy, and Environmental Aspect)

Use of micro CHP system not only reduce the cost by replacing the distribution and transmission network and maintenance but also reduce the cost of production by utilizing cheaper biomass for electricity production (Korsgaard et al. 2008a, b; Mathiesen and Lund 2009). In spite of these, micro CHP systems for residential application are still not favorable because of their higher investment costs as compared to conventionally used thermal and electrical systems. Therefore, development of cheaper micro CHP systems with easy-to-use technology is still under process (De Paepe et al. 2006). It has been proposed that although different CHP technologies are mature enough but the installation and operation costs are still required to be further reduced up to 50 % to make them suitable for residential applications. Therefore, the main limitations for the growth of biomass fueled cogeneration are high costs, low conversion efficiency, and availability of biomass feed stock (Sadrul Islam and Ahiduzzaman 2012). Cogeneration systems have several advantages but their industrial applications do not prove to be much beneficial due to unsuitable system scheduling and lack of proper system configuration in controllable strategies are required for industrial implementation. Moreover, if the capacity of the cogeneration system is kept higher to meet the demand of commercial sector, it will jeopardize the economics of the system by increasing the investment costs, making the system unable to be implemented. On the other hand, if the system capacity is kept lower than the optimal level, it will not be able to meet the demands for peak load. Liu et al. (2013) proposed some constraints for the optimal design of a distributed energy system. Firstly, cogeneration equipment should have balanced mass and energy. Secondly, primary energy consumption should meet local energy limitations. Thirdly, energy production must be large enough to meet the demands of end user and fourthly, the equipment size should be capable to overcome peak loads.

Different investigations have been performed to compare the energy requirements for domestic electrical and thermal appliances and the output from micro CHP systems. Generally, energy demands in residential applications of CHP systems are highly inconsistent depending on changing climatic conditions and uncertainties in human activities, which pose a great challenge for the optimal design of successful cogeneration system. In a typical CHP system, different prime mover technologies like ICE, SE, FC, and MGT are employed for electricity production while the thermal demands are fulfilled by the high temperature exhaust gases released from prime movers. Absorption and compression chillers (heat pumps) are used in reversible configuration to produce heat and cooling in winter and summer accordingly from the exhaust gases. These chillers or heat pumps provide more constant energy supply, satisfying the energy demands even on daily temperature variation bases. Even though, the heating and electricity requirements cannot be completely achieved by the cogeneration system, supplementary gas boilers and external power grid can be aided to fulfill the heat and electricity needs of the application area. Li et al. (2008) performed a sensitivity analysis on varying energy demands to determine the influence on working efficiencies of combined cooling heat and power (CCHP) system. It was found that the fluctuation in energy demands has a small impact on economics of the selected CCHP system and the economic evaluation of the system largely depends on average energy demands. A residential energy microgrid could be introduced by connecting several cogeneration systems to meet the demands for peak load that can interchange heat and electricity between the subdivisions of microgrid. Figure 17.13 represents the energy supply chain through microgrid within different subgroups of households, satisfying heating, cooling, and electrical demands of the application area.

Previously, micro CHP systems were using diesel as their fuel which cause more CO_2 emissions. Now, diesel fuel has been replaced by raw biomass which is more environmental friendly. Electricity generation by using biomass as fuel has become well known all around the world as it is capable of producing lesser emissions, up to 14–90 % as compared to fossil fuels. CO_2 released during the combustion of

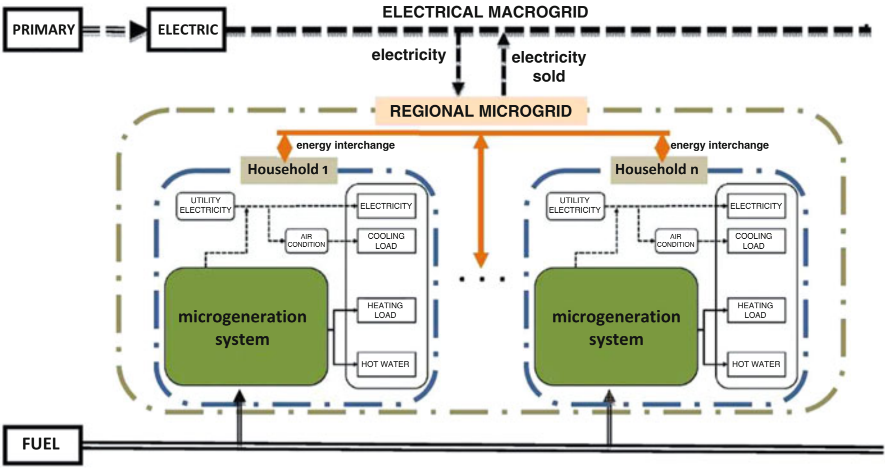


Fig. 17.13 Energy supply chain network for micro CHP system (Kopanos et al. 2013)

Table 17.5 Comparison between conventional generators and biomass fueled generator (Kartha and Larson 2000)

Fuel and technology	Generation efficiency (%)	Grams of CO_2 per KWh
Diesel generator	20	1,320
Coal steam cycle	33	1,000
Natural gas combined cycle	45	410
Biogas digester and diesel generator (with 15 % diesel pilot fuel)	18	220
Biomass steam cycle (biomass energy ratio[a] = 12)	22	100
Biomass gasifier and gas turbine (Biomass energy ratio[a] = 12)	35	60

[a] The energy of the biomass produced divided by the energy of the fossil fuel consumed to produce the biomass

biomass for cogeneration can be reutilized in photosynthesis of newly grown biomass. So, the process continues and biomass can be renewed within a short interval of time (Sadrul Islam and Ahiduzzaman 2012). The reduction in carbon containing emissions from cogeneration plants largely depends upon the efficiency of biomass fueled CHP systems as well as on the type of biomass used and the amount of fossil fuel use to produce biomass for cogeneration purpose. Biomass fueled generation produces far less carbon containing emission as compared to conventional power generation systems (Kartha and Larson 2000; Van Der Linden and Romero 2009). Table 17.5 shows comparison between conventional generators and biomass fueled generators in terms of generation efficiency and grams of CO_2 emissions per kWh. The comparison clearly depicts that biomass fueled gas turbine and steam cycle have generation efficiencies comparable to coal and natural gas systems (up to 35 %) while carbon dioxide emissions are far less (up to 60 g/kWh) than conventional generators (up to 1,320 g/kWh). On the other hand, comparison among different prime mover technologies of CHP systems in terms of carbon dioxide saving reveals that ORC and MGT are proven to be least CO_2 saving whilst solid oxide FC has the highest potential where it can save CO_2 emission up to 0.85 t per annum.

17.5.2 CHP Usage in Different Countries

In a survey held in 2009, it was estimated that world's total renewable power capacity has reached up to 1,230 gigawatts (GW) while the contribution of electricity produced from biomass was only 52 GW in 2009. In 2007, Organization of Economic Cooperation and development (OECD) accounted to produce a total biomass electricity of 42 Terawatt-hours (TWh) out of which the USA generated more than 34 % of electricity from solid biomass. Among other OECD countries, Japan generated 16 TWh of electricity while Germany produced 10 TWh. In late 2009, 80 biomass power plants installed in different states of the USA generated around 8.5 GW power capacity. Recently, the USA started to convert most of its conventional coal and gas-fired power plants to biomass-fired cogeneration plants (Bouchard et al. 2013). Germany and other European countries also started to produce increasing amount of electricity from biomass. Europe's total electricity production from biomass has tripled its production in 2001. In early 2010, Europe installed 800 solid biomass power plants having a capacity to produce 7 GW of electricity. Scandinavia has highest number of solid biomass power plants while Austria and Germany are also not behind in this growing race. It is considered that CHP systems are largely responsible for the development and increase of biomass power capacity (Sadrul Islam and Ahiduzzaman 2012). In 2008, Sweden, Finland, and Germany produced more than half of the total biomass electricity produced in all European countries (Sahlin et al. 2004; Sandberg and Bernotat 2005). Germany being top producer among others boosts its electricity production from biomass up to 20-folds between 2002 and 2008. Finland is producing 20 % of its electricity from biomass generation. Several developing countries, comprising India, Mexico, Tanzania, Brazil, Costa Rica, Thailand, and Uruguay, are also trying to increase their biomass electricity. China increased its biomass power capacity up to 3.2 GW by the year of 2009 and is planning to boost it to 30 GW by 2020. India is generating 1.9 TWh of electricity with solid biomass by the year of 2008. At the end of 2009, India installed 835 MW of biomass fueled power plants from agricultural residues and around 1.5 GW of bagasse cogeneration plants. It was planned to increase the production up to 1.7 GW of capacity by 2012. Brazil had produced more than 14 TWh of electricity from 4.8 GW capacity cogeneration plants using waste biomass of sugar mills (Fig. 17.14).

Different investigations were performed in various countries to compare the power efficiency of different CHP systems with the traditional energy systems. Micro CHP systems have more scope in the areas where heat demand is quite higher.

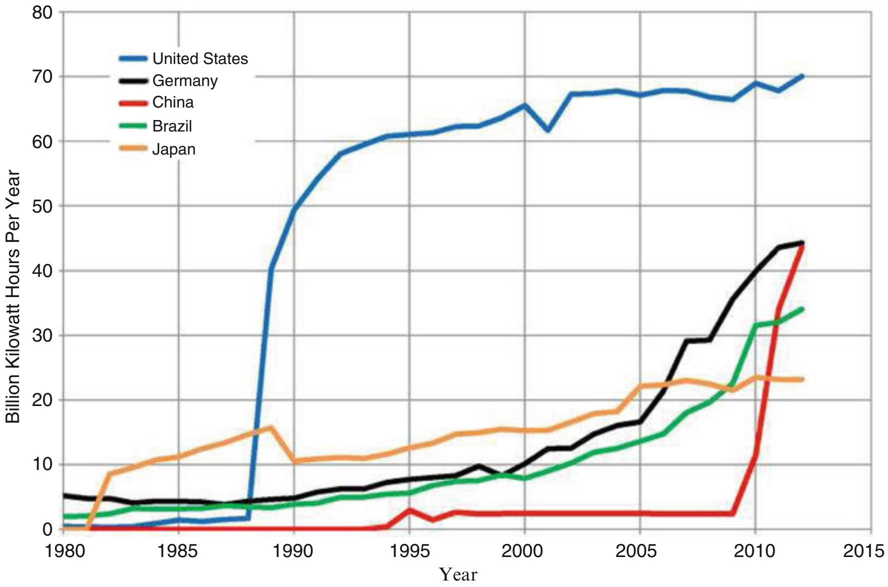


Fig. 17.14 Trends in top five countries for the production of biomass fueled power generation (Sahlin et al. 2004)

Mago et al. (2010) studied the use of ORC based CHP system for small-scale commercial buildings and found that ORC based CHP systems can recuperate the exhaust heat into useful electricity that is usually released to the atmosphere in conventional power generation systems. As a result, increasing the overall system efficiency can be increased leading to the reduction in the cost and greenhouse gas emissions. Moreover, results also revealed that performance of a CHP system largely depends on buildings thermal requirements which in turn are responsible for different weather conditions and climatic variations. Additionally, cost of electricity produced by CHP systems also influenced by the location depending upon the variation of economy in different countries. ORC based micro-cogeneration can allow energy saving up to 25 % and emission reduction of 40 % as compared to conventional systems (Possidente et al. 2006). De Paepe et al. (2006) reported the use of five different kinds of CHP systems (two types of MGTs, two types of Stirling engines, and a fuel cell) from various brands for two different type of houses (terraced and two storey apartment) in Belgium. He found micro gas engines showing best performance as compared to other CHP systems while the economic analysis proved that fuel cells are still too expensive to be utilized for residential small-scale applications in Belgium as the investment is very high as compared to return rate. Algieri and Morrone (2013) investigated the energy analysis of biomass fuelled ORC based CHP system for application in Italian residential sector and found that ORC based CHP's are good alternate to conventional heating boilers fulfilling the need for heat as well electricity requirements of the residential buildings, producing the thermal output of 14.8 kW_t with the electrical power of 2.2–5.0 kW_e. It has been observed that higher efficiency of ORC based CHP systems depend highly upon suitable operating conditions along with appropriate working fluids.

17.6 Conclusion

Biomass is one of the largest renewable sources in the world including forest residues, agriculture residues, municipal solid wastes, and wild plant growth. The utilization of biomass in power sector is beneficial in various aspects including energy economy and environment. The most appreciable benefits of using biomass in power generation are its highly energy efficient and environmentally friendly behavior. CHP generation is the most appropriate mean to exploit biomass energy to produce heat and electricity in an efficient manner. CHP systems are efficient enough to work with primary energy saving of up to 90 % and almost neutral for CO_2 production as the CO_2 produced during CHP process is utilized again during the harvesting of biomass. Various countries are trying to increase their biomass fueled production of electricity day by day which will result in low consumption of fossil fuels and less greenhouse gas emissions. Investigation revealed that considerable work has been carried out for the development of various prime mover technologies for CHP but more research and development is still needed to implement it for residential applications.

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Chapter 18
Application of Biomass-Derived Catalyst

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Contents

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Abstract Due to the high cost and complex synthesis of existing heterogeneous-base catalysts such as supported alkaline catalysts, alkali earth oxides, mixed metal oxides, dolomites, perovskite-type catalysts, zeolites, hydrocalcites etc., carbon-based sulfonated catalyst (CBSC) was widely studied and showed high catalytic activities in many chemical reactions, including hydrolysis, dehydration, esterification, alkylation, condensation, oxathioketalization, dimerization, benzylation, and trimethylsilylation. The enhanced activity of heterogeneous CBSC ascribed to the high stability of its acid sites, high density, carbon sheets hydrophobic property, existence of –OH and –COOH groups in its molecular structure and loose irregular network are some of the structural properties that are usually not present in the homogeneous catalyst. A variety of technique is used to characterize the catalysts structure. As both transesterification and esterification reactions are being simultaneously catalyzed by these catalysts, hence it is considered as a viable alternative for the production of biodiesel from the waste cooking oil or any feedstock having high free fatty acid (FFA) concentrations. Performance of various solid acid catalysts is influenced by method of preparation such as calcinations temperature within 500–800 °C range. The best way to produce biodiesel is provided by solid acid biomass-derived sulfonated catalyst. These solid acid catalysts are found to be recoverable and reusable which are more eco-friendly and greener than a catalyst in a liquid phase. Many research nowadays focused on production of biodiesel involving renewable "green catalyst" prepared either from biomass or from waste generated in the households.

Keywords Sulfonated catalyst • Transesterification • Biodiesel • Cellulose hydrolysis

18.1 Introduction

Among the characteristics of activated catalysts that are bio-based, the number of acidic sites shows the most dramatic effect on the catalytic activity while surface area has much less significant effect on the catalytic activity. The solid phase is the most common for heterogeneous catalysts; hence, the surface area of the catalyst is very critical and important as it determines the catalytic site. Carbon-based sulfonated catalysts (CBSCs) are the heterogeneous acid catalyst. Heterogeneous catalysts work by lowering the activation energy of a reaction. Reactant molecules are normally adsorbed at active sites onto the surface of the catalyst. Weakened structured bond is formed which is then converted to another complex, which is exclusively the product attached to the catalyst. At the end, this complicated molecule then breaks down to release product molecules and leaves the catalyst surface by moving away, get ready to interact with another reactant molecule. Although, these catalysts are more expensive than mineral acids, advantages such as minimized corrosion and environmental effects due to acid waste streams and ease of product separation compensate for their high costs (Gates 2008). The catalytic active sites in the CBSCs are chemically bound; in the case of biodiesel production, both the resultant biodiesel and glycerol by-product will be free of catalyst contaminants (Emrani and Shahbazi 2012).

The high activity of CBSCs due to hydrophobic property of its carbon sheets, stability of acid sites, loose irregular network, high density, and the existence of –OH and –COOH groups that assists hydrophilic reactants accessing toward the $-SO_3H$ groups, which would be in favor of effective catalytic performance. The interaction between the active sites of the catalyst and surface hydrophobicity makes solid acid-catalyzed esterification distinct from the homogeneous catalysis (Trakarnpruk 2012; Wilson et al. 2000). Solid acid catalysts (both Lewis-type such as the mixed and sulfated oxides and Brønsted-type such as sulfonic acid-containing materials) combine the advantages of heterogeneous base catalysts and mineral acids (Lotero et al. 2005).

Carbon catalyst with high surface area showed improved catalytic activity in the reactions of large molecule, e.g., esterification of aliphatic acids with longer carbon chains and benzylation of toluene (Liu et al. 2010a, b; Kitano et al. 2009a, b). The important factor that determines the catalytic performance of amorphous carbon-bearing SO_3H catalysts is the carbonization temperature of the starting material and the specific surface area of the carbonized activated carbon (Sani et al. 2014). However, the catalytic activity for some small molecule reactions (e.g., esterification of acetic acid with ethanol) was found to be independent of the specific surface area, but related to acid density of the carbon catalyst.

18.2 Biodiesel and Cellulose Hydrolysis Reaction

The most important applications of biomass-derived activated sulfonated carbon catalyst involve biodiesel production and cellulose hydrolysis reaction.

18.2.1 Biodiesel Production

Utilization of nonedible biomass as a feedstock is expected to increase to meet the growing demands of catalyst and their applications for biofuel production, maintenance of high stability and high density of strong protonic acid sites is essential, when considerable amounts of free fatty acids (FFAs) are present in the waste cooking oil used as feedstocks, there is a need to consider this solid acid catalyst in this situation.

Biodiesel synthesis reaction using heterogeneous base catalysts including silica, KOH–NaY, K_2CO_3–Al_2O_3, Li–MgO, $CaZrO_3$ requires anhydrous refined oil as feedstock having less than 0.5 % FFA, making the biodiesel highly expensive (Emrani and Shahbazi 2012). The sulfonated activated carbon catalyst consists of sulfonic group and carboxylic group as a high density functional group after the sulfonation of the catalyst and these are referred as CBSC. Owing to their properties such as chemical inertness, high mechanical and thermal stability, these carbon-based solid acids are considered as ideal catalysts for many chemical reactions (Konwar et al. 2013). Both transesterification and esterification reactions can be simultaneously catalyzed by this activated catalyst so it is highly useful for the conversion of feedstock with high FFA concentration to biodiesel. A flexible carbon-based framework supporting dispersed polycylic aromatic hydrocarbons having sulfonic acid groups constitutes the solid acid catalyst. Although it is the sulfonate group that is the active catalyst site, rest of the functional groups results during the preparation step of the catalyst has not a significant advantage. This type of bio-based catalyst structure allows behaving it as enzymes in taking a substrate such as fatty acid in their active site, catalyzing its esterification and then releasing it into the reaction medium. CBSCs are the most promising solid acids and used extensively for the transesterification and esterification of vegetable oils and animal fats (lipid feedstocks) with alcohol usually with methanol and ethanol. Consequently, the sulfonated carbon catalysts could be considered as a viable alternative to H_2SO_4 owing to their low material cost and high catalytic activity. This type of catalysts shows a great tendency to convert raw vegetable oils composed of triglycerides, free higher fatty acids, and water into biodiesel and glycerol very directly through the transesterification reaction by-products with minimal and limited energy consumption. The reported catalyst was successfully recycled in five consecutive experiments and exhibited high thermal stability and could be used as a potential substitute for corrosive, concentrated H_2SO_4 currently employed for acid oil pretreatment (Konwar et al. 2013).

These bio-based small sulfonated aromatic hydrocarbon catalysts however are not stable as catalysts because aromatic molecules leach out of them over time. In order to prevent leaching, catalysts with larger molecular size are prepared starting from macromolecular carbohydrate. Solar energy converted into plant materials or into chemical energy by absorbing CO_2 to produce cellulose, starch, higher fatty acids, triglycerides, lignin, and saccharides. However, plant seeds containing triglycerides and higher fatty acids cannot be directly combusted hence are converted into biodiesel that consume energy through chemical reaction; however in the case of $LCA > 1$, life cycle assessment (LCA) of the "biodiesel", it is nonrenewable energy and also not a carbon neutral material (Hara 2010). According to the American Society for Testing and Materials (ASTM), biodiesel can be defined as a monoalkyl ester of fatty acids obtained from renewable waste feedstocks such as vegetable oils and fats (Demirbas 2009). Broadly biodiesel composed of higher fatty acid derivatives or higher fatty acids in plant materials or animal fat (Hara 2010). Several recent researches have focused on the involvement and the applications of heterogeneous catalysts for biodiesel production, because of their environmental and economic advantages. The simultaneous esterification and transesterification reactions are fully established and are remarkable with the utilization of only one solid acid catalyst. Nonedible vegetable oils regarded can be a promising substitute for traditional edible and nonedible food crops for the production of biodiesel. The utilization of nonedible oil sources as the feedstocks for the biodiesel production and the resulting catalyst obtained from nonedible waste products show great probability to improve the future production of biofuel or biodiesel.

18.2.2 Steps of Biodiesel Production

The transesterification of vegetable oil for the production of biodiesel is carried out as follows (Ali and Tay 2013):

1. Alcohol (methanol) and catalyst mixing
2. Vegetable oil reaction with alcohol/catalyst
3. Biodiesel and glycerol separation
4. Separation of alcohol
5. Washing of methyl ester
6. Purification of biodiesel produced

The schematic representations of biodiesel production with heterogeneous catalysts have been illustrated below in Fig. 18.1. Advantages of these catalysts stem from reduction of environmental pollution because they are made from waste, they are active and stable, and they lower the biodiesel cost by using waste grease containing water and fatty acids (Emrani and Shahbazi 2012).

18.2.3 Transesterification (Alcoholysis) Reaction

Generally nontoxic, renewable, biodegradable sources, such as refined and waste vegetable oils and animal fats, are used for biodiesel production and it is considered as a renewable alternative substitute for petrodiesel fuel. Chemical process known as transesterification reaction employed to obtain biodiesel, virtually involving any triglyceride feedstock, in the presence of a catalyst, to produce fatty acid alkyl esters or biodiesel. The process is termed as methanolysis reaction if methanol is used and further it is ethanolysis if instead of methanol, ethyl alcohol is used in the reaction. Reduction of the viscosity of vegetable oil and for conversion of the triglycerides into ester, transesterification reaction is considered. The transesterification reaction is shown in Fig. 18.2 (Ellis et al. 2007). Transesterification is the best example of reversible reactions and mainly involves the mixing of the reactants to proceed the

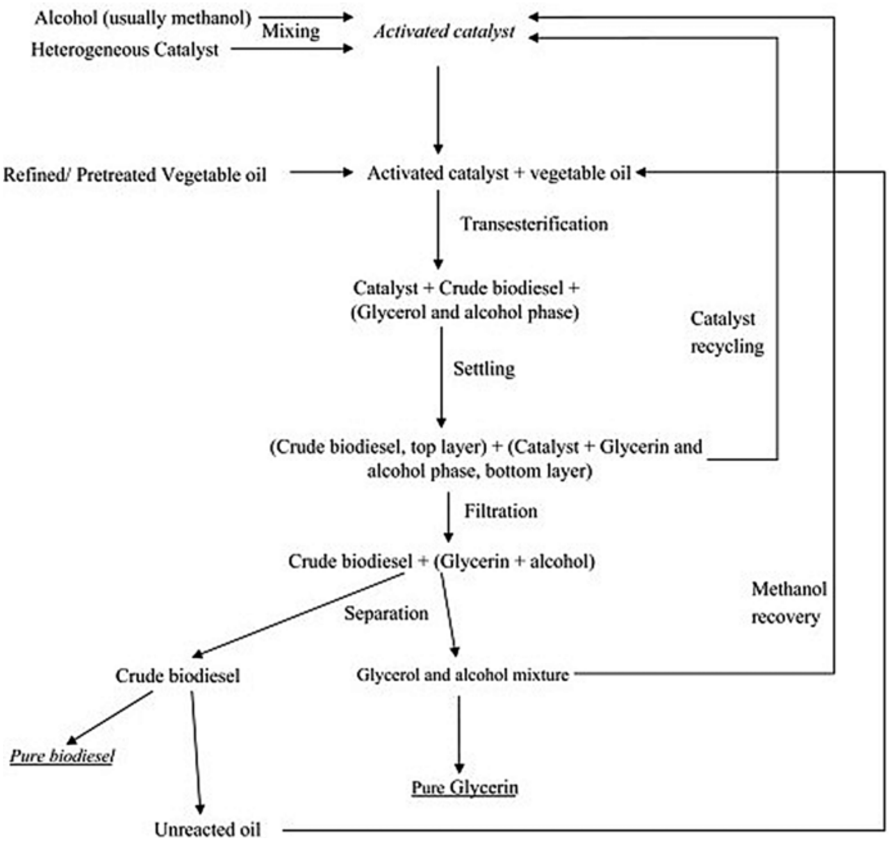
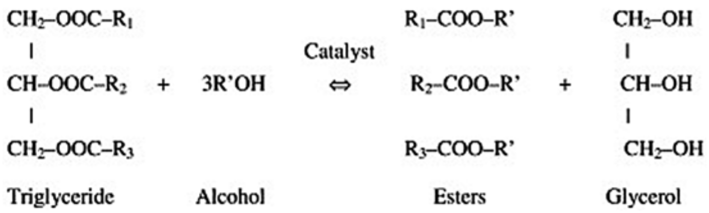


Fig. 18.1 Schematic block diagram of heterogeneous biodiesel production (Konwar et al. 2014, with permission)



$$\begin{array}{ccccccc} CH_2\text{–}OOC\text{–}R_1 & & & & R_1\text{–}COO\text{–}R' & & CH_2\text{–}OH \\ | & & & \text{Catalyst} & & & | \\ CH\text{–}OOC\text{–}R_2 & + & 3R'OH & \Leftrightarrow & R_2\text{–}COO\text{–}R' & + & CH\text{–}OH \\ | & & & & & & | \\ CH_2\text{–}OOC\text{–}R_3 & & & & R_3\text{–}COO\text{–}R' & & CH_2\text{–}OH \\ \text{Triglyceride} & & \text{Alcohol} & & \text{Esters} & & \text{Glycerol} \end{array}$$

Fig. 18.2 Transesterification of triglyceride (Ellis et al. 2007, with permission)

reaction. To shift the equilibrium to the product side an excess of alcohol is required. Obtained ester or biodiesel through transesterification reaction possesses similar physical properties, almost identical to those of commercial diesel fuel (Yaakob et al. 2013). Figures 18.3 and 18.4 show the general equation of transesterification and transesterification of triglycerides (Meher et al. 2006).

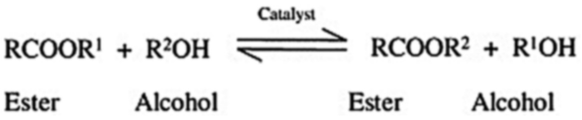


Fig. 18.3 General equation of transesterification (Meher et al. 2006, with permission)

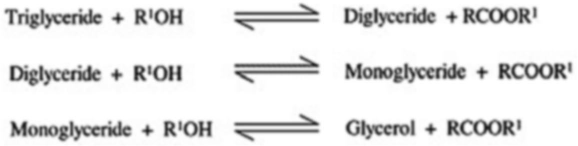


Fig. 18.4 General equation for transesterification of triglycerides (Meher et al. 2006, with permission)

A catalyst generally enhances and fastens the rate of reaction and yield. The glycerine as glycerol is the by-product of transesterification. Biodiesel fuel obtained by triglyceride transesterification contains several individual FAME species (Hoekmana et al. 2012). The ^{1}H nuclear magnetic resonance spectroscopy (NMR), gas chromatography (GC), high-performance liquid chromatography (HPLC), and near-infrared spectroscopy (NIR) are generally used as technical tool and process for monitoring the transesterification reactions. The presence of catalyst at appropriate temperature, 1 mol of fatty acids will react with 1 mol methanol to produce 1 mol methyl esters and 1 mol of water. Alcohol in excess is required to carry the reaction forward since this is reversible order reaction. Both the forward and backward reactions follow second-order kinetics. FAMEs and water produced from the reaction can be separated by using reduced pressure distillation or by the rotary vacuum evaporation techniques.

The sulfonated carbon materials were utilized as catalysts for pretreatment of acid oils (oils containing 8.17–43.73 wt% of FFAs). The catalysts could be used to convert FFA present in acid oils into corresponding methyl esters within 6–8 h at 80 °C, thus reducing the FFA content to desirable levels below 2 wt% (Konwar et al. 2013). The catalysts were filtered, washed, with hot ethanol and diethyl ether, successively, dried at 180 °C for 1 h at the end of each reaction and further can be reused deprived of loss of its catalytic activity or leaching in five consecutive reactions. Variety of catalysts can be used for biodiesel production techniques and are classified as Homogeneous-catalyzed transesterification, Heterogeneous-catalyzed transesterification, Enzyme-catalyzed transesterification, and Noncatalyzed transesterification.

18.2.3.1 Homogeneous-Catalyzed Transesterification

This method involves the use of catalyst in liquid form, mainly acid and alkali catalysts. The basic factor in the acid catalysis is the protonation of the carbonyl group in triglycerides and the alcohol attacking the protonated carbon to create a tetrahedral intermediate. In a homogeneous-base catalyzed reaction, the main factor is to create nucleophilic alkoxide from the alcohol to attack the electrophilic part

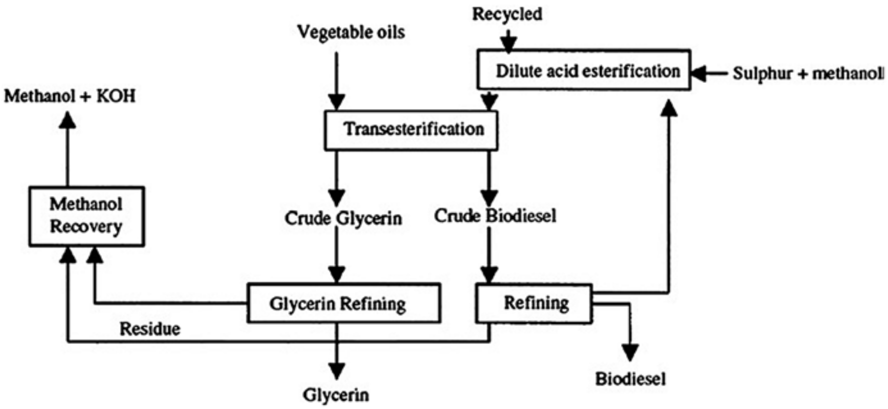


Fig. 18.5 Basic scheme for biodiesel production (Marchetti et al. 2007, with permission)

of the carbonyl group of the triglycerides (Schuchardt et al. 1998). The use of homogeneous catalysts is the first conventional method applied in the biodiesel production industry.

18.2.3.2 Heterogeneous-Catalyzed Transesterification

The application of heterogeneous (solid) catalysts in biodiesel production alleviates the problems associated with homogeneous catalysis. Glycerol as by-product with a purity of greater than 98 % is produced from heterogeneous process compared to about 80 % from the homogeneous process (Helwani et al. 2009). The basic scheme for biodiesel production is depicted in Fig. 18.5 (Marchetti et al. 2007).

18.2.3.3 Enzyme-Catalyzed Transesterification

The efficiency of biocatalyzed process is mainly reliant on enzyme source and its operational conditions. The use of organic solvents, such as *n*-hexane, *n*-heptane, petroleum ether, and cyclohexane, is another certain factor that influences the efficiency of biocatalysis (Soumanou and Bornscheuer 2003). Biocatalysis is mediated by lipases, a group of enzymes (EC 3.1.1.3), produced by microorganisms, animals, and plants (Gog et al. 2012; Antczak et al. 2009).

18.2.3.4 Noncatalyzed Transesterification

A temperature above the critical temperature of alcohol is required to carry out the transesterification reaction in the absence of any catalyst through a supercritical method. Application of extreme temperature and pressure converts the methanol into supercritical fluid state. The reaction temperature is mostly greater than 250 °C since the critical temperature of methanol is 240 °C (D'Ippolito et al. 2007). In order to drive the reaction toward forward in this method, a molar ratio in higher value is required. The probability of producing biodiesel from crude Jatropha oil by utilizing the supercritical method on methanol and ethanol has been investigated (Rathore and Madras 2007) with molar ratio 50:1 alcohol to oil considered best ratio under 20 MPa at 300 °C. The prime importance of this method is that no purification step is required to remove the catalyst enabling to push the production of biodiesel from laboratory to large industrial scale (Kulkarni and Dalai 2006). Hence further studies, investigations, research, and economic evaluations are still to be considered in the production steps for large scale.

18.2.4 Equipment or Reactor for Biodiesel Production

The advanced technology introduces a large number of equipment for the production of biodiesel. Microwave reactor and ultrasound-assisted reactor are the latest equipment although the conventional reflux method and auto clave are the two most common or conventional methods to produce biodiesel. Time by a factor of 15–40 gets reduced for the transesterification when compared with conventional batch reactors (99 % yield for 5 min or less agitation) through ultrasonic reactor. The high chemical activity of an ultrasonic reactor reduces the consumption of excess alcohol and the amount of catalysts required in its processing (Singh et al. 2007).

A reaction system where membranes and chemical reactions are combined are called membrane reactor. This reactor is used for carrying out a reaction and a membrane-based separation simultaneously in a particular physical enclosure or in close proximity. This method has been decidedly advantageous over conventional means as it ends with an FAME-rich phase (Aransiola et al. 2014). The minimization of the wastewater produced during the process at an industrial scale by membrane reactors (MRs) is well established; thus, it is more eco-friendly (membrane flux of 30–40 L/m^2/h, residence time of 15 min). The quality and color of methyl ester and glycerin are also improved and enhanced by MRs (below the levels specified by the ASTM D6751/EN 14214 standards) (Falahati and Tremblay 2012).

Many other continuous reactors, such as oscillatory flow reactors (OFRs), rotating packed bed, supercritical methanol, and gas–liquid reactors, are more effective in biodiesel production (Thanh et al. 2010). The cost of "biodiesel" most probably gets reduced by these improvements in technology enabling it more realistic and strong opponent to commercial biodiesel fuel. Chemical reaction and thermodynamic separation are combined in a single unit in Reactive distillation (RD) reactor; hence, it is a promising multifunctional reactor to improve an ordinary process (Kiss et al. 2008). Moreover, it is a valuable process intensification technique that can be applied successfully to the production of biodiesel as the reactions are controlled by the chemical equilibrium leading to the end product.

One of the important types of continuous reactor is OFRs, consisting of tubes containing equally spaced orifice plate baffles, which can be considered novel reactor. An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficient heat and mass transfer, while maintaining plug flow. The degree of mixing does not depend on the net flow, allowing long residence time to be achieved in a reactor of greatly reduced length-to-diameter ratio in the OFRs (Harvey et al. 2003). Production of biodiesel in the OFR using heterogeneous catalyst is commendable and advantageous as the OFR found to be perfect for suspending particles of solid catalyst or polymer-supported catalyst. The residence time shorter than that of batch processes in OFR can also be achieved (Fabiyi and Skelton 2000).

18.3 Optimization of Parameters for Transesterification Reaction

Transesterification (also called alcoholysis) involves the formation esters and glycerol by the reaction between feedstock (oil or fat) and an alcohol. To increase the reaction rate and yield a catalyst is employed. The process of biodiesel production by the transesterification reaction involves various parameters such as FFA content, stirrer speed, reaction rate, catalyst concentration or catalyst loading, temperature, type of alcohol used, alcohol-to-oil molar ratio, water content, catalyst type, etc. (Gnanaprakasam et al. 2013).

18.3.1 The Effect of Molar Ratio of Alcohol

The yield of ester production is affected by several variables and among them major variable is the molar ratio of alcohol to triglyceride. The transesterification to stoichiometric ratio involves three moles of alcohol and one mole of triglyceride to produce three moles of fatty acid alkyl esters and one mole of glycerol (Tariq et al. 2012).

18.3.2 The Effect of Catalyst

Alkali, acid, or enzyme catalyst is the major classification for catalysts. Acid-catalyzed are much slower than alkali-catalyzed transesterification. If water and FFA contents are present in excess in the glyceride, acid-catalyzed transesterification found to be more favorable (Sprules and Price 1950; Freedman et al. 1984). The catalytic activity of calcium methoxide, barium hydroxide, magnesium oxide, calcium hydroxide, calcium oxide, and for comparison, sodium hydroxide was investigated during the transesterification of rapeseed oil, although sodium hydroxide exhibited the highest catalytic activity in this process. The production of fatty acid methyl esters from the rapeseed oil through transesterification, several attempts have been made to use basic alkaline-earth metal compounds. The catalyzed reaction involving alkaline-earth metal, alkoxides, and oxides and hydroxides proceeds slowly (Tariq et al. 2012). Triglycerides transesterification either in nonaqueous or aqueous systems can be catalyzed by enzymatic catalysts such as lipases very effectively. However, other alkali or acid has the production cost relatively less than that of the lipase catalyst (Smith 1949).

18.3.3 Water Content

The water content in the waste cooking oil plays an important role in accelerating the hydrolysis reaction and simultaneous reduction in the yield of ester formation (Arun et al. 2011). In the acid-catalyzed reaction, water content is more critical than base-catalyzed reaction (Lotero et al. 2005). Certain amount of water even lesser than monolayer amount of water molecules around the enzyme molecules is the requirement for some enzymes to be active (Shah et al. 2003). If raw material contains more water beyond this limit, it will automatically affect the extent of conversion by deactivating the lipase (Kumari et al. 2009).

18.3.4 Free Fatty Acid

The fatty acid content or composition is a vital factor greatly affecting the performance of biodiesel in an engine and also affects the rate of transesterification and esterification reactions. If content of FFA exceeds 3 % in the feedstock (waste cooking oil), then even with homogenous base catalyst, transesterification reaction will not proceed (Ahmad et al. 2010). Using of heterogeneous catalyst and pretreatment through acid homogenous catalyst might solve this problem (Feng et al. 2011; Zhang et al. 2010; Jiang 2010; Liu et al. 2010a, b; Sherbiny et al. 2010; Knothe and Steidley 2009) or heterogeneous catalyst (Rice et al. 1998; Corro et al. 2010) by esterification to form FFA ester. Solid acid (heterogeneous) catalysts, thus, show a unique advantage in esterification and transesterification reactions for synthesis of biodiesel with the use of high acid value oil as feedstock.

18.3.5 The Effect of Reaction Time and Temperature

The conversion rate increases with the reaction time. The effect of reaction time on transesterification of beef tallow with methanol is being studied. Due to the mixing and dispersion of methanol into beef tallow, the reaction was very slow during the first minute. From 1 to 5 min, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1 to 38 % (Ma et al. 1998). Conversion increases over a temperature range of 30–55 °C for enzymatic reaction.

The temperatures 45 and 60 °C show no difference in conversion as observed by Freedman et al. (1986). The rate of the transesterification reaction and yield of esters produced are influenced by reaction temperature (Ahmad et al. 2011). The acceleration of the saponification reaction of triglyceride decreases the amount of biodiesel/ester produced the reaction temperature goes beyond the optimal temperature (Leung and Guo 2006; Eevera et al. 2009). To avoid vaporization of alcohol, the temperature should not exceed the boiling point of alcohol (Li et al. 2009). Viscosity of biodiesel will increase if the reaction temperature is maintained below 50 °C (Kapilakarn and Peugtong 2007). More considerably to get maximum yield of biodiesel, the microwave heating are used to shorten the reaction time (Chen et al. 2012). The temperature higher than 323 K had a negative impact on the product yield for neat oil, but had a positive effect for waste oil with higher viscosities (Leung and Guo 2006). Optimal temperature ranges from 50 to 60 °C, primarily depending on the type of oil used (Ahmad et al. 2011; Freedman et al. 1984; Leung and Guo 2006). The minimum vaporization reaction is ensured when the temperature is less than the boiling point of alcohol (Tariq et al. 2012). About 99 % of yield can be obtained, depending on the accessibility of reactants in the reaction mixture only when the reaction was carried out for a longer time. To lower the production cost reaction time should be optimized. Chances for the backward reaction increase when parameters of the reaction are not properly managed, which subsequently decrease the product formation (Hossain et al. 2010a, b; Refaat 2010).

18.3.6 Stirrer Speed

To ensure the completion of transesterification reaction and to increase the yield of ester formation, the mixing of reactants plays important role (Canakci and Gerpen 2003). The reaction time lengthened when decrease in stirrer speed was accounted (Jiang et al. 2010) and this subsequently decreases the conversion (Adeyemi et al. 2011). The 200 rpm is the optimum speed using enzymatic reaction for production of biodiesel (Kumari et al. 2009). In the transesterification reaction mode of stirring too plays a vital role. Moreover, when magnetic stirrer (1,000 rpm) was replaced with mechanical stirrer (1,100 rpm), yield of biodiesel increased from 85 to 89.5 % (Sharma and Singh 2008).

18.3.7 Catalyst Loading

Nature of oil and the catalyst employed in the transesterification process determined the catalyst content. Optimum load of alkali catalysts, such as NaOH, for WCO transesterification is approximately 1.0 wt% (Phan and Phan 2008; Meng et al. 2008) whereas for acid catalysts, the load approximately 4 %. Research study stated that with increasing enzyme content the enzymic activity increases. It has been obvious from study that most feasible loading for obtaining the highest possible biodiesel yield is 25 % enzyme load (Wang et al. 2006; Chen et al. 2009).

Table 18.1 Comparison of the properties of fatty acid methyl ester and fatty acid ethyl ester

Fuel property	Units	Ref	FAME	FAEE
Density at 15 °C	kg/m^3	834	887	878
Kinematic viscosity at 40 °C	cSt	2.72	5.16	4.92
Gross heating value	MJ/kg	45.54	39.26	39.48
Lower heating value	MJ/kg	42.49	36.59	36.81
Acid number	mg KOH/g	0.1	0.55	0.27
% C	wt.	86.13	76.95	77.38
% H	wt.	13.87	12.14	12.19
% O	wt.	0	10.91	10.43
Sulfur content	ppm/wt.	34	0	0
Water content	ppm/wt.	57	466	420
Molecular weight		211.7	293.2	306.7
Iodine number		–	97.46	105.6

FAME fatty acid methyl ester, *FAEE* fatty acid ethyl ester, *REF* reference fuel
Source: Lapuerta et al. (2008b)

18.3.8 Types of Alcohol

Important reactants in transesterification reactions are the alcohol. In this reaction, most generally primary and secondary monohydric aliphatic alcohols (with 1–8 carbon atoms) are used. However, methyl alcohol (methanol) and ethyl alcohol (ethanol) (Banerjee and Chakraborty 2009) are most commonly used in the transesterification of biodiesel. In most cases, recovery from the final product is much easier in the case of methyl alcohol; hence, it is commonly used for the production of biodiesel (Mathiyazhagan et al. 2011). Methanol yields more biodiesel from waste cooking oil than other alcohols (ethanol and butanol) (Hossain et al. 2010a, b) and viscosity of biodiesel obtained using other alcohols (ethanol and butanol) is greater than that of biofuel obtained from methanol (Hossain et al. 2010a). Table 18.1 compares the properties of fatty acid methyl ester and fatty acid ethyl ester (Lapuerta et al. 2008b). Distillation process gets more difficult for the separation of water from alcohol, when ethanol or isopropanol is used, since it forms azeotrope with water (Gerpen 2005). Obtained biodiesel using methanol (fatty acid ethyl ester, FAME) has higher pour and cloud points than that produced using ethanol (fatty acid methyl ester, FAEE), which decreases the storage ability of biodiesel (Lam and Lee 2011).

18.3.9 Effect of Using Organic Cosolvents

Many cosolvents, such as tetrahydrofuran, 1, 4-dioxane, and diethyl ether, were tested to carry out the reaction in single phase. As THF boiling point 67 °C is only 2° higher than that of methanol, hence it is most commonly used. The unreacted methanol and THF can be codistilled and recycled at the end of each reaction (Boocock et al. 1996).

18.3.10 Effect of Specific Gravity

Higher value of the specific gravity of the end product shows the incompletion of reaction and presence of heavy glycerine. The influence of temperature, catalyst quantity, and molar ratio on the specific gravity of the biodiesel was studied by many researchers (Miao and Wu 2006).

18.3.11 Catalyst Concentration

High temperature conditions are required for the conversion of waste cooking oil into biofuel, when catalysts are not present (Tan et al. 2011). Increasing the catalyst concentration, the yield of the product will also increase because of the enhancement in rate of reaction. It has been found that conversion decreases, with excess catalyst concentration, as the viscosity of the reaction mixture gets increased (Kiakalaieh et al. 2013). About 1.5 % concentrations of catalyst CuVOP can be used for the production of biodiesel from soya bean oil (Chen et al. 2011). Type and nature of raw material and catalyst greatly influenced the optimum catalyst concentration (Highina et al. 2011).

18.4 Analysis of Biodiesel Fuel Properties

Many of the fuel properties, such as density, acid value, kinematic viscosity, and calorific value, were quite similar irrespective of fatty acid compositions of various oils (Chattopadhyay and Sen 2013). Quality of biodiesel can be defined by some standard general parameters as shown in Table 18.2 (Meher et al. 2006). Biodiesel's flash point and its heating value can be analyzed by using an oxygen bomb calorimeter measured with a Pensky–Marten closed-cup flash point tester. To measure the kinematic viscosity of the fuel, a capillary viscometer is employed. Conradson carbon residue analyzer determine carbon residue in unit of wt%. A Distillation temperature analyzer (HAD-620 model, Petroleum Analyzer Inc., USA) usually used to determine the distillation temperature of the biodiesel sample (Benjumea et al. 2008).

Table 18.3 shows the fuel properties of ASTM No. 2D diesel (Lin and Fan 2011). Research shows that the oil containing lesser saturated fatty acids showed more cold filter properties (pour point and cloud point), whereas unsaturated fatty acid-rich oils have less oxidation stability (Leung et al. 2010). Oil containing higher amount of unsaturated fatty acids was found to be better feedstock in terms of the fuel properties of biodiesel produced from it. Low viscosity, high cetane value, low acid value, specific gravity, and high flash point are the important parameters used to determine the quality of biodiesel (Chattopadhyay and Sen 2013).

Table 18.2 General parameters of the quality of biodiesel (Meher et al. 2006, with permission)

Parameters	Austria (ON)	Czech republic (CSN)	France (journal official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Density at 15 °C g/cm^3	0.85–0.89	0.87–0.89	0.87–0.89	0.875–0.89	0.86–0.90	–
Viscosity at 40 mm^2/s	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	1.9–6.0
Flash point (°C)	100	110	100	110	100	130
CFPP (°C)	0/−5	−5	–	0–10/−20	–	–
Pour point (°C)	–	–	−10	–	0/−5	–
Cetane number	≥49	≥48	≥49	≥49	–	≥47
Neutralization number (mg KOH/g)	≤0.8	≤0.5	≤0.5	≤0.5	≤0.5	≤0.8
Conradson carbon residue (%)	0.05	0.05	–	0.05	–	0.05

Table 18.3 Fuel properties of ASTM No. 2D diesel

Fuel properties	ASTM No. 2D diesel
Heat of combustion (MJ/kg)	46.2
Flash point (°C)	72
Kinematic viscosity (mm^2/s)	3.61
Water content (wt.%)	0.006
Carbon residue (wt.%)	0.055
Peroxide value (meq/kg)	
Acid value (mg KOH/g)	

Source: Lin and Fan (2011)

18.4.1 Density

Density is the relationship between the mass and volume of a liquid or a solid and can be expressed in units of grams per liter (g/L). ASTM Standard D1298 and EN ISO 3675/12185 test methods are used to measure the density of the biodiesel (Atabani 2013).

18.4.2 Heat of Combustion

Higher heat of combustion value of a fuel possesses lower mass fuel consumption rate for the same engine output. Diesel fuel’s refining process relative to the biodiesels required higher operating temperature and pressure may also cause smaller water and impurity content leading to higher heat of combustion value of the fuel.

18.4.3 Flash Point

The temperature at which fuel will ignite when exposed to a flame or spark is termed as flash point of oil; also, it can be regarded as the lower or minimum temperature at which a fuel produces sufficient vapor to ignite momentarily and give the first flash, thus determines the fuel flammability. Safer transportation and storage of the fuel are associated with the higher flash point. Flash point is measured according to ASTM D93 and EN ISO 3679 (Sanford et al. 2011; Masjuki 2010; Fernando et al. 2007). Liquid fuel with a lower flash point is more likely to result in autoignition at a high surrounding temperature while transportation or storage (Lin and Fan 2011).

18.4.4 Sulfur Content

Emissions of sulfur oxides occur during combustion of the fuel, causes if the fuel contained the sulfur. It is important parameter and need to specify for engine operability (Singh and Singh 2010; Balat and Balat 2010; Atadashi et al. 2010; Masjuki 2010; Schinas et al. 2009).

18.4.5 Kinematic Viscosity

The tendency to resist the fluid flow is the viscosity of that fluid. The extent of both atomization and fuel fluidity are affected by Kinematic viscosity generally, when the liquid fuel utilization is at a low temperature. When the kinematic viscosity value is higher it creates pumping difficulty along with improper fuel injection (Lin and Fan 2011). Larger saturated fatty acid content in the FAME possesses greater kinematic viscosity (Knothe 2005).

18.4.6 Water and Sediment Content

Suspended water or dissolved water droplets are the two forms for the existence of water and the sediments, corrosion and damage of vital fuel system components, injector pumps, fuel tubes, fuel pumps, etc. results due to presence of water content in biodiesel which apparently decreases the heat of combustion. The standards ASTM D 2709 and EN ISO 12937, respectively, are the standards of water content and sediment for biodiesel (Atabani et al. 2013).

18.4.7 Cetane Number

Ignition properties or a characteristic represents the cetane number. The ease of ignition and the smoothness of combustion results are measured by the cetane number. Cetane number greatly affect the ignition properties, higher its value, better it is in its ignition properties. Cetane number of biodiesel is greater than conventional diesel fuel, which leads to its increase in combustion efficiency (Meher et al. 2006).

18.4.8 Carbon Residue

Presence of various additives, impurities, and ash in liquid fuel following a burning process produces carbon residue. Higher amount of carbon residue in the hydrocarbon fuel is observed due to the presence of larger proportion of aromatic compounds in the hydrocarbon fuel (Arisoy 2008). Although the burning of the biodiesel left less carbon residues than the commercial biodiesel, the amount of carbon residue specified in the ASTM D6751-09 biodiesel standard is less than 0.05 wt%.

18.4.9 Distillation Temperature

The significant indicators for combustion characteristics are the distillation temperature and boiling point of liquid fuel is directly related to it (Lin and Fan 2011).

18.4.10 Neutralization Number

To determine proper ageing properties of the fuel, neutralization numbers are considered; it is also regarded as a good manufacturing process. Neutralization number reflects the presence of FFAs or acids used in manufacture of biodiesel and also biodiesel degradation due to thermal effects (Meher et al. 2006).

18.4.11 Phosphorus, Calcium, and Magnesium Content

These are minor components that are associated with the phospholipids and gums that usually act as emulsifiers or cause sediment, lowering yields during the transesterification process (Vera et al. 2011). ASTM D4951 and EN 14107 are used for the phosphorous determination, whereas magnesium and calcium are determined using EN Standard 14538 (Sanford et al. 2011; Masjuki 2010).

18.4.12 Acid Value

Existence of FA or FFA in the fuel indicates the acid value AV of fuel (Chattopadhyay and Sen 2013). If acid value of biodiesel is higher, then it is evident that it has more FFAs and less oxidative and thermal stability, causing faster formation of oxidation products such as hydroperoxides and conjugated dienes and which further causes the quicker degradation of properties of fuel and its burning properties (Lin and Fan 2011). The presence of higher amount of FFA led to corrosion in engine which consequently reduced and affects engine efficiency (Chattopadhyay and Sen 2013). Temperature, storage time, and water content results in increase in the acid value of a biodiesel (Lin and Fan 2011).

Following equation can be used to calculate the acid value:

$$\mathrm{AV} = \left(56.1 \times N \times V\right) / m$$

where N is the ethanolic KOH normality (0.1 N), V is the volume used to titrate, and the sample mass is m (2 g).

18.4.13 Peroxide Value

Determination of peroxide value indicates the extent of lipid oxidation. When the peroxide value is higher, it indicates oxidative stability has a lower degree causing the faster deterioration of lipid properties under the same storage or operating conditions (Lin and Fan 2011).

18.4.14 Weight Composition of Fatty Acid Content

The linoleic acid (C18:2) and oleic acid (C18:1) constitutes the fatty acids of the commercial biodiesel. The exhibition of inferior oxidative and thermal stability of the biodiesel having larger weight fraction of poly-unsaturated fatty acids with more than three double bonds are observed. The various oxidative products such as conjugated dienes, water, and hydroperoxides of the biodiesel compounds, are susceptible to get contaminated in both the combustion chamber and fuel feeding system causing a prior blockage of the injection pump and also engine breakdown (Arisoy 2008).

18.4.15 Cold Filter Plugging Point

Cold filter plugging point (CFPP) of a fuel represents its performance in cold weather. Fuel gets thicken and lowers the flow property thus greatly affects the performance of fuel pumps, fuel lines, and injectors when the operating temperature of

Table 18.4 Comparison of fuel properties between diesel and biodiesel (Lapuerta et al. 2008a, with permission)

Fuel property	Biodiesel	Diesel
Lower heating value (MJ/kg)	36.5–38	42.5–44
Kinematic viscosity (cSt) at 40 °C	3.5–5.5	2–3.5
Acid number (mg KOH/g)	0–0.60	
Density (kg/m^3) at 15 °C	870–895	810–860
Water content (mg/kg)	0–500	
Ester content (%w/w)	>96	
Glycerin content (%w/w)	0–0.25	
Cold filter plugging point (°C)	−5 to 10	−25 to 0
Sulfur content (mg/kg)		15–500
Cloud point (°C)	−5 to 10	−20 to 0
Pour point (°C)	−15 to −10	−35 to 0
Cetane number	45–65	40–55

fuel is low. CFPP also defines the fuels limit of filterability (Meher et al. 2006). In some of the cases, CFPP of a fuel is higher than its cloud point; usually it is lower than its cloud point. The ASTM D6371 is employed for CFFP determination (Sanford et al. 2011).

18.4.16 Calorific Value

Another important parameter is the calorific value (CV) or heat of combustion. Calorific value is the number of heat evolved by the complete combustion per unit weight of fuel. To calculate calorific value bomb calorimeter was usually used (Chattopadhyay and Sen 2013).

18.4.17 Iodine Number

Iodine number is the index of the number of double bonds. It determines the extent of unsaturation of the biodiesel. The cetane number, cold flow, and biodiesel viscosity characteristics are also correlated directly to iodine value and CFPP (Atabani et al. 2013). Several properties of biodiesel do not resemble any significant change during storage, while others, such as viscosity and peroxide value, change more dramatically. To demonstrate the nature of the starting product and the related changes, rancimat induction period is used (Meher et al. 2006). Table 18.4 shows the comparison of fuel properties between diesel and biodiesel (Lapuerta et al. 2008a).

18.5 Cellulose Hydrolysis Catalysis Reaction

Breaking cellulose to produce glucose in an environmentally friendly fashion and at low cost is a major challenge nowadays. Once broken to glucose, glucose can be fermented to produce various liquid and gas fuels and just about all the commercially available organic chemicals. Bio-based catalysts, which can be made by the sulfonation of cellulosic agricultural waste, can efficiently catalyze hydrolysis reactions in both economical and environmentally friendly way. CBSC bearing –SO_3H, –COOH, and –OH function was perfect catalyst for the hydrolysis reaction of the pure crystalline cellulose. A lot of work have been published on catalytic conversion of cellulose with various CBSCs (Suganuma et al. 2008, 2012; Nakajima and Hara 2012; Dora et al. 2012; Onda et al. 2009; Zhang et al. 2013; Onda 2012; Yamaguchi et al. 2009). The activation energy for cellulose hydrolysis process (110 kJ/mol) is less than the activation energy for reaction involving H_2SO_4 (170 kJ/mol) as the catalyst. H_2SO_4 as catalyst can break down the cellulose, but the challenge is the separation of the products from the aqueous mixture. A solid sulfonated catalyst can easily be separated by filtration.

Artificial neural network (ANN) and a response surface methodology (RSM) analyses revealed that the catalytic hydrolysis of cellulose and cellulose saccharification using amorphous carbon-bearing SO_3H, OH, and COOH groups proceeds using conc. H_2SO_4; the reaction depends largely on the amount of water (Yamaguchi et al. 2009). Amorphous solid carbon catalyst bearing SO_3H, COOH, and OH groups gave 10 % glucose yield at 373 K after 3 h (Kitano et al. 2009a, b; Yamaguchi et al. 2009). Bio-based catalysts in combination with silica or other supports have been able to break down cellulose. The hydrolysis efficiency of cellulose increases with increasing reaction temperature first; however, too much high temperature (>363 K) would result in degradation of the cellulose surface, which prevents efficient hydrolysis of cellulose (Yamaguchi et al. 2009). It has also been found out that hydrolysis of cellulose into water-soluble β-1,4 glucan by carbon material bearing SO_3H, COOH, and phenolic OH groups, and its further hydrolysis into glucose by the carbon material are highly remarkable (Suganuma et al. 2008). A wide range of solid catalysts is investigated for the hydrolysis of cellulose into saccharides shows a great potential and widespread application in the environmentally benign saccharification of cellulose (Suganuma et al. 2008).

Secondary groups on the structure allows the bio-based catalysts to behave as enzymes in taking a substrate such as fatty acid in their active site catalyze its esterification and then release it into the reaction medium. Hydrolysis of cellulose or the formation of bio-based catalyst with sulfonic, carboxyl, and hydroxyl groups on polyaromatic graphene rings is shown in Fig. 18.6 (Suganuma et al. 2008). Selectively hydrolysis of cellulose with β-1, 4-glycosidic bonds into glucose in the catalytic hydrothermal reactions at temperatures around 423 K by a group of a sulfonated activated carbon catalyst is well established. The excellent catalytic properties of the prehydrothermal-treated sulfonated activated carbon catalyst attributes toward the high hydrothermal stability and the strong acid sites of sulfo functional groups, resulted in glucose

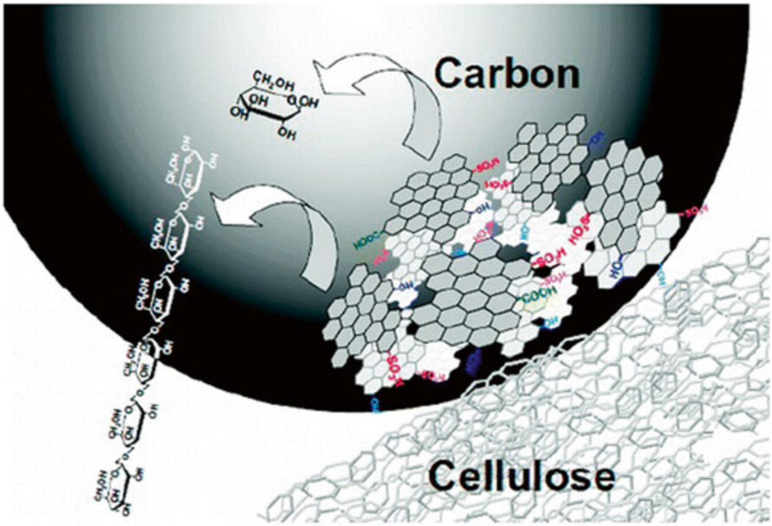


Fig. 18.6 Hydrolysis of cellulose or the formation of bio-based catalyst with sulfonic, carboxyl, and hydroxyl groups on polyaromatic graphene rings (Suganuma et al. 2008)

yields of about 40 C-% and the product selectivity of about 90 C-% (Onda et al. 2009). The Carbonaceous solid (CBS) catalysts with SO_3H, COOH, and phenolic OH groups also prepared by incomplete hydrothermal carbonization of cellulose followed by either sulfonation with H_2SO_4 to give carbonaceous sulfonated solid material or by both chemical activation with KOH and sulfonation to give activated carbonaceous sulfonated solid material. The prepared carbonaceous sulfonated solid material possess high catalytic activity for a hydrolysis from hemicellulose to xylose and glucose. The hydrolysis reaction rate and conversion increase with temperature (85 % in 2 h at 120 °C vs. 65 % and <5 % for 111 °C and 93 °C, respectively) and can be analyzed by kinetic analysis. Declination in the catalytic activity after one recycling ~14 is observed. Loss in activity was attributed to acid site leaching (Ormsby et al. 2012).

18.6 Dehydration from Xylose to Furfural

X-ray photoelectron spectroscopy, ^{13}C solid state nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, energy dispersive X-ray spectroscopy, thermo gravimetric analysis, and surface area analysis suggested that the sulfonic acid groups were the key active sites for high temperature production of furfural in water (Lam et al. 2012). The poisoning of acidic sites by water is responsible for these catalysts to lose their activity in water (Okuhara 2002). Figure 18.7 shows the pathway for the conversion of hemicellulosic materials to xylose and then furfural (Corma et al. 2007). Most widely used soluble acid,

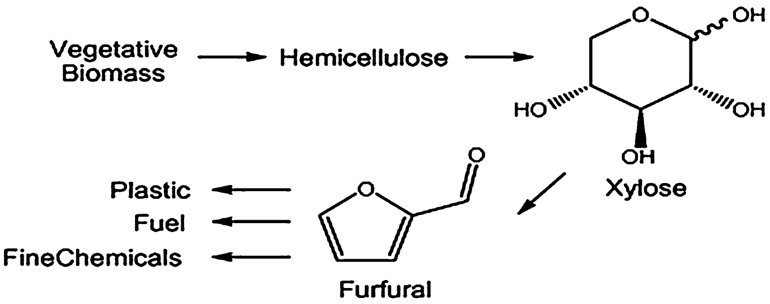


Fig. 18.7 Conversion of hemicellulosic materials to xylose and then furfural (Corma et al. 2007)

such as sulfuric acid and formic acid at 200 °C, are used to produce furfural with yields of ~60 % when the reactions are carried out in water (Oefner et al. 1992; Lamminpää and Tanskanen 2009). However, intermediate-stabilizing anions lead to increase the yield up to 80 % on addition (Marcotullio and De Jong 2010; Smuk and Zoch 1965).

18.7 Dehydration from Fructose to Furfural and Hydroxyl Methylfurfural

The dehydration from fructose to furfural and hydroxyl methylfurfural (HMF) in the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) are being investigated by many researchers (Qi et al. 2012). A novel carbon-based solid acid, which was prepared by a facile and eco-friendly approach from glucose and *p-toluenesulfonic* acid (TsOH), also catalyzes fructose dehydration into 5-hydroxy methyl furfural (HMF) for the first time and exhibits excellent catalytic performance. As high as 91.2 % yield of HMF was achieved in dimethyl sulfoxide (DMSO) at 130 °C after only 1.5 h. Besides, this catalyst also displayed a good reusability. Some other solvents, including dimethyl formamide (DMF), dimethyl acetamide (DMA), *N*-methylpyrrolidone (*N*-MP), and water, were also used (Wang et al. 2011). As shown in Fig. 18.8, the synthesis of HMF starts with replacement of one or two water molecules from fructose to form partly dehydrated intermediates (Kuster 1990; Roman-Leshkov et al. 2006). A further removal of water from these intermediates results final product (HMF), but intermolecule reaction leads to a condensation products from these intermediates, such as soluble polymers and insoluble humins (Kuster 1990). The HMF hydrolysis (rehydration) to give levulinic acid leads to increase in the HMF selectivity is the other alternate way of by-product formation.

It has been found that for various solid acid catalysts this method is quite effective including heteropolyacid, zeolite, amberlyst-15 resin, and other acidic resins.

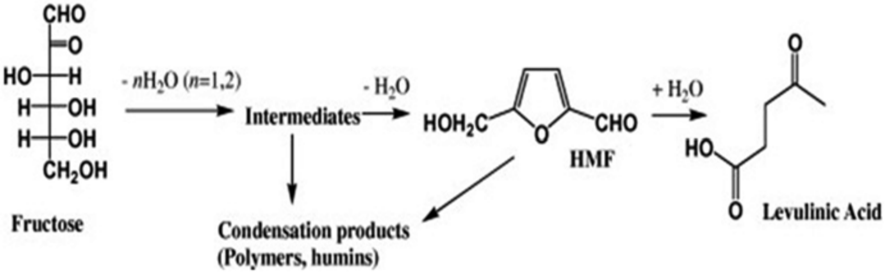


Fig. 18.8 The dehydration of fructose to HMF (Ken-ichi et al. 2009, with permission)

A series of carboxylic acid esters were well hydrolyzed by carbon-based solid acid and the CBSC showed higher conversions than the typical Amberlyst-15 resin, Nafion catalysts (Ji et al. 2011; Fu et al. 2011). The activities of the catalyst for methyl acetate hydrolysis were quite similar to the acid density, and the conversion ratio of hydrolysis decreased with the increase in length of carbon chain of carboxylic acid esters (Fu et al. 2011). The use of carbon as sulfonated carbon catalyst provides a greener and effective process for hydrolysis or conversion of cellulose to number of valuable by-products.

18.8 Acid-Catalyzed Alkylation Reaction

By employing a molar excess of carbon dioxide ($P_c = 71.8$ bar; $T_c = 31.1$ °C), supercritical 1-butene/isobutene, alkylation reaction can be perfectly carried out. Alkylation reaction resulting in virtually steady alkylate (trimethylpentanes and dimethylhexanes) production on mesoporous activated solid acid catalysts for experimental durations of about 2 days could be performed at temperatures relatively lower than the critical temperature of isobutane (<135 °C). Thus, an environmentally and eco-friendly safer alternative for alkylation reaction to conventional alkylation that employs liquid acids is promised by fixed-bed, carbon dioxide based, and solid acid alkylation process (Clark and Subramaniam 1998). Racemic tertiary halooxindoles proceed to enantioenriched oxindoles bearing all-carbon quaternary stereocenters as a result of a catalytic enantioselective stereo ablative process, this application allows for the rapid asymmetric construction of biologically significant alkaloid core motifs (Ma et al. 2009).

18.9 Conclusion

CBSC produced directly from biomass would own potential advantage. It has been established that solid acid-catalyzed biodiesel production is far from perfection than basic-catalyzed reaction. Better catalytic activity for making biodiesel type molecules was found to be due to the large surface area and mesoporous structure of the activated carbon which probably increase the contact of reactant with catalytic active sites. As reported by different researches owing to its high thermal stability, unique surface, and structural properties, it can be utilized as a support for the variety of active catalysts (metal, metal oxide, and so on). Sulfonation method played an important role in determining strong acid site ($–SO_3H$) density and hence catalytic activity. CBSC has shown high catalytic effects in many chemical reactions, including hydrolysis, dehydration, esterification, alkylation, condensation, oxathioketalization, dimerization, benzylation, and trimethylsilylation. CBSC becomes a popular solid acid catalyst. In addition, the reported catalyst could also be used repeatedly without severe decrease in its catalytic activity resulting from strong covalent attachment between $–PhSO_3H$ groups and carbon material. An overall economic study and comparison with the traditional solid acid catalyst are required before this kind of catalyst can be considered on an industrial scale and solid acid catalysis needs to be comprehensively explored and exploited.

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