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Mohammad Jawaid
Umer Rashid *Editors*

Biomass and Bioenergy

Processing and Properties

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ISBN 978-3-319-07640-9 ISBN 978-3-319-07641-6 (eBook)
DOI 10.1007/978-3-319-07641-6
Springer Cham Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014945123

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Foreword

The present volume is a well-written account of highly important aspects of Biomass and Bioenergy. The book comprises of 20 chapters from distinguished scientists/researchers around the tropics, reporting the diversity of untapped biomass resources and their value added as a bio-based feedstock in a sustainable economy. This book eloquently highlighted the usefulness of biomass residues that are mostly known in the tropical world. By doing so, the present volume achieved one of the very important objectives of a book, which is to reach out to a large community comprising of academic, industrial, and social-economic experts. This distinct nature of the contribution of numerous authors from their own community based biomass resources made this book unique and one-of-a-kind.

The editors have noticed the gap existed in the systematic reporting of tropical biomass and agricultural residues in the production of potential materials and made a very compelling case in editing this book with 20 chapters. In this book, the inclusion of a broad range of bast fibers, for example, Kapok, pine apple leaf, Indian date fiber, mainly existing in tropics with untapped potential of vast and wide range value-addition in an energy-intensive world makes perfect sense.

Last but not the least, the importance of the book as a collective knowledge of many coauthors is a result of their collaboration with editors and the publisher. Fully committed to rural and local economic development in the greater part of the globe, the editors and authors are fully devoted to providing their readers a rich knowledge of rural and tropical biomass residue solutions.

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Preface

Since the early times of human civilizations, biomass has been a major source of energy for the world's people. Biomass energy or bioenergy, the energy from organic matter, is being used by human beings since thousands of years, ever since people started burning wood to cook food or to keep warm. Today still non-wood, forest residues, and agricultural biomass are our largest biomass resources. Biomass includes plants, residues from agriculture or forestry materials. So, the proper utilization of biomass can be environmentally friendly because, it will not only be able to solve the disposal problem but also can create value-added products from this biomass. It is also a renewable resource because plants to make biomass can be grown over and over and certainly as alternative source of energy. The use of agricultural biomass is constantly growing and will likely to continue to grow in future. It is estimated that utilization of biomass can also reduce global warming compared to fossil fuel. Energy crops, such as fast-growing trees and grasses, are called *biomass feedstocks*. The use of biomass feedstocks can also help to increase profits for the agricultural based industries.

Biomass obtained from agricultural residues or forest can be used to produce different materials and bioenergy required in a modern society. As compared to other resources available, biomass is one of the most common and widespread resources in the world. Thus, biomass has the potential to provide a renewable energy source, both locally and across large areas of the world. It is estimated that the total investment in the biomass sector will reach up to $104 billion from 2008 to 2021. Presently bioenergy is the most important renewable energy option and will remain so in the near and medium-term future. Previously several countries try to explore utilization of biomass in bioenergy and polymer composite sector. Biomass has the potential to become the world's largest and most sustainable energy source and will be very much in demand. Bioenergy is based on resources that can be utilized on a sustainable basis all around the world and can thus serve as an effective option for the provision of energy services. In addition, the benefits accrued go beyond energy provision, creating unique opportunities for regional development.

The present book "Biomass and Bioenergy," volume 1, provides an up-to-date account of processing and properties of non-wood, forest residues, agricultural biomass (natural fibers) and its composites and bioenergy to ensure biomass utilization and reuse.

We wish to express our gratitude to all the contributors from all over the world for readily accepting our invitations and sharing their knowledge and expertise. We are thankful to authors for helping us to formulate diverse fields and also admirably integrating their scattered information from diverse fields in composing the chapters and enduring editorial suggestions to finally produce this venture that we hope will be a success. We greatly appreciate their commitment.

We are highly thankful to Springer-Verlag team for their unstinted cooperation at every stage of the book production.

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Khalid Rehman Hakeem
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Chapter 1
Processing and Properties of Date Palm Fibers and Its Composites

**Faris M. AL-Oqla, Othman Y. Alothman, M. Jawaid,
S.M. Sapuan, and M.H. Es-Saheb**

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_1,

Abstract Date palm (*Phoenix dactylifera*) fibers are considered as one of the most available natural fiber types worldwide. Large quantities of date palm biomass wastes are annually accumulated without proper utilization. These quantities are of potential interest to support the industrial sustainability by producing alternative cheap eco-friendly materials. The competitiveness of the date palm fibers in several applications particularly in automotive industrial sectors was illustrated. Date palm fiber can be considered the best regarding several evaluation criteria like specific strength to cost ratio if compared to other fiber types. The effects of using date palm fibers in natural fiber composites with different polymer matrices were demonstrated. Criteria that can affect the proper selection and evaluation of the natural fibers as well as the composites for particular applications were discussed. The benefit of natural fibers' modifications on physical, mechanical, and other properties were also explored. Selecting the proper date palm fiber reinforcement condition can dramatically enhance its future expectations and widen its usage in different applications.

Keywords Date palm fibers • Natural fiber composites • Composites performance • Evaluation criteria

1.1 Introduction

Date palm cultivation and their fruit utilization had been investigated by several studies and works. Unfortunately, little information and details are available regarding the utilization and implementation of the date palm fibers and wastes in producing desirable commercial natural fiber composites. Consequently, the intention of this chapter is to introduce a comprehensive discussion on the value of the date palm fibers and their composites in addition to their properties and competitiveness from different physical, chemical, mechanical, and engineering point of views. This is presented here to focus a light on one of the most important fiber types that can be utilized as an eco-friendly raw alternative material for different engineering applications.

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Table 1.1 Characteristics of the date palm production system (Dakheel 2003; Jain 2007)

1	Its sustainability in harsh climatic
2	High efficiency in resource utilization
3	High productivity
4	High nutritional value of date fruit
5	Long productive life
6	Enhance agriculture development by creating equable microclimate within oasis ecosystems
7	Helpful in reducing desertification risks

Date palm (*Phoenix dactylifera* L.) trees as one of mankind's oldest cultivated plants belong to the family of Palmae (Arecaceae). It has played a vital role in daily life activities in the Middle East particularly the Arabian Peninsula since 7,000 years (Ahmed et al. 1995). Recently, the worldwide production of date palm fruits is continuously increasing which indicates the importance of the date palm trees. The utilization and industrialization of dates are distributed among several countries such as Egypt (1,352,950 metric tons), Saudi Arabia (1,078, 300 metric tons), Iran (1,023,130 metric tons), UAE (775,000 metric tons), and Algeria (710,000 metric tons) (Chandrasekaran and Bahkali 2013).

Date palm trees have government support, social acceptance, and positive view in most countries (Al-Oqla and Sapuan 2014). Such reasons can sufficiently express why there are more than 120 million date palm trees in different countries worldwide. Over two-thirds of such trees are in Arab countries. Each tree has the ability to grow and produce fruits for more than 100 years (Al-Khanbashi et al. 2005). For instance, date palm trees have positive points of view and government support due to several reasons such as to produce the raw materials for local industries (furniture and home accessories), and produce valuable food for human beings (Jain 2007). Moreover, date palm trees can contribute to the national economy of several countries. For instance, the income for Saudi Arabia from the date fruit production was about $2.12 billion according to the base price of 2006 (Alshuaibi 2011). Due to the unique characteristics of date palm it is usually called the tree of life (Jain 2007). That is, it is very beneficial and connected with the survival and well-being of humans living particularly in hot arid environments under harsh climatic conditions. The date palm production systems have several distinguished characteristics as shown in Table 1.1. Moreover, the rich date fruit plays a crucial role in providing nutrition to human kinds under hot and arid conditions. Date fruits are rich source of fructose, sweeteners, fat, proteins, glucose, and vitamins (Al Eid 2006; Jain 2007) in addition to other minerals. Therefore, date palm fruits are considered as an ideal food for human beings as it provides several kinds of essential nutrients and potential health benefits. In addition, date palm trees are usually utilized for garden decorations in Arabian Peninsula. Consequently, it can be deduced that such reasons can ensure the continuous availability of the date palms and their residuals and fibers as renewable raw materials with low prices to be used in different industrial applications.

1.2 Natural Fiber Composites

Materials have critical roles in engineering design and applications that can lead to successful sustainable products. The proper compatibility between the material and products' functions, performance, and recyclability became critical for engineering applications. Moreover, finding new materials with desirable distinctive characteristics can expand new design possibilities (Ashby 1992). On the other hand, several criteria and limitations usually affect the usage of a specific type of material in a particular application (Ashby 1992). Thus, selecting a proper material type for a particular application is a matter of multi-criteria decision making problem (Dweiri and Al-Oqla 2006) where proper decisions have to be carried out based upon several factors.

Recently, due to the tremendous need and awareness of environmental impact and as a result of the governmental emphasizing on the new regulations regarding the environmental impact issues and sustainability concepts as well as the growing of social, economic, and ecological awareness (Faruk et al. 2012; Kalia et al. 2011a, b), the utilization of natural resources was strongly encouraged (Govindan et al. 2014). Consequently, the natural fiber reinforced polymer composites (NFRPC), (simply NFC), became a valuable alternative material type for wide range of applications. In this NFC, natural fibers (such as jute, hemp, sisal, oil palm, kenaf, and flax) are utilized to be fillers or reinforcing material for polymer-based matrices. Such utilization of natural fibers can decrease the amount of waste disposal problems, and enhance reducing in environmental pollution (Kalia et al. 2011b). Such materials are attractive from environmental point of view where they can be used as an alternative to the traditional glass/carbon polymer composites (Faruk et al. 2012; Kalia et al. 2011a, b). They can be used in different applications such as packaging, disposable accessories, furniture, building, insulation, and automotive industries (Al-Oqla and Sapuan 2014). Moreover, these NFC have several advantages over the traditional types of materials like the low costs and density as well as acceptable specific strength and modulus (Alves et al. 2010; Faruk et al. 2012; Kalia et al. 2011b) which can lead to low weight products.

Furthermore, natural fiber composites are acceptable from environmental points of view because they can participate in producing recyclable and biodegradable products after use (Alves et al. 2010; Kalia et al. 2011a; Mir et al. 2010). Comparable to synthetic fiber composites, NFC are much cheaper, good thermal as well as acoustic insulating properties that can widen their industrial applications (Alves et al. 2010; Faruk et al. 2012). On the other hand, natural fibers have several advantages over the traditional glass fibers such as: availability, CO_2 sequestration enhanced energy recovery, reduced tool wear in machining, and reduced dermal and respiratory irritation (Al-Oqla and Sapuan 2014; Faruk et al. 2012; Kalia et al. 2011b; Sarikanat 2010). Despite of that, natural fibers have some considerable drawback demonstrated in poor water resistance, poor bonding with the matrix, and low durability, The weak interfacial bonding between natural fibers and the polymer matrix can lead to undesirable properties of the composites and thus limited their industrial usage. Therefore, different ways have been performed to improve their compatibility

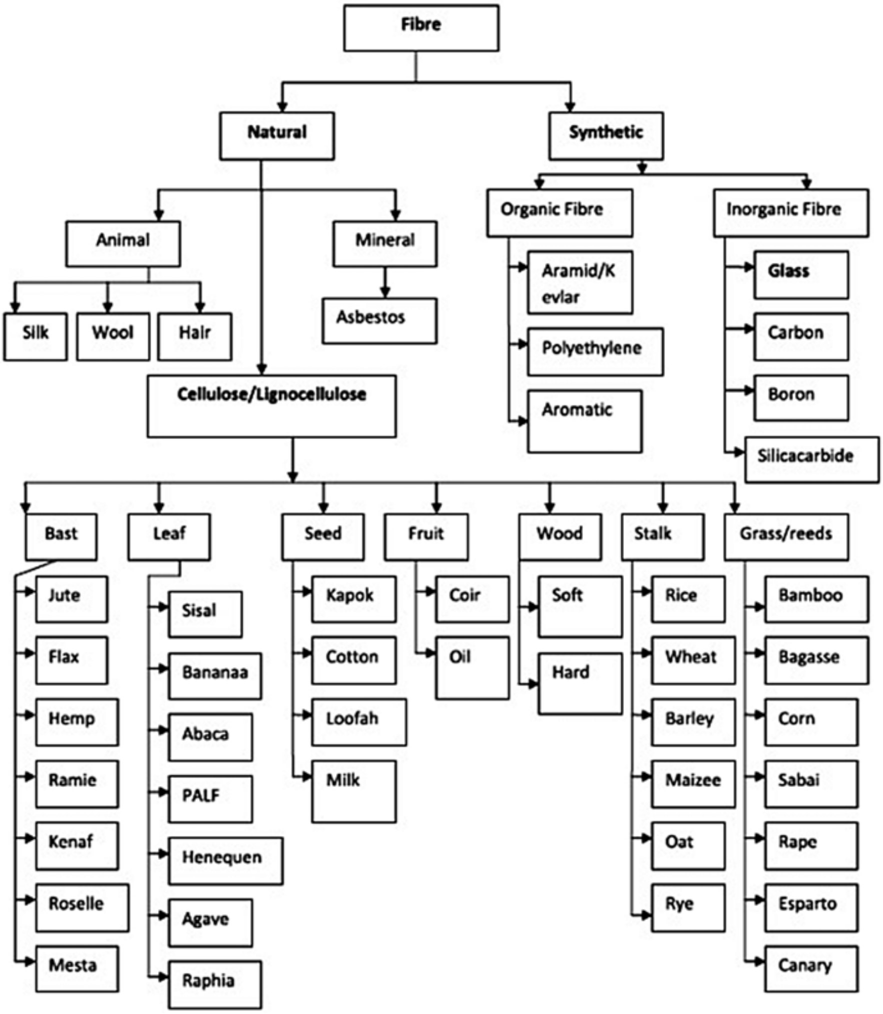


Fig. 1.1 General classifications of fibers (Jawaid and Abdul Khalil 2011)

and bonding. Consequently, the usage of the coupling agents and surface treatments via mechanical, chemical, and/or physical modifications was implemented (Al-Khanbashi et al. 2005; Arbelaiz et al. 2005; Faruk et al. 2012). A general classification of the natural fibers can be classified based upon their origin as bast fibers, leaf fibers, fruit, and seed-hair fibers as seen in Fig. 1.1. Wide different natural fiber types had been used to reinforce different polymer matrices. Such fibers include wood, cotton, bagasse, rice straw, rice husk, wheat straw, flax, hemp, pineapple leaf, coir, oil palm, date palm, doum fruit, ramie, curaua, jowar, kenaf, bamboo, rapeseed waste, sisal, and jute (Jawaid and Abdul Khalil 2011; Majeed et al. 2013). A schematic diagram of the general classifications of natural fibers is shown in Fig. 1.1.

1.3 Date Palm Fibers

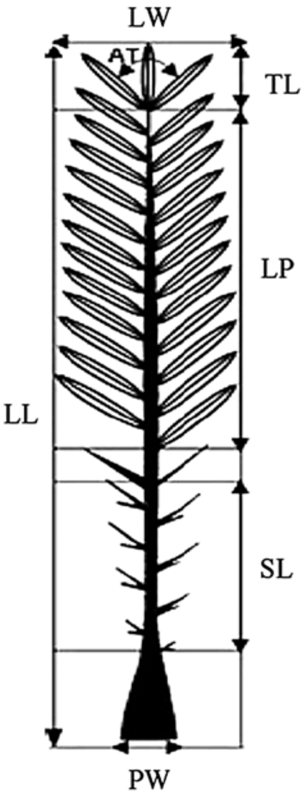
The date palm biodiversity is obvious all around the world where about 5,000 date palm cultivars can be found (Jaradat and Zaid 2004). Based on botanical descriptions, about 1,000 cultivars can be found in Algeria, 400 in Iran, 370 in Iraq, 250 in Tunisia, 244 in Morocco, and 400 in Sudan, as well as many additional cultivars in the other countries (Benkhalifa 1999; Osman 1983; Zaid and De Wet 1999). The date palm trees (*Phoenix dactylifera* L.) is the tallest *Phoenix* species, it can be found with heights of more than 30 m and has fruit reaching up to 100 mm × 40 mm in size. The fruits are very tasty and nutritious (Jaradat and Zaid 2004). Date palms have characteristics that adapt them to varied conditions. Date palm trees can grow well in sand, but it is not arenaceous. It can also grow well where soil water is close to the surface because they have air spaces in their roots. Although date palm tree can grow well in saline conditions, it can do better in higher quality soil and water. The leaves of the date palm are adapted to hot and dry conditions, but it is not a xerophyte and requires abundant water (Benkhalifa 1999; Jaradat and Zaid 2004).

The date palm tree is characterized by numerous offshoots produced at its trunk's base. The trunk of the date palm tree is covered with persistent grayish leaf bases. It is surmounted by a handsome array of pinnate divided long leaves and needle sharp fronds. Usually, around 10–20 new leaves are produced annually. The leaves of the date palm are subtended by a cylindrical sheath of reticulate mass of tough, fibrous material, at their bases. These together form a tight protective envelope for the terminal bud (Benkhalifa 1999; Dakheel 2003). A young actively bearing date palm tree showing offshoots is shown in Fig. 1.2 and fruit of the date palm is seen in Fig. 1.3. Detailed morphological traits of date palm tree leaf can be shown in Fig. 1.4, where different parameters of the leaf can be demonstrated like the leaf length, thickness, angle, length of leaflet part, rachis thickness, leaf lets number as well as others (Salem et al. 2008).

Once the date palms' fruit are harvested, large quantities of date palm rachis and leaves wastes accumulated every year in agricultural lands of different countries. These amounts of important and valuable biomass wastes are of potential interest in different countries since they can be considered as new cellulosic fiber sources. Thus, innovative ways of valorizing this abundant renewable resource should be found (Chandrasekaran and Bahkali 2013). One of these ideas is to use such natural fibers in natural fiber composites suitable for different industrial applications. This can be one way of meeting the increasing demand in renewable and biodegradable materials. Therefore, the agricultural residues of date palms mainly rachis and leaves can be viewed as sources of reinforcing fibers for polymeric matrices in composite. The competitiveness of the date palm fibers in forming natural composites suitable for automotive industrial applications was demonstrated (Al-Oqla and Sapuan 2014). On the other hand, several studies proved that date palm fibers have the potential to be an effective filler in both thermoplastics and thermosetting materials to be used in different industrial applications (Abdal-hay et al. 2012; Agoudjil et al. 2011; Al-Oqla and Sapuan 2014).

Fig. 1.2 Date palm tree

Fig. 1.3 Date palm fruit



Key to the diagram

Parameter	Label
Leaf length	LL
Leaf width	LW
Leaf angle	LA
Spineted part length	SL
Length of leafleted part	LP
Petiole width	PW
Rachis thickness between the last spine and the first leaflet	RT
Leaf lets number	LN
Terminal leaflet length	TL
Terminal leaflet width	TW
Ventral angle of middle leaflet	VA
Middle leaflet width	WM
Middle leaflet length	LM
Leaflets spacing index at the middle	LI
Angle of leaflets on both sides of the terminal one	AT
Spine number	SN
Middle spine width	WS
Middle spine length	LS

Fig. 1.4 Detailed morphological traits of date palm tree leaf (Salem et al. 2008)

Date palm tree can produce annually large number of natural fibers that can be utilized in different industries. It is estimated that the annual date palm agricultural wastes are more than 20 kg of dry leaves and fibers for each date palm tree (Al-Oqla and Sapuan 2014). Moreover, the date palm tree produces another type of wastes as date pits which are about of 10 % of the date fruits (Barreveld 1993). Unfortunately, these agriculture wastes are not properly utilized in any biological process or industrial applications, in most of countries, despite of their contents of potential amount of cellulose, hemicelluloses, lignin, and other compounds. Typical date palm fibers can be seen in Fig. 1.5.

1.3.1 *Chemical Composition of Date Palm Fiber*

It is known that the chemical composition of the natural fibers is of paramount in determining their suitability for different industrial applications particularly for NFRPC. That is, several characteristics of these composites like degradability and

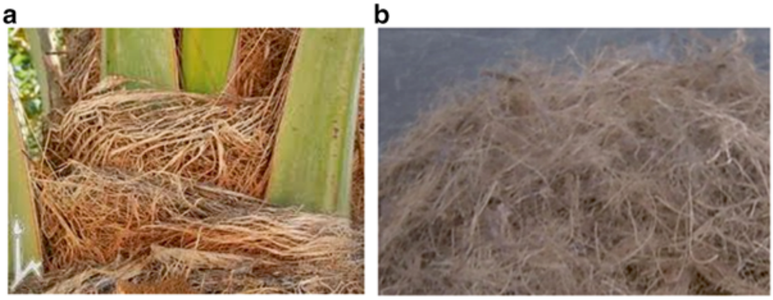


Fig. 1.5 Date palm fibers (**a**) on the tree, (**b**) separated

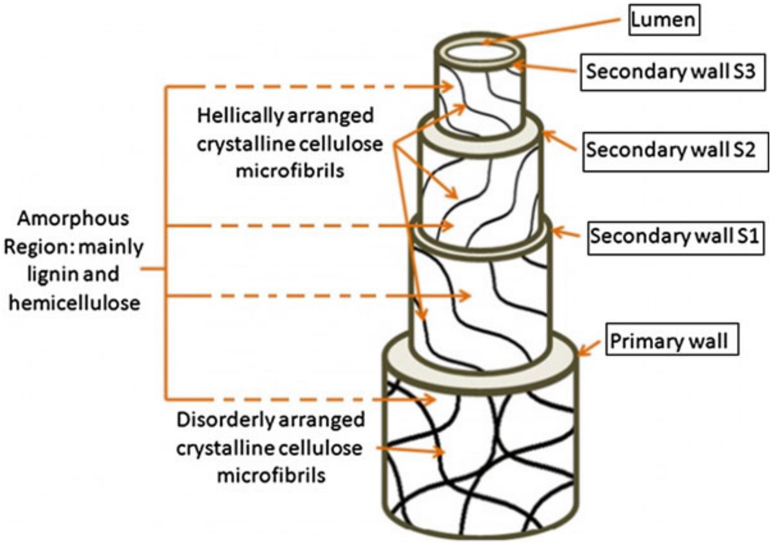


Fig. 1.6 Structure of bio-fiber. Adapted from Azwa et al. (2013)

recyclability, weather resistance, fungi attack, etc., strongly depend on the chemical composition of filler (fiber) (Al-Oqla and Sapuan 2014; Azwa et al. 2013). Actually, a variation in the fiber quality can be achieved for the same fiber type due to several factors. Some of these factors are: soil quality, fiber location on the plant, weather conditions, crop variety, fertilization, climate, and harvest timing (Dittenber and GangaRao 2011; Kalia et al. 2011b). In addition, extraction processing methods, fibers cross-sectional area variation, and the differences in drying processes will also affect the quality of the natural fibers (Dittenber and GangaRao 2011). Consequently, differences of natural fiber chemical and physical properties can be found in literature. Plant fibers consist mainly of cellulose fibrils embedded in lignin matrix. The bio-fiber structure is shown in Fig. 1.6. A primary cell wall and other

Table 1.2 The average weight percentage of chemical composition of the date palm fibers from leaf (leaflet and rachis) (Mirmehdi et al. 2014; Sbiai et al. 2010)

Constituents		Cellulose		Hemicelluloses		Lignin		Ash		Extractive	
Leaflet	Leaf[a]	40.21	54.75[a]	12.8	20.00[a]	32.2	15.30[a]	10.54	1.75[a]	4.25	8.2[a]
Rachis		38.26		28.17		22.53		5.96		5.08	

[a] Values are from Sbiai et al. (2010)

three secondary walls form the fiber's complex layered structure whereas secondary thick middle layer of the cell walls consists of a series of helically wound cellular micro-fibrils formed from long chain cellulose molecules can determine the mechanical properties of fiber. Each cell wall is formed from three main components which are cellulose, hemicelluloses, and lignin. The lignin-hemicelluloses have a matrix-like role while the micro-fibrils which are made up of cellulose molecules act as fibers (Dittenber and GangaRao 2011; John and Thomas 2008). Pectin, oil, and waxes can be found as other components (John and Thomas 2008; Wong et al. 2010). Due to the existence of Lumen, the natural fiber has a hollow structure unlike synthetic ones (Liu et al. 2012).

Cellulose and lignin are the most important structural components in many natural fibers. In plants, cellulose is usually found as a slender rod like crystalline micro-fibrils and aligned along the fiber's length (Azwa et al. 2013). Although Cellulose is resistant to hydrolysis, strong alkali, and oxidizing agents, it is degradable to some extent when exposed to chemical treatments (Azwa et al. 2013). Lignin is a complex hydrocarbon polymer. It usually gives rigidity to plant and assists in water transportation. It is hydrophobic, resists most of microorganisms attacks as well as acid hydrolysis, it is usually soluble in hot alkali, readily oxidized, and easily condensable with phenol. The nature of cellulose and its crystallinity can determine the reinforcing efficiency of natural fibers (John and Anandjiwala 2007). Filaments are bonded into a bundle by lignin and are attached to stem by pectin. Lignin and pectin are weaker polymers than cellulose. They have to be removed by retting and scotching for effective composite reinforcements (Dittenber and GangaRao 2011). The average weight percentage of chemical composition of the date palm tree frond and their fiber properties (Mirmehdi et al. 2014; Sbiai et al. 2010) are shown in Table 1.2.

It can be noticed that there are some variation in the measured values of the date palm fiber's chemical composition due to inherent parameters mentioned previously. A comparison between average values of both cellulose and lignin for the date palm fiber with other natural fibers can demonstrate the appropriateness and competitiveness of the date palm fibers for being potential type of fillers for natural fiber composites. Such comparison is demonstrated in Fig. 1.7.

It can be seen from the comparison that the date palm fiber has an added value over both hemp and sisal, because it has less cellulose content than they do which reduces the ability of the date palm fiber to absorb water comparing with hemp and sisal (Al-Oqla and Sapuan 2014). On the other hand, this can give the date palm fiber more desired mechanical properties over the coir one. Moreover, the cellulose content in date palm fiber is greater than that of lignin, which allows it to be competitive for automotive applications (Al-Oqla and Sapuan 2014).

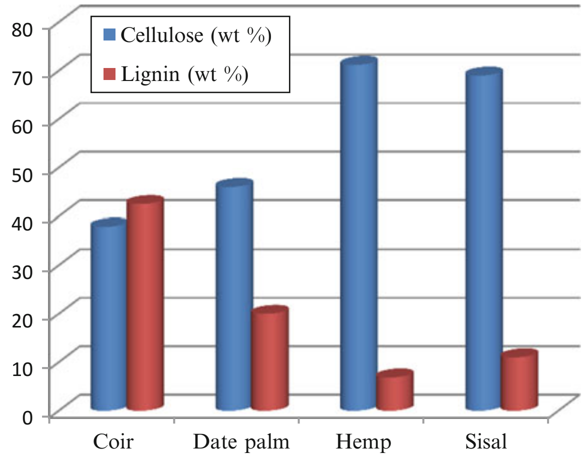


Fig. 1.7 Comparing the date palm's cellulose and lignin contents with other natural fiber types. From Al-Oqla and Sapuan (2014)

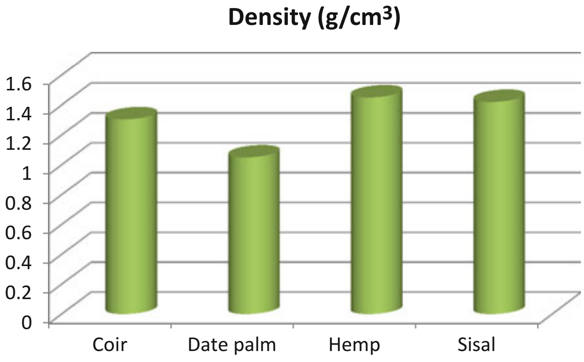


Fig. 1.8 Date palm fiber's density compared with other natural fibers types used in automotive industry. From Al-Oqla and Sapuan (2014)

1.3.2 Physical Properties of Date Palm Fiber

Physical properties of the natural fibers are crucial in determining their suitability for different industrial applications as well as natural fiber composites. Fiber's length, diameter, and density as well as aspect ratio, thermal conductivity, cost, and availability are considered as key criteria and properties that can determine the potential usage of any natural fiber type in different industrial applications (Al-Oqla and Sapuan 2014; Al-Khanbashi et al. 2005; Alves et al. 2010). Date palm fiber can be considered as one of the most available natural type comparing to other natural fiber used in polymer composites for automotive industry. It can be estimated that the annual world production of the date palm fiber is about 42 times more than that of coir and about 20 and 10 times more than hemp and sisal production respectively. On the other hand, the fiber density is one of the most important physical properties that contribute implementing natural fibers in different applications. That is, it can lead to lower weight composites suitable for automotive and space applications. A comparison between the date palm fibers with other natural types regarding the density property is demonstrated in Fig. 1.8. It is noticed that date palm fiber have a lower density as compared to other natural fibers which give it an added value in the field of natural fiber composites.

Table 1.3 Physical properties of the date palm fibers with other natural types

Fiber type	Coir	Date palm	Hemp	Sisal
Density (g/cm^3)	1.15–1.46	0.9–1.2	1.4–1.5	1.33–1.5
Length (mm)	20–150	20–250	5–55	900
Diameter (μm)	10–460	100–1,000	25–500	8–200
Specific modulus (approx.)	4	7	40	17
Annual world production (10^3 ton)	100	4,200	214	378
Cost per weight (USD/Kg)	0.3	0.02	1.2	1
Thermal conductivity (W/m K)	0.047	0.083	0.115	0.07

Adopted from Al-Oqla and Sapuan (2014)

On the other, hand, several researches had reported the significance of the aspect ratio (length/diameter) on the properties of final composite materials. Studies had investigated and proved that this aspect ratio of the date palm fiber has an intermediate value regarding other natural fiber types which can attribute its usage in different industrial applications (Al-Oqla and Sapuan 2014). Table 1.3 provides useful physical properties of the date palm fibers with other natural types. The physical properties such as length, diameter, density, and micro-fibril angle of the date palm fibers made it potential for wide range of applications (Al-Oqla and Sapuan 2014; Faruk et al. 2012; Sbiai et al. 2010).

1.3.3 Mechanical Properties of Date Palm Fiber

Mechanical properties of natural fibers can be strongly affected and determined by several important variables such as structure, microfibrillar angle, chemical composition, cell dimensions, and defects (Azwa et al. 2013; Dittenber and GangaRao 2011; John and Anandjiwala 2007; Wong et al. 2010). Microfibrillar angle is the angle between fiber axis and the micro-fibrils. These angles are responsible for the mechanical properties of the fibers. The smaller the angle the higher strength and stiffness of the fiber while larger angles provide usually higher ductility. Generally, natural fibers with higher mechanical strength possess higher cellulose content, longer cell length, higher degree of polymerization of cellulose, and lower microfibrillar angle. Important mechanical properties like tensile strength and Young's modulus usually increase as cellulose content and cell length increase (John and Thomas 2008; Methacanon et al. 2010). The mechanical properties of the date palm fiber and other natural fiber types can be shown in Table 1.4.

1.3.4 Treatment of the Natural Fibers

It was proved that the properties of the natural fiber composites depend on constituents (fiber/matrix) and their interfacial bonding (Agoudjil et al. 2011; Al-Khanbashi et al. 2005; Huda et al. 2008; Kalia et al. 2011b). The interfacial

Table 1.4 Mechanical properties of date palm and other natural fibers

Properties	Diameter (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Jute	25–200	393–773	13–26.5	1.16–1.5
Flax	10–40	600–2,000	12–85	1–4
Sisal	50–200	468–640	9.4–22.0	3–7
Coir	100–450	131–175	4–6	15–40
Raw date palm fiber	100–1,000	58–203	2–7.5	5–10

From Alawar et al. (2009)

bonding between the reinforcing natural fibers and the polymer matrix in the composite has a vital role in determining its final mechanical properties. That is, the reinforcement efficiency depends upon the stress transfer between the matrix and fibers. Most of the thermoplastic polymers are nonpolar, hydrophobic compounds whereas natural fibers are polar, hydrophilic ones. Because of this inherent dissimilarity, the NFRPC are usually not compatible and interfacial adhesion in these composites tends to be poor. Therefore, the surfaces of the natural fibers are usually treated via different means in order to improve the interfacial bonds between the fibers and the matrix. Several methods of surface modification by physical, chemical, or mechanical means have been investigated to improve the fiber properties and to increase the bond ability as well as the wettability between the cellulosic fibers and the polymer matrix. Such used methods of treatment are tabulated in Table 1.5.

Several studies had proved the efficiency of such surface treatments on the date palm fibers for different polymer matrices when treated with suitable means of treatments particularly the chemical one (Abdal-hay et al. 2012; Al-Khanbashi et al. 2005; Alsaeed et al. 2012; Sbiai et al. 2010; Shalwan and Yousif 2014). The effect of different treatment process on the data palm fiber was investigated by several studies (Alawar et al. 2009) where different concentrations of alkali treatment were used to modified the fiber surface (Alawar et al. 2009), a range from 0.5 to 5 %, and acid treatment with 0.3, 0.9, and 1.6 N were used and performed at 100 °C for 1 h. Results demonstrated that the surface morphology was improved. NaOH treated fibers showed an increase in tensile and considerable advancement in surface morphology. On the other hand, fibers treated with hydrochloric acid were found to be unfavorable due to its negative impact on tensile strength and surface morphology. Microscopic examinations were demonstrated the effectiveness of the chemical treatment on the date palm fiber as can be shown in Fig. 1.9 where untreated fibers are demonstrated having a weak outer layer that can prevent strong bonding with the polymer matrix in one hand, and another treated one where the weak outer layer was removed through the treatment process which can lead to stronger bonding with the matrix.

It is worthy to note that the proper treatment conditions like the suitable solution type, concentration, and time can dramatically enhance the mechanical properties of the fiber. The effect of the chemical treatment of the date palm fiber on its mechanical

Table 1.5 Physical and chemical treatments methods for cellulosic natural fibers

Physical treatments	Physical treatments processes change the fiber's structural and surface properties; thereby influence the mechanical bonding with the matrix. Such treatments involve surface fibrillation, electric discharge (corona, cold plasma), etc. The Cold plasma method is a very effective one that can clean the bio-fibers and modify its surface imparting different functional groups and changes in surface energies. Steam treatment of the natural fiber can be performed by applying of high pressure steaming, where heating at high temperatures and pressures are preformed, then mechanical disruption by violent discharge or explosion is usually used (Kalia et al. 2011b; Arbelaiz et al. 2005)
Chemical treatments Alkaline treatment Liquid ammonia treatment Silanization	Natural fibers are highly polar-owing to the hydroxyl groups. Such groups are readily available for chemical bonding (hydrogen bonding) with compatible polymer matrices and physical interlocking (wetting) with the nonpolar matrices. Several chemical treatments were investigated having potential to remove both waxes and oils from the fiber's surface in one hand, and to make it rough, and stop the water uptake
Graft copolymerization Esterification Acrylation and maleic anhydride treatment and treatment with isocyanates	*Alkaline treatment*: Alkaline treatment (mercerization) is one of the most popular chemical treatments of natural fibers. The major modification done by this treatment is the disruption of hydrogen bonding in the network structure, herewith increasing surface roughness. Alkaline treatment by adding of aqueous sodium hydroxide (NaOH) to natural fiber can remove a certain amount of lignin, wax, and oils covering the external surface of the fiber cell wall, depolymerizes cellulose, and exposes the short length crystallites (Mohanty et al. 2001; Nouira and Frein 2014). Thus, alkaline processing can directly affect the cellulosic fibril, the degree of polymerization, and the extraction of lignin and hemi cellulosic compounds (Li et al. 2007; Osman 1983)
	Liquid ammonia treatment: Liquid ammonia has the ability to penetrate quickly to the interior of cellulose fibers, forming a complex compound after the rupture of hydrogen bonds. This ability of ammonia is due to its low viscosity and surface tension. In addition, the relatively small molecule of ammonia is able to increase the distances between cellulose chains and penetrate crystalline regions. Therefore, the liquid ammonia treatment can change the original crystal structure of cellulose I into cellulose III. Then, after hot water treatment, cellulose III changes into cellulose I again (Pickering 2008; Rachini et al. 2012). This type of treatment results in deconvolution and smoothing of the natural fibers' surface. At the same time, the fiber cross-section becomes round and lumens decrease (Kozlowski and Wladyka-Przybylak 2004; Rowell et al. 1997)
	Silanization: Silane is a chemical compound with chemical formula of SiH_4. Silanization of cellulosic fibers can minimize the disadvantageous effect of moisture on the properties of fiber composites in one hand and can increase the adhesion between the fiber and its polymer matrix. Thus, upgrading the composite strength, proper conditions like the type of silane used, its concentration in solution, time and temperature of fiber silanization, in addition to the moisture content, can determine the effectiveness of the silanization (Li et al. 2007; Osman 1983)

(continued)

Table 1.5 (continued)

	Graft copolymerization: Grafting copolymerization can be used to modify the surface of the natural fibers. The cellulose is treated in this process with an aqueous solution containing selected ions and is exposed to a high-energy radiation. After that, cellulose molecules crack and radicals are formed (Bledzki and Gassan 1997; Salem et al. 2008). Afterwards, the radical sites of the cellulose are treated with a suitable solution usually compatible with the polymer matrix type like, vinyl monomer, acrylonitrile, and methyl (Kalia et al. 2011b; Arbelaiz et al. 2005)
	Esterification: Esterification is a popular chemical treatment method usually involves the reactions with organic acids or anhydrides. Many esters are possible to be used depending on the nature of the organic acid involved in the reaction. Esters containing 1–4 carbon atoms are formate, acetate, propionate, and butyrate; laurate has 12 carbon atoms and stearate has 18 carbon atoms. Maleate and fumarate are esters of dicarboxylic acids containing double bonds in the carbon chain. Such treatment modification can alter polarization of the fibers to make them more compatible to nonpolar matrix (Kalia et al. 2011b; Arbelaiz et al. 2005)
	Acrylation and maleic anhydride treatment and treatment with isocyanates: Other types of chemical natural fiber's treatment can be performed by Acrylation and Maleic Anhydride Treatment and Treatment with Isocyanates to enhance the mechanical properties of cellulose fiber silanization (Arbelaiz et al. 2005; Kalia et al. 2011b; Li et al. 2007; Osman 1983)

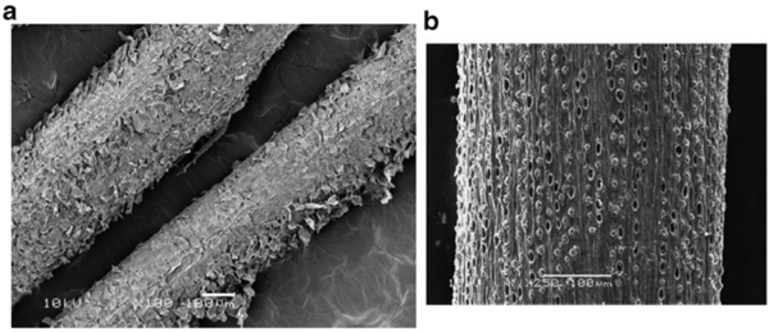


Fig. 1.9 Scanning electron microscope (SEM) for (**a**) untreated date palm fiber, (**b**) treated date palm fiber with 1.5 % NaOH. Form Alawar et al. (2009)

properties is demonstrated in Fig. 1.10 where proper treatments demonstrate a dramatically enhancement of the tensile strength as well as the Young's modulus of the fiber. Stress/strain diagrams of date palm fibers treated with different NaOH concentration can be shown in Fig. 1.11.

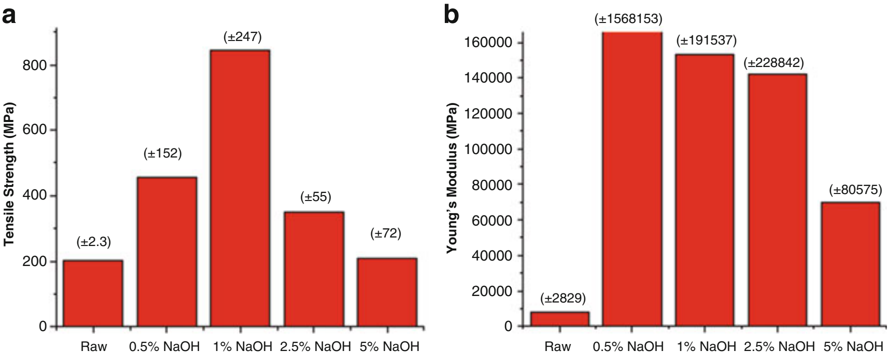


Fig. 1.10 The effect of NaOH treatment on (**a**) the date palm fiber's tensile strength and (**b**) the fiber's Young's modulus. From Alawar et al. (2009)

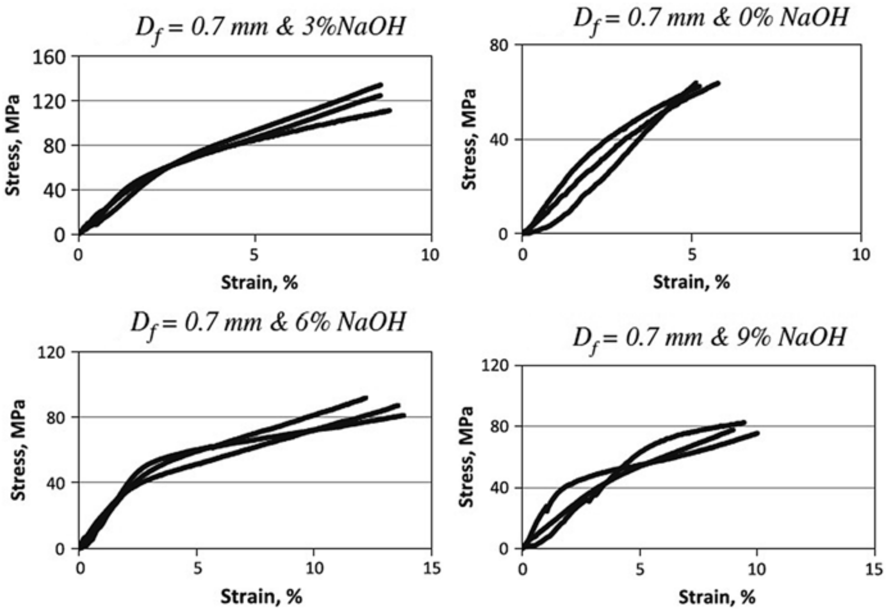


Fig. 1.11 Stress/strain diagram of date palm fiber with 0.5 mm diameter treated with different NaOH concentration. From Shalwan and Yousif (2014)

1.4 Matrices for Date Palm Fibers

The composites' shape, appearance, as well as the environmental and overall durability are dominated by the matrix type whereas fillers carry most of the structural loads hereby they provide macroscopic stiffness and strength. Polymers dominated the market of the commodity plastics with about 80 % consuming materials based on nonrenewable resources (Faruk et al. 2012). Due to the public awareness of the environment as well as the limited fossil fuel resources, alternative matrices of the conventional petroleum-based ones are emphasized by different governing and industrial sectors. Therefore bio-based plastics that consist of renewable resources have experienced a revival in the past few decades. Polymers and their composites have recently emerged in wide different applications of modern industries due to their desirable properties like: low weight, low cost, recyclability, biodegradability, availability, and high specific properties (Alves et al. 2010; Faruk et al. 2012).

The petrochemical-based matrices such as thermoplastics and thermoset were extensively investigated for natural fiber composites. Thermoplastics such as Polyethylene (PE) (Alawar et al. 2009), polypropylene (PP) (Rachini et al. 2012), polystyrene (PS) (Singha and Rana 2012), and PVC (polyvinylchloride) (Huang et al. 2012) were used as polymeric base of the natural fiber composites, whereas Phenol formaldehyde (Zhang et al. 2012), Polyester (Al-Khanbashi et al. 2005), Epoxy resin (Shalwan and Yousif 2014), and Vinyl esters (Huo et al. 2012) were widely used as thermosets matrix.

Due to the undesirable properties as well as the technical drawback of natural fibers such as high moisture absorption and anisotropic characteristics (Arbelaiz et al. 2005), and the low permissible processing temperature, proper polymer matrices have to be selected for a particular fiber type to avoid the possibility of any lignocellulosic degradation and to prevent volatile emissions that could hurt composite characteristics (Rowell et al. 1997). Different mechanical properties, deformations, thermal analysis, degradability, weather resistance, and thermo-mechanical properties of different composites were studied (Abdal-hay et al. 2012; Abu-Sharkh and Hamid 2004; Agoudjil et al. 2011; Al-Khanbashi et al. 2005; Alawar et al. 2009; Dehghani et al. 2013; Ibrahim et al. 2014). In these studies, researchers used date palm fibers with different matrix such as Polypropylene, Polyester, Epoxy, High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE), Polyester, and ethylene terephthalate. Moreover, date palm fibers were used with other types of fibers to make completely biodegradable hydride natural fiber composites like flax fibers and starch-based composites (Ibrahim et al. 2014). A typical SEM micrograph of fracture surface of date palm fiber/polyester composite is shown in Fig. 1.12 using raw date palm fiber.

Generally, it was reported that using date palm fibers with different polymer types can enhance the beneficial desired characteristic of the composites like the tensile strength, Young’s modulus, flexural strength and modulus, thermal and acoustical properties (Abdal-hay et al. 2012; Al-Kaabi et al. 2005; Al-Khanbashi et al. 2005; Shalwan and Yousif 2014) which can with no doubt demonstrate the effectiveness and competitiveness of the date palm fibers to be used in different natural fiber composites for wide industrial applications (Al-Oqla and Sapuan 2014). Data of a single fiber pull out treated date palm fiber/Epoxy composite with different NaOH concentrations to determine the maximum stress is shown in Fig. 1.13.

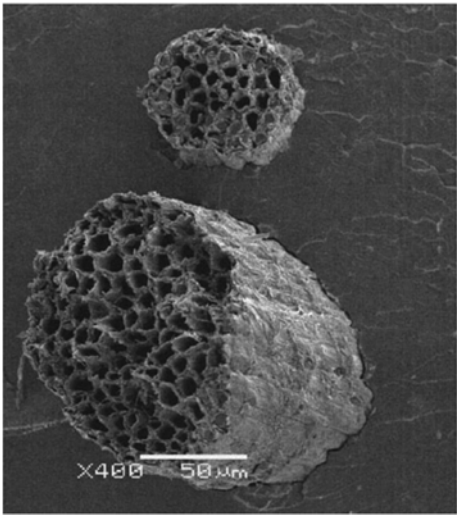


Fig. 1.12 A typical SEM micrograph of fracture surface of date palm fiber/polyester composite. From Al-Kaabi et al. (2005)

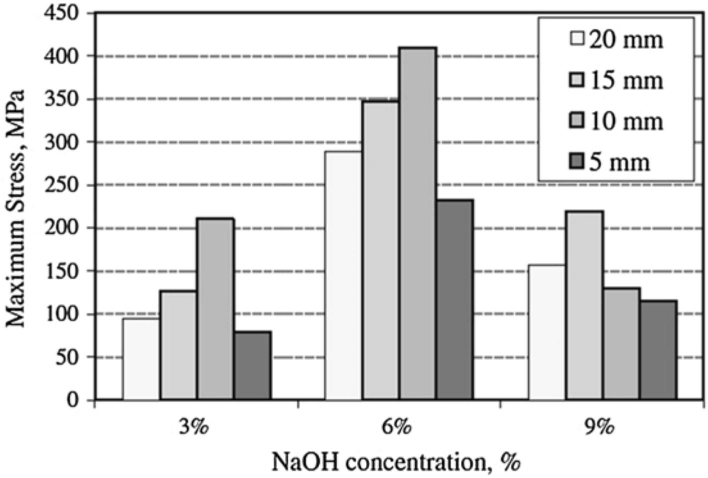


Fig. 1.13 Single fiber pull out data of treated DPF/Epoxy with different NaOH concentrations showing the maximum stress. From Alsaeed et al. (2012)

1.5 Performance of Bio-composites

Different characteristics and properties of the natural fiber composites have to be investigated in order to maximize their potential usage and implementation in various applications. Adopting of any new material type in a certain application is limited by several factors that affect its suitability in that particular application (Al-Oqla and Sapuan 2014; Dweiri and Al-Oqla 2006).

It is of paramount importance to know various physical, chemical, mechanical, and biological as well as economic and environmental properties of the composite in order to determine its compatibility with a particular application to ensure its contribution to the industrial sustainability (Al-Oqla and Sapuan 2014).

1.5.1 Factors Influence the Composite Performance

Unlike isotropic materials, the functional requirements can affect the design of components made of composites. And because natural fibers play a critical role in achieving the desired specific requirements of the composites as engineered materials and because the incorporation of these fibers in matrix polymers have been found helpful in determining the properties of the final composites, the appropriate selection of the reinforcement and the polymer as well as other technical aspects should be fairly executed and optimized. That is, several criteria affect the final desired characteristics of the natural fiber composites to be suitable for particular application. These criteria were classified into levels by AL-Oqla and Sapuan (Al-Oqla and Sapuan 2014) to be as:

1. The Natural Fiber Level: where different properties regarding natural fibers have to be concerned.
2. Matrix Level: where different properties regarding the polymer matrix have to be concerned.
3. The Composite Level: where different properties regarding the composite itself have to be concerned. That is, the characteristics of the final composites are not necessarily being exactly similar to any of these for fibers or matrix.
4. The General Performance Level: where different properties regarding the composite performance have to be taken into account such as mechanical properties, weather resistance, bio stability, life cycle, etc.
5. The Specific Performance Level: where particular requirements regarding a specific desired function and application should be considered. For instance, for automotive applications: composites' weight, thermal and acoustic insulation properties, occupational health and safety properties have to be considered. An illustrative diagram of the suggested levels is shown in Fig. 1.14.

The classified criteria that affect the proper selection of the natural fiber composites are shown in Tables 1.6 and 1.7. According to these criteria, it was approved that date palm fibers are one of the most potential and available fiber types that can be utilized to form attractive natural fiber composites for different applications particularly in the automotive industry (Al-Oqla and Sapuan 2014).

Fig. 1.14 Levels of factors that affect the proper selection NFC materials. From Al-Oqla and Sapuan (2014)

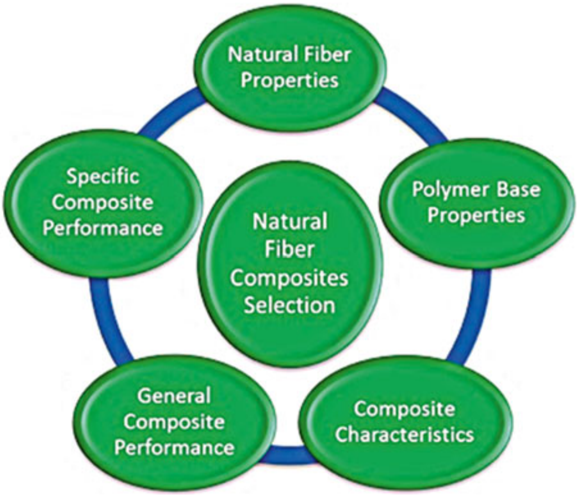


Table 1.6 Criteria affect the selection of products made from natural fiber composite materials on composite characteristics level (Al-Oqla and Sapuan 2014)

Level 1	Level 2	Level 3
Category	Property/characteristic	Criteria
Composite characteristics	Physical	Total density, surface topology, texture, surface roughness, coefficient of thermal expansion, specific heat, electrical conductivity, color and esthetic, reflective index, opacity, and translucency
	Chemical and biological	Biodegradability behavior, bio stability, toxicity, storage (on shelf storage), recyclability, life cycle time, water absorption behavior, weather resistance, sunlight and UV resistant, possibility of thermal recycling
	Mechanical/structural	Elastic modulus, shear modulus, flexural modulus, yield strength, compressive strength, Poisson's ratio, fracture toughness, fatigue strength, creep resistance, hardness, elongation to break, impact strength, hardness
	Technical	Fabrication knowledge and time, fabrication cost, reproducibility, product quality, sterilizeability, packaging, process parameters (pressure, temperature, cure time, and surface finish requirements), thermal stability, secondary processability, level of automation, labor protection and safety, life cycle cost, cost of performance improvement, Possibility of producing homogenous/non homogenous composites

Table 1.7 Criteria affect the selection of products made from natural fiber composite materials: specific composite performance level (Al-Oqla and Sapuan 2014)

Level 1	Level 2	Level 3
Category	Property/characteristic	Criteria
Specific composite Performance	Specific requirements based on the desired function or application (Here, Automotive industry)	Total weight, thermal insulation properties, acoustic insulation properties, ease of maintenance, crash behavior, social impact (acceptance and positive image), occupational health and safety, good resistance to micro cracking, low tearability, dirt resistance

1.6 Future Developments

Renewable energy and steps toward achieving more sustainable societies are the key drivers for conducting more scientific research regarding different aspects of natural resources. A proper utilization of the available resources can enhance better living standards as well as reducing energy consumption behavior. Implementing natural fibers for getting more bioenergy as an alternative source to the fossil fuel energy, as well as utilizing the natural fiber/nanoclay reinforced polymeric materials are emphasized by several governing and industrial sectors. Achieving the optimum desired properties for the completely recyclable hybrid composites are the future game of the world to expand the sustainable design possibilities that can widen the applications of such composite to reach all aspects of the modern living standards. Hybrid recyclable packaging material from natural fiber developed at lower cost but contributes to the sustainability as well as functionality. Mechanically stronger materials are recommended for the packaging as well as gas sensitive materials such as electronic and pharmaceutical packaging. Although those hybrid materials are degradable, the poor interfacial adhesion and the lack of compatibility between the filler and the matrix limited their widespread commercial impact.

1.7 Summary

NFC as eco-friendly materials, have been emerged as an alternative to the traditional glass/carbon-reinforced polymer composites. They are attractive materials for different applications like packaging, furniture, and automotive industries. Such materials have several advantages like, the low cost, acceptable mechanical properties, good thermal and acoustic insulating properties, availability, CO_2 sequestration enhanced energy recovery, etc. The properties and performance of the final natural fiber composites depend on the properties of both the matrix and filler as well as their interfacial bonding.

Both physical and mechanical treatment processes were performed on the cellulosic fibers to enhance the interfacial bonding characteristics of the natural fiber composites. Different factors and criteria can affect the performance of the produced natural fiber composites. Some of these criteria affect the selection of the composite constituents (matrix and fillers), whereas others can determine the final performance of the produced product of such materials. Wide range of physical, biological, mechanical, environmental as well as economic properties of the polymer composite have to be investigated to optimize and widen their potential applications.

The petroleum derived thermoplastics and thermosets are widely used for producing different natural fiber composites oriented for various industrial applications. The potential and competitiveness of the palm fiber was proved for different industrial applications particularly the automotive ones. It can be considered that date palm fiber is one of the most available natural fiber types all over the word. It can be utilized with different polymer matrices to produce satisfactorily strong composites. The effect of the chemical treatment of the date palm fiber had been proven to increase its final mechanical properties as well as its reinforced polymer composites.

1.8 Conclusions

The NFRPC became recently a valuable type of materials due to their desirable eco-friendly characteristics. Adopting the natural wastes and resources in finding alternative low cost materials can enhance the industrial sustainability as well as reducing the environmental pollution. Biodegradability, low cost, low relative density, and the high specific strength characteristics are the main added value steps of the natural fiber composites. Widening the application of such materials can contribute to the human living standards as well as the green environmental indices. Many potential natural fiber types are still undiscovered due to the improper evaluations of such fibers. Date palm fiber is one of the most competitive fiber types for producing natural composites. Several studies had demonstrated its capability to produce different composites with various thermo plastics and thermoset polymers. Proper fiber treatment can enhance the role of date palm fiber in supporting the natural composites with more desirable characteristics to contribute the sustainable industrial applications. Further research is required to improve the natural fiber performance and to overcome their drawbacks like the moisture absorption, inadequate toughness, and reduced long-term stability for outdoor applications.

Acknowledgment The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this work through research group no RGP-VPP-133.

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Chapter 2
Bamboo Fiber Processing, Properties, and Applications

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Contents

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_2, © Springer International Publishing Switzerland 2014

Abstract Bamboo fiber is a cellulosic fiber that is regenerated from bamboo plant. It is a great prospective green fiber with outstanding biodegradable textile material, having strength comparable to conventional glass fibers. Bamboo used for fiber preparation is usually 3–4 years old. Fiber is produced through alkaline hydrolysis and multi-phase bleaching of bamboo stems and leaves followed by chemical treatment of starchy pulp generated during the process. Bamboo fiber has various micro-gaps, which make it softer than cotton and increase its moisture absorption. They are elastic, environment-friendly, and biodegradable. The fiber is bacteriostatic, antifungal, antibacterial, hypoallergenic, hydroscopic, natural deodorizer, and resistant against ultraviolet light. Furthermore, it is highly durable, stable and tough and has substantial tensile strength. Due to its versatile properties, bamboo fibers are used mainly in textile industry for making attires, towels, and bathrobes. Due to its antibacterial nature, it is used for making bandages, masks, nurse wears, and sanitary napkins. UV-proof, antibiotic and bacteriostatic curtains, television covers, and wallpapers and many other things are also prepared from bamboo fibers to lessen the effects of bacteria and harm of ultra violet radiations on human skin. Bamboo fibers are also used for decoration purpose.

Keywords Bamboo • Bamboo fibers • Tensile properties • Mechanical properties • Processing

2.1 Introduction

Bamboo is a common term applied to approximately 1,250 species of large woody grasses, ranging from 10 cm to 40 m in height (Scurlock et al. 2000). Bamboo is considered to be the second largest resource of forestry in the whole world because of its rapid growth potential. Bamboo forests are distributed extensively in tropical and sub-tropical climates in frigid zones. The area covered by bamboo forestry is estimated to be around 20 million hectares. China is considered to be rich in bamboo resources and there are about 40 families and 400 species of bamboo found only in China. This rich resource of bamboo in China covers an area of about 7 million hectare; 35 % of the area covered by bamboo forests in the whole world (Yao and Zhang 2011). Bamboo is called a cash crop because the time required for its cultivation is less, can be grown in deprived regions and has a variety of uses. Furthermore, the plant is harvested after 3–4 years (Erdumlu and Ozipek 2008). Bamboo is observed to produce an adult tree in only 1 year.

Bamboo is supposed to be one of the best functionally gradient composite materials available. It is observed that in a piece of bamboo, 1 mm^2 area near outer periphery contains approximately eight fibers and inner periphery contains two fibers (Ray et al. 2005). Bamboo fiber is a new kind of natural material, which has high potential in textile field due to some of its specific properties (Liu and Hu 2008). Bamboo fibers are also known as breathable fabric as they resemble puffball of light and cotton in untwisted form (Yao and Zhang 2011). These fibers are cellulosic in nature and are obtained from natural, reproducible resource of bamboo plants. Bamboo fibers are made from pulp of the plant, which is extracted from the plant's stems and leaves.

Total culm of bamboo comprises of 60 % parenchyma, 40 % fibers, and 10 % conducting tissues (vessels and sieve tubes). Bamboo culm constitutes 60–70 % of fiber content by weight (Liese 1992). Bamboo fibers consist of cellulose, hemi-cellulose, and lignin in the ratio 2:1:1 (Tung et al. 2004; Fukushima et al. 2003). Bamboo monofilament has four layers where crystallized cellulose micro-fibrils (MF) are aligned longitudinally with reverence to the axis of the fiber. MFCs are bonded together with lignin and hemi-cellulose (Fukushima et al. 2003). Lignin is hydrophobic and plays an important role in formation of fibers in the form of matrix whilst MFCs play a role in reinforcement. The overall structure appears to have a hydrophilic surface with hydrophobic lignin core (Jain et al. 1992).

Bamboo fibers have good properties of moisture adsorption, moisture desorption, and air permeability (Yao and Zhang 2011). Being natural they are available in abundance, have high strength, are biodegradable and renewable (Deshpande et al. 2000). The current scenario of research and investigation on bamboo fibers is limited because of limited extraction of fibers from bamboo plant (Jain et al. 1992; Jindal 1988).

2.2 Bamboo Fiber Preparation

Bamboo fiber preparation methods can be divided into two types:

1. Mechanical method
2. Chemical method

Mechanical methods give natural bamboo fibers and involve flax production whereas chemical methods are of two types namely Bamboo Viscose Rayon method and Bamboo Lyocell method.

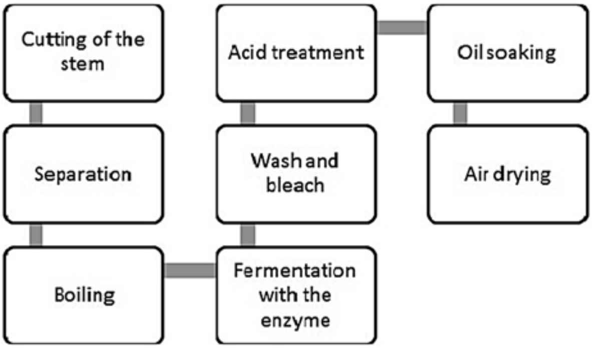

Fig. 2.1 Bamboo fiber preparation procedure

The preparation of rough and fine bamboo fiber is different. Rough bamboo fiber preparation does not involve harsh treatments like the use of bleaches and acids and soaking in oil. Preparation of rough bamboo fiber involves the following steps (Yao and Zhang 2011; Fig. 2.1):

1. Cutting of the stem
2. Separation
3. Boiling
4. Fermentation with the enzyme

The preparation of fine bamboo fiber is much similar to that of rough but also includes additional steps. The overall process involves (Yao and Zhang 2011):

1. Boiling
2. Fermentation with enzyme
3. Wash and bleach
4. Acid treatment
5. Oil soaking
6. Air-drying

2.3 Bamboo Fiber Processing

Bamboo processing is a lengthy process and has the following requirements:

1. Machine for separating rough bamboo fiber
2. High temperature pressure-cooking pot
3. Pool for bleaching and softening
4. Steam boiler
5. Equipments for washing
6. Drying room
7. Dehydrator

Table 2.1 Yield and quality of bamboo fibers depending upon their processing technique

Fiber processing procedure	Yield of fiber	Quality of yielded fiber
Rolling	High yield	Good
Mechanical comb fiber technology	Low yield	Good
Degumming defibrase system	High yield	Bad
Chemical mechanical processing technology	Low yield	Good
Processing technology by cracking	High yield	Good

Several technologies are available for the processing of bamboo fibers. Each of them has its own merits, demerits, and specifications and employs a different process. The following paragraphs include the details of the five of the technologies used for the processing of the bamboo.

2.3.1 Processing by Rolling

Rolling technology slices bamboo, which is then softened by steam so that lignin middle lamella separates out. The bonding of the fiber is then weakened through rolling or hammering. Through mechanical friction, bamboo is eventually decomposed (Yao and Zhang 2011). Quality and yield of fiber produced by this method is shown in Table 2.1.

2.3.2 Mechanical Comb Fiber Technology

With the help of mechanical equipments, bamboo is ground to make bamboo fiber. Although the strength and flexibility of the fiber is considerably damaged during the mechanical treatment process but the fiber produced is thick and short and is used in the production of bamboo fiberboard and some other low value products (Yao and Zhang 2011). Quality and yield of fiber produced by this method is shown in Table 2.1.

2.3.3 Degumming Defibrase System Technology by Explosion

As bamboo plant has high lignin content so it is difficult to perform degumming on it. Therefore, liquid water is taken and bamboo is treated at high temperature and pressure. Although this method is chemical and pollution free, has high fiber rate and uniform fiber recovery, but the process is intricate and costly and the fibers obtained are also dark colored (Yao and Zhang 2011). Quality and yield of fiber produced by this method is shown in Table 2.1.

2.3.4 Chemical Mechanical Processing Technology

In this method, bamboo is pretreated with chemical substances to dissolve the lignin, glia, and hemi-cellulose and to weaken the binding force between fibers. The fibers are then formed by mechanical external force. Deshpande introduced a chemical mechanical processing system, which can extract the bamboo fiber. It combines traditional techniques to molding grinding processes. The extracted bamboo fiber can be used for processing of isotropic composite material. This method has low fiber rate, requires more chemicals, fiber has a certain pH, and the process is complex and costly (Yao and Zhang 2011; Deshpande et al. 2000).

The above-mentioned method of production of bamboo fiber can be used as strengthening method to make a variety of composite materials. The products are further developed, and bamboo fiber produced in these methods cannot be used for weaving (Yao and Zhang 2011).

2.3.5 Processing Technology by Cracking

In 2005, Yao Wenbin and Zhang Wei of Zhejiang Forestry College put forward the cracking technology of bamboo fiber pyrolysis and separating (Yao and Zhang 2011).

Firstly, using high pressure-cooking vessel softens bamboo slices and then micro-cracks are formed. The slices are delaminated by splitting the bamboo through machine and the cracks and delamination expand along the direction parallel to the fiber leading to bamboo detaching. In external load synergies, the macro-crack of bamboo continues to expand, achieve its interfacial debonding stratified and obtain crude fiber bamboo. Coarse bamboo fibers become fine fibers after softening, carding and a series of processes (Yao and Zhang 2011).

The notable feature in this method is small damage to the fiber intensity, fiber product has even type, and also very adaptable. Bamboo fiber processed by this method has the length of 50–90 cm and the fineness of 0.06 mm (Yao and Zhang 2011). The quality and yield of bamboo fiber produced by this method is shown in Table 2.1.

2.4 Properties of Bamboo Fiber

2.4.1 Durability

The durability of bamboo fiber reinforced polypropylene can be increased by hybridizing it with small amount of glass fiber (Thwe and Liao 2002a). Bamboo glass fiber reinforced polypropylene composites have a very high fatigue resistance, which results in its extremely good durability (Thwe and Liao 2003).

The durability of bamboo fiber depends on high tensile strength, flexural strength, tensile load, moisture absorption, and molding capacity (Thwe and Liao 2002a). Unlike vegetal materials, bamboo durability is not affected by high pH. Bamboo fibers are set into concrete prisms and exposed to wetting and drying for 24 h. Then specimens without concrete and specimens with concrete are immersed in tap water. Different mechanical properties are measured after 7, 15, 30, 45, and 60 cycles. The results showed that there is no considerable change in these mechanical properties. These aggressive tests thus attest the durability of bamboo fibers (Lima et al. 2008).

2.4.2 Elasticity

Elasticity of bamboo culms is observed to increase with age. Specific modulus for elasticity measured for 1-year culm is 16,268, for 3 year culm is 14,346, and for 5 year culm is 17,414. This proves that elasticity in bamboo culms is enhanced with age. Elasticity of bamboo culms is directly proportional to specific gravity. When outer layer of bamboo is removed, specific gravity is lowered and hence elasticity decreases (Li 2004). The highest elasticity is observed in steam exploded bamboo filaments put into poly lactic acid matrix (Tokoro et al. 2008). There is a significant decrease in modulus of elasticity between longitudinal and transverse directions. Modulus of elasticity of longitudinal direction is 16.1 GPa and that of transverse direction is 5.91 GPa in the cell walls (Yu et al. 2007). Increase in filler loading increases the elasticity of bamboo fibers (Ismail 2003). Dynamic modulus of elasticity increases with increase in density, drilling resistance, modulus of elasticity, and modulus of rupture (Lin et al. 2006). As the surface area percentage of fiber band becomes larger, the modulus of elasticity increases (Sheng-Xia et al. 2005). Bamboo fibers owe their elasticity to combination of fiber rich outer part and compressible inner part (Obataya et al. 2007).

2.4.3 Elongation

Bamboo when treated with caustic soda of different concentration, show significant decrease in percent elongation at break with the increase in concentration of caustic soda (Das and Chakraborty 2008).

2.4.4 Flexural Strength

Bamboo fiber reinforced mortar laminates with reformed bamboo plate on bottom as tensile layer and a fiber reinforced mortar sheet at the top as compressive layer are exposed to have flexural strength of upto 90 MPa (Yao and Li 2003). Flexural strength shows a considerable increase at 50 % volume fraction of extracted bamboo fibers in composites (Chattopadhyay et al. 2010). Flexural strength of bamboo fiber reinforced epoxy resins is calculated to be 230.09 MN m^{-2} (Jain et al. 1992). Flexural strength of maleic anhydride treated bamboo polyester composite is increased by 50 % (Kushwaha and Kumar 2010). Autoclaved bamboo fibers reinforced cement composites have a flexural strength greater than 18 MPa. By screening out fines found in original bamboo pulp, flexural strength can be increased upto 20 MPa (Coutts and Ni 1995). Flexural strength of bamboo fibers shows a significant increase on addition of amino propyl trimethoxysilane and tetramethoxy orthosilicate after alkali treatment (Lee et al. 2009). Bamboo glass composite fibers at bamboo to glass ratio of 1:4 show flexural strength of 140 MPa (Dieu et al. 2004). Bamboo fiber reinforced cementitious plate (FRC) is found to have a very high flexural strength, which may be upto 96 MPa (Li et al. 2002).

2.4.5 Hardness

Bamboo fibers owe their hardness to the presence of cobble like polygonal cellulose nano grains with a diameter of 21–198 nm in their cell walls. These nano grains are basic building blocks of bamboo fibers. It is observed that nano grain structured fibers are not brittle (Zou et al. 2009). A continuous increase in hardness from center to outer surface is observed (Chand et al. 2006). Hardness of bamboo fibers is same in longitudinal as well as transverse directions. Measured hardness for parenchyma cell wall is 0.23 GPa. Hardness shows a decrease when moving from outer layer to inner layer (Yu et al. 2007). Research has also exposed that young bamboo culms are harder as compared to old culms and have high fracture toughness. The hardness of bamboo culms can be judged by crack deflection and crack bridging (Low et al. 2006). The hardness of bamboo reduces due to steaming treatment (Lin et al. 2006). Tangled micro-fibrillated cellulose fibers when added to poly lactic acid/bamboo fiber composites, increase the hardness and prevent crack development (Naoya et al. 2004). Bamboo is 23 % harder than oak and 13 % harder than rock maple. Fracture toughness of bamboo is measured to be 56.8 MPa $m^{1/2}$ (Amada and Untao 2001).

2.4.6 Impact Strength

Impact strength of bamboo fiber concretes is distinctly higher (Ramaswamy et al. 1983). The impact strength of steam exploded bamboo fiber filaments is very high (Tokoro et al. 2008). Bamboo fiber reinforced epoxy resins have impact strength of 63.54 KJ m^{-2} (Jain et al. 1992). The impact strength of poly lactic acid/bamboo fiber composites increases after addition of micro-fibrillated cellulose (MFC) (Naoya et al. 2004). The high percentage of alkali content in bamboo fibers reduces their impact strength (Kushwaha and Kumar 2009).

2.4.7 *Linear Density*

The linear density of bamboo fiber is calculated to be 1.44 (Erdumlu and Ozipek 2008). It is approximately one eighth of the density of mild steel whereas its tensile strength is higher than mild steel. Hence this fiber can be used as an alternate of plastic fibers for formation of many materials (Jindal 1986). Linear density of autoclaved bamboo fiber reinforced cement composites is 1.3 g cm^{-3} (Coutts and Ni 1995). Bamboo zephyr boards (BZB) exhibit less thickness and low density under dry wet conditioning cycles (Nugroho and Ando 2000). The density decreases with increase in amount of bamboo fibers in short bamboo fiber reinforced epoxy composites with varying fiber content (Rajulu et al. 2004). The linear density of BZB exhibits a huge effect on moduli of elasticity and rupture, internal bond strength, water absorption, and thickness swelling. The linear density is not seen to have any effect on linear expansion (Nugroho and Ando 2000).

2.4.8 *Moisture Absorption*

The process of moisture absorption in bamboo is observed to follow the kinetics described in Fick's theory (Kushwaha and Kumar 2010). The moisture absorption of bamboo fibers is observed to be 13 %, which is more than that of cotton, lyocell, viscose rayon, modal, and soybean (Erdumlu and Ozipek 2008). Bamboo fiber provides a reservoir of moisture, which usually diffuses into interfacial regions and decreases the shear strength (Chen et al. 2009). The moisture absorption of bamboo epoxy composite is 41 % and when it is subjected to benzoylation, moisture absorption decreases to 16 % (Kushwaha and Kumar 2010). The moisture absorption in bamboo fibers after 9 days of water immersion results in decrease in interfacial shear strength (IFSS) to at least 40 % (Chen et al. 2009). Bamboo possesses very high moisture content; green bamboo has 100 % moisture with innermost layers having 155 % moisture (Li 2004). *Phyllostachys bambusoides*; bamboo specie has moisture content of 138 %. Increased moisture absorption in bamboo/vinyl ester composite fibers leads to a decrease in IFSS. This reduction in IFSS is due to the fact that bamboo strips provide reservoir of moisture which diffuse to interfacial area and inhibit the hardening of composite (Chen et al. 2009). Moisture absorption in bamboo can be decreased from 41 to 26 %. Silane treatment also reduces the water absorption (Kushwaha and Kumar 2010).

2.4.9 *Specific Gravity*

The specific gravity of bamboo varies between 0.4 and 0.8 depending on its anatomical structure. The specific gravity of 1-year-old bamboo is very low as compared to 3- or 5-year-old bamboo culms. The average specific gravity increases about 58 %

from 1 to 3 years of age. The specific gravity value of outer layer of bamboo is observed to be twice than that of inner layer (Li 2004). The specific gravity of bamboo fiber reinforced plastic composite is measured as 0.924 (Jain et al. 1993).

2.4.10 Specific Strength

Bamboo fiber extracted by steam explosion method has a very high specific strength. The specific strength of steam exploded bamboo fiber is equivalent to conventional glass fiber (Okubo et al. 2004). The specific strength of bamboo fibers is higher than plastics, which makes them a very good choice for preparation of many substances including furniture (Lakkad and Patel 1981). Bamboo fiber's specific strength when compared with specific strength of mild steel is 3–4 times higher. Bamboo fiber reinforced plastic composites possess a very high specific strength (Jindal 1986). The specific strength of bamboo fibers can be increased by making a composite with maleic anhydride grafted polyethylene (Mohanty and Nayak 2010). A remarkable increase in specific strength of bamboo fibers is observed when they are reinforced with aluminum alloy sheets (Li et al. 1994).

The specific strength of bamboo decreases with increase in age. The best strength is observed in the bamboos of 3–6 years (Li 2004). The strength is also observed to increase with height. The strength increases from central to outer part (Li 2004). BZB is seen to have a higher specific strength than many of the commercially available wood fibers (Nugroho and Ando 2000).

2.4.11 Tensile Load

Short bamboo fiber reinforced epoxy composites with varying fiber length, when tested for resistance to acetic acid, hydrochloric acid, toluene, carbon tetrachloride, benzene, ammonia, sodium carbonate, sodium hydroxide, and nitric acid show variation in tensile load. This proves that bamboo fiber length affects the tensile load. The tensile load is found to be maximum at the fiber length of 30 mm (Rajulu et al. 1998).

2.4.12 Tensile Modulus

The tensile modulus of permanganate treated bamboo polyester fiber is seen to be increased by 118 % and that treated with benzoyl chloride is 118 % (Kushwaha and Kumar 2010). Bamboo fiber reinforced polypropylene composites show a significant increase in tensile modulus after addition of maleic anhydride polypropylene (MAPP) content in concentration of 24 % by weight. The composite is shown to have the tensile modulus of 5–6 GPa (Chen et al. 1998). Due to high tensile modulus, bamboo fibers are excellent material for making composites (Rao and Rao 2007). By the addition of glass fiber by 20 % mass the tensile modulus of bamboo glass fiber reinforced polypropylene composite increases by 12.5 %. The reduction of tensile modulus in bamboo glass fiber reinforced poly propylene hybrid composites is two times more than reduction of tensile modulus in bamboo fiber reinforced poly propylene composites after 1,200 h of aging in water (Thwe and Liao 2002b). Tensile modulus of poly propylene based bamboo composites which use steam exploded fibers increases to about 30 %, due to well impregnation and reduction in void numbers (Okubo et al. 2004). The tensile modulus improves significantly with the addition of silane coupling agent Si69 in bamboo fibers (Ismail et al. 2002).

2.4.13 Tensile Strength

The tensile strength of bamboo fibers is observed as 56.8 MPa, which is higher than that of aluminum alloy (Amada and Untao 2001). Bamboo fibers reinforced polypropylene composites and bamboo glass fiber reinforced polypropylene hybrid composites, when exposed to water, show a decrease in tensile strength and elastic modulus (Thwe and Liao 2003). The high density bamboo fibers are shown to have increased tensile strength when fabricated with maleated polyethylene contents (Han et al. 2008). The tensile strength of bamboo fiber obtained from bamboo fiber blocks is higher than that of separated fiber bundles. This is due to interaction between components in bamboo in which parenchyma cells can pass loads (Shao et al. 2010).

Poly butylene succinate bamboo fiber (PBS/BF) composite has a tensile strength of 21 MPa. When bamboo fiber esterified with maleic anhydride is added in the concentration of 5 %, the tensile strength increases to 28 MPa (Lee and Ohkita 2005). Alkali treated bamboo fiber reinforced composite is shown to have a reduction in tensile strength (Kushwaha and Kumar 2010). Bamboo fiber reinforced plastic composites have a measured tensile strength of 102.6 MN m^{-2} (Jain et al. 1993). The tensile strength of bamboo fiber reinforced epoxy resins is calculated to be 200.5 MN m^{-2} (Jain et al. 1992). The tensile strength of short bamboo glass fiber reinforced polypropylene composites is best at the fiber length of 1–6 mm (Thwe and Liao 2002b).

The tensile strength of outer periphery of bamboo fibers is approximately 160 kg mm^{-2} and that of inner periphery is approximately 45 kg mm^{-2} (Ray et al. 2005). The tensile strength of steam exploded bamboo fiber can be increased by impregnation and reduction in number of voids (Okubo et al. 2004). Green composites made from bamboo fibers show the tensile strength of 330 MPa at the fiber volume of 70 %. This tensile strength is observed to be higher than that of the composites prepared from biodegradable resins (Cao and Wu 2008). The tensile strength of permanganate treated bamboo polyester fibers is increased by 58 % and that treated with benzoyl chloride is 71 % (Kushwaha and Kumar 2010).

The tensile strength of bamboo fiber reinforced poly propylene composite after aging of 1,200 h at 25 °C temperature is reduced by 12.2 % and that of bamboo glass fiber reinforced poly propylene composite is reduced by 7.5 %. The strength reduction can be suppressed by using MAPP residues (Thwe and Liao 2003).

2.4.14 Thermal Resistance

The heat resistance of bamboo fibers is extremely good. The thermal resistance of fibers is increased by reinforcing it with epoxy resins (Shih 2007). The chemically modified water bamboo fibers when reinforced with biodegradable PBS show an improvement in thermal resistance of the resultant composite (Shih et al. 2006). Cotton/bamboo fiber composites when subjected to heat reveal that as the concentration of bamboo increases, their thermal conductivity reduces and resistance increases (Majumdar et al. 2010). Thermogravimetric analysis reveals that thermal stability of polypropylene bamboo/glass fiber reinforced hybrid composites increases as the amount of bamboo increases in the composite (Nayak et al. 2009).

2.4.15 Weight

Bamboo fibers are lightweight fibers and due to this property they can be used for the formation of composites (Rao and Rao 2007). Bamboo fiber strips when treated with sodium hydroxide solution show that increase in the percent of alkali results in decreasing the weight of strips (Das et al. 2006). Bamboo fibers have high strength to weight ratio. This ratio can be increased by reforming the bamboo (Yao and Li 2003). Increase in bamboo weight is directly related to aging (Li 2004).

2.4.16 Biodegradability

Bamboo fibers reinforced composites with poly lactic acid and poly butylene succinate are easily degraded by enzymes like proteinase K and lipase PS. Degradation rate of these composites is reduced by the addition of lysine based diisocyanate (LDI), which also enhances their tensile properties, water resistance, and inter facial adhesion (Lee and Wang 2006). Bamboo fibers obtained from compression molding technique and roller mill technique are reinforced into unidirectional composites of polyester. These composites are highly degradable by the use of enzymes (Deshpande et al. 2000). Water bamboo husk and poly butylene succinate novel reinforced composites are biodegradable in nature (Shih et al. 2006). Bamboo fiber filled poly lactic acid composites are ecocomposites as they are biodegradable and save the environment from pollution (Lee et al. 2005). Micro-sized bamboo fibers and modified soy protein resin are used to fabricate environmentally friendly composites.

These composites have increased fracture stress and young's modulus. These composites are fully biodegradable and have a great potential to replace traditional and expensive petroleum based materials in many applications (Huang and Netravali 2009). Bamboo fiber reinforced in poly butylene succinate matrix produces long fiber unidirectional composites. These composites have high values for tensile and mechanical properties. The mechanical properties are enhanced as the amount of bamboo fiber is increased. Young's modulus of these composites is predicted by laminate theory but experimental results show that ratio obtained by laminate theory is lower than the actual (Ogihara et al. 2008).

2.5 Applications of Bamboo Fibers

2.5.1 Biofuel Production

Bamboo is observed to be more productive as compared to many biofuel producing vegetable plants. Bamboo is suitable for fuel production because it has low alkali index and ash content. Moreover it has low heating value than many of the woody biomass feed stocks. Further research is required on bamboo fibers for commercialization of biofuel (Scurlock et al. 2000). Pyrolysis of bamboo in the presence of high temperature steam and inert atmosphere containing nitrogen produces a product. The product when analyzed indicates exploitation of derived char as activated carbon precursor or solid fuel for gasification. The composition of liquid fraction reveals it to be a biofuel (Kantarelis et al. 2010). The treatment of bamboo fibers with cold sodium hydroxide/urea disrupts the recalcitrance of bamboo fibers effectively and leads to generation of highly reactive cellulosic material. This material, on enzymatic hydrolysis is converted into bio-ethanol. Bamboo fiber derived bio-energy products include charcoal, biofuel, pyrolysis, firewood, gasification, briquettes, pellets, and biomass (Li et al. 2010). Bamboo hemi-cellulosic fibers having 2.4 % hemicellulose content have been extracted and pulped. The pulp produce can be used to produce biofuel and bio-ethanol after further modification (Vena et al. 2010).

2.5.2 Construction Material

Bamboo is one of the oldest and most versatile constructing materials. Bamboo has certain qualities due to which it can be used for construction purposes. These qualities include its hardness and lightweight. Bamboo does not require processing or finishing. Bamboo constructions are strong and resistant to even earth quakes (Jayanetti 2000). Bamboo fibers are used in concrete reinforcement, bamboo fencing, and housing (Diver 2001). It can be used as reinforcement alternative to steel in concrete due to its high specific strength, tensile strength, tensile modulus, hardness, and other mechanical properties (Youngsi 2007). Studies on microstructure of bamboo reveal that bamboo is functionally gradient material. This property can be used for the formation of reinforced concrete composites, which can be used in construction of strong buildings (Ghavami 2005; Aziz et al. 1981). Bamboo is used for concrete composite reinforcement (Lima et al. 2008).

2.5.3 Food and Feedstock

Fresh bamboo shoots and shoot fibers are used as foods. Bamboo shoots and fibers are very popular in Asian stir-fry and as pickled condiment. Most important genus for production of edible shoots is *Phyllostachys*. Bamboo fiber derived food products include bamboo tea, bamboo wine, bamboo vinegar, and charcoal coated dry fruits (Diver 2001). Bamboo fibers are also used for preparation of food packaging material like cellophane. The nutritive value of bamboo exposes that total carbohydrate content of bamboo leaves decreases throughout the growing season, remains stable for some time and increases during winter. Unlike carbohydrates, crude protein content is high in growing season and is decreased in winter season. The concentration of fiber and proteins make it a good source for feedstock. The bamboo has a potential for winter forage for goats and some other livestock. Bamboo also reduces the exposure of livestock animals to gastrointestinal parasites (Halvorson et al. 2011).

2.5.4 Musical Instruments

Grass bamboo can be used in preparation of musical instruments like wind, string, and percussion instruments. Bamboo is ideally suited for manufacture of xylophone bars and chimes, flutes and organs, violins and zithers and violin bows. Bamboo plates can be used for forming body and neck of acoustic guitar as it is easily available and is economical (Wegst 2008). Bamboo is nearly immutable, and hence resistant to change. Bamboo is straight and cylindrical; this structure is best suited for production of musical instruments like flute (Grame 1962). Bamboo used for formation of musical instruments should be harvested at 3–5 years of age for high strength and durability (Diver 2001). Bamboo culms are also used for production of wind chimes (Perdue 1958).

2.5.5 Paper Industry

The shape, chemical composition and structure of bamboo are very suitable for pulping. Pulping performance and pulp strength make bamboo fibers one of the most suitable materials for paper production. Bamboo pulp mill may result in improvement in paper industry like substituting pulping techniques. The paper produced from bamboo has certain advantages, which include reduction in pressure of wood demand, less pollution, and environmental protection (Kefu 2002). Bamboo pulp produced from hemi-cellulosic fibers can be used potently for the production of paper. In paper industry, bamboo fiber pulp can be used in the formation of newsprint, bond paper, toilet tissue, cardboard, cement sacks, and coffee filters (Vena et al. 2010).

2.5.6 Pharmaceutical Industry

Bamboo fibers have an excellent characteristic of inhibition of bacterial growth, absorption of peculiar smells, and hygroscopicity. Due to these characteristics, bamboo fibers are used as non-woven medical and hygienic materials (Yi 2004). Flavones can be extracted from bamboo leave fibers by leaching method. These flavones are used in preparation of many drugs (Gang et al. 2000). Chemical contents of bamboo fiber are bacteriostatic and bacteriolytic (Zhong-Kai et al. 2005). Eating bamboo fiber reduces the rate of intestinal natural flora and pathogens. This property is applied to produce a bamboo drug for gastrointestinal infections (Anping et al. 2005). Moreover bamboo fibers can also be used for the production of sanitary towels, gauze, bandages, absorbent pads, surgical wear, doctors' coats, and medical masks. Bamboo fibers have gentle make up, due to this reason only a few people are allergic to bamboo fibers; this property plays a role in production of masks etc. It is light, durable, and inexpensive (Bamboo Groove 2008).

2.5.7 Textile Industry

Natural bamboo fibers have some of the excellent properties, which make it a very potent material to be used in textile industry. Refined bamboo fibers with low non-cellulosic content can be used in textiles (Liu et al. 2011). Bamboo fiber luster is closer to that of silk. It can be used for knitting and weaving purposes (Yi 2004). Study on bamboo fibers revealed that its chemical composition is same as that of all the bast fibers, which means cellulose content is in majority and lignin content is present in small amount. The structural properties of bamboo are different from those of other textile producing plants. Bamboo is shown to have high potential in textile industry (Yueping et al. 2010). They are used for the formation of socks, under wears, T-shirts, bathing suits, bathing suit cover ups, towels, Sleep wear, face masks, sanitary napkins, bed sheets, pillows, baby diapers, bullet proof vests, table cloth, blinds, and mattresses. Bamboo fibers are observed to have excellent characteristics for spinning and weaving (Hengshu 2004). Dyeability of bamboo can be enhanced by plasma treatment. Longer the treatment time, higher the roughness and hence higher is the dyeability, which leads to increase in potential to be used as textile.

2.5.8 Cosmetic Industry

The potential of bamboo can be used in cosmetic industry (Liese 1992). Bamboo fibers are widely used in cosmetic industry in the formation of cosmetics for acne prone people (Qin-Rong 2006).

2.5.9 Sports Industry

Bamboo fibers can be used as reinforced composite materials in the formation of sports goods like polo balls, base balls, etc. These sport items made from bamboo fiber composites are highly durable and strong (Subic et al. 2009).

2.6 Conclusion and Future Prospects

Research and investigation regarding use of bamboo fiber for the well-being of human beings is limited because of limited availability and tough extraction process. The techniques used for bamboo fiber extraction nowadays give low fiber yield or low quality fiber. Studies are further required for improving the extraction, preparation, and processing techniques for bamboo fiber. Bamboo fiber is a potent fiber to be used for many applications. It is an outstanding biodegradable textile material, which does not absorb ultraviolet and infrared rays. For commercializing bamboo based products much research and knowledge is required so that the world may get benefit from an inexpensive source of fibers.

Super strong and durable bamboo is being used presently for flooring and paneling. Its stability, hardness, flexibility, and strength are its most remarkable qualities. Bamboo has a bright future as an alternate to wood for formation of furniture and construction material. Bamboo fiber can also serve as an alternate to cement and concrete in near future. As bamboo is easily pulped, it can be used efficiently for paper production and may benefit us with less cost and high availability. Textile industry is expected to get huge advantages from bamboo fibers in near future, as bamboo is lightweight, environmental friendly, and bacteriostatic. Also it is antiallergenic and soft like silk which makes it best suited for its use in textile industry.

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Chapter 3
Abaca Fiber: A Renewable Bio-resource for Industrial Uses and Other Applications

Waseem Shahri, Inayatullah Tahir, and Burhan Ahad

Contents

Abstract Of the various fibers obtained from natural sources, fibers obtained from abaca offer a great potential to be used as a renewable bio-resource for various industrial or extra-industrial applications due to their high mechanical strength, durability, flexibility, and long fiber length. The fiber is obtained from the leaf sheaths or petioles of the abaca plant (*Musa texitilis*), a plant native to Asia (Philippines). The plant grows well in shady and humid areas (altitude below 500 m and temperature 27 °C) and requires well-drained loamy soil for cultivation. It can be propagated by seeds, suckers or corm, or through tissue culture techniques. Since the cultivation of abaca is mainly confined to Philippines and other adjacent areas, it has also been introduced to other regions like Malaysia, Indonesia, etc. The topmost producer of abaca fiber is Catanduanes province. As far as its extent of cultivation is concerned, it is being grown on about 172,524 ha providing employment to a large number of farmers and other associated traders, exporters, or manufacturers.

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_3,

The harvesting and extraction of fiber from abaca is laborious process which involves many operations like tuxying, stripping, drying, and final processing. Stripping and drying of fibers is either done manually or mechanically. After extraction, different grades of fibers are obtained which are then accordingly used for different set of industrial activities. Abaca fiber is chemically composed of cellulose, pectin, lignin, and significant quantities of glycerides, ketones, fatty acids, and other compounds. Being regarded as the strongest natural fiber in the world, it can be put into various modern sophisticated technologies like automobile industry and as a raw material for other important industries like paper and pulp industry, textile industry, and furnishing industry, besides being used as a fuel. Now-a-days, abaca-reinforced polymers are used and preferred over synthetic polymers. In the ecological perspective, the products obtained from abaca fibers are eco-friendly and the production of abaca-fiber composites is energy-efficient as it has been found to save 60 % energy besides reducing CO_2 emissions. Moreover, abaca plantations are used to prevent soil erosion and in promoting biodiversity rehabilitation. Waste material produced from abaca plants is also used as organic fertilizers to replenish the soil fertility.

Keywords Bio-resource • Cordage • Eco-friendly • Fiber • Polymer • Propagation • Textile

3.1 Introduction

Today we are familiar with a number of natural fibers obtained from various plant sources like cotton, jute, cannabis, pineapple, sisal, bamboo, coconut, etc. These fibers because of their extraordinary mechanical and tensile properties find their use in many industries for the production of numerous commodities like fabrics, carry bags, and also as filling material for furniture items (Pothan et al. 2003). Despite the advantages of using these natural fibers, their mechanical degradation or thermal degradation during processing makes them unsuitable for various applications and thus limits their utility (Espert et al. 2004; Majid et al. 2008). Of the various fiber-yielding plants, abaca is one of the potential candidates that offer a good quality fiber with high mechanical strength and durability and is regarded as the strongest natural fiber in the world (Umali and Brewbaker 1956; Hadi et al. 2011). Keeping in view the applications of natural fibers like abaca fibers in various industrial and miscellaneous activities, there is a need to present a comprehensive review on the various aspects of abaca ranging from its morphology, cultivation, fiber extraction, applications, and other related aspects. In the present chapter, we therefore attempt to consolidate the information scattered in various research papers, conference proceedings, and FIDA (Fiber Industry Development Authority, Philippines) annual reports to discuss the role of abaca as a potential renewable bio-resource for various applications of industrial and other domestic importance.

3.2 Morphology of Abaca (*Musa textilis*) Plant

Botanically *Musa texitilis* and commonly known as abaca or Manila hemp or Cebu hemp or Davao hemp belongs to family Musaceae (Moreno 2001). The plant is native to Asia (Philippines) and is widely distributed in the humid tropics and grows abundantly in Philippines, Ecuador, and Costa Rica (Ocfemia 1930). Philippines is the leading producer of abaca in the world followed by Ecuador (Umali and Brewbaker 1956; Hadi et al. 2011). Morphologically the plant resembles the banana plant (*Musa sapientum*) which grows from the rootstock producing about 25 fleshy stalks (fiberless) and forms a circular mat called as "mat" or "hill." About 12–25 leaves are produced from each stock and these leaves have overlapping petioles that cover the stalk to give a shrubby appearance and form a "false trunk" or "pseudostem." The diameter of the pseudostem is about 30–40 cm and the leaves grow in acropetal succession. The leaves are bright green on the adaxial surface and yellowish green on the abaxial surface whose length ranges from 1 to 2.5 m (3–8 ft) and width ranges from 20 to 30 cm. The plant grows to a height of about 12 ft (4–8 m) as the oldest petioles develop from the base of the stalk while the younger ones develop successively from the higher points on the stalk. The sheaths or petioles yield the valuable abaca fibers whose length range from 1.5 to 3.5 m and are variously colored including white, brown, red, black, or purple which is reported to depend on the plant variety and the position of petiole. It has been found that the fibers obtained from outer sheaths are darkest in color than those obtained from the inner sheaths. A mature abaca plant produces an inflorescence of small dark red flowers arranged in spikes which ultimately develop into banana-like fruits. These fruits (8 cm long and 2.5 cm in diameter) are inedible having green skins with white pulp inside consisting of large and black seeds (Fig. 3.1).

3.3 Abaca Cultivation

Abaca grows well in the regions having an altitude below 500 m with an average rainfall and temperature of 2,000–3,200 mm/annum and 27 °C respectively and 75–80 % relative humidity. The latitudinal extent of its successful cultivation is approximately 5°S and 15°N (Moreno 2001). However, the areas with average temperature ranging from 20 to 27 °C and having altitudinal extent upto 1,000 m are also suitable for cultivation (Halos 2008; Sievert 2009). The plants require fairly rich, well-drained loamy soil for cultivation. The plants have been reported to thrive well in shade and show improvement in plant height, leaf area, length and girth of pseudostem and more importantly the fiber yield which has been found to be significantly increased (upto 165 %) under shady conditions (Bande et al. 2012). Recent results have also shown that 50 % reduction in light quality leads to significant improvement in plant height, pseudostem length, and cumulative leaf area.

Fig. 3.1 Some morphological features of abaca: abaca plant (**a**), petiole (**b**), flower (**c**), heart (**d**), fruit with black seeds (**e**) and extracted fibers (**f**) (Note: photographs downloaded from the Internet)

The increased productivity of abaca under shady conditions has been suggested to be due to decrease in photoinhibition and photooxidative damage (Bande et al. 2013). The plants are propagated by seeds and by vegetative propagules like suckers, corm or tissue culture; but the vegetative propagation is the widely adopted practice (Sievert 2009). Suckers are traditionally used for replantation of old plantations and corms are preferred for new plantations. The mature rootstock pieces or vegetative propagules are usually planted at the start of the rainy season with the average distance of 2.0 m × 2.0 m and 2.5 m × 3.0 m for smaller and larger varieties respectively. It has been reported that intercropping abaca plants with leguminous plants leads to increased yields as they provide shade effect besides enriching the soil with nitrogenous fertilizers by the symbiotic nitrogen fixers associated with their root nodules (Halos 2008; Bande et al. 2013). The plants are initially allowed to grow for about 12–26 months after which the fibers (petioles) are harvested every 3–8 months. The plants are allowed to grow for a maximum lifespan of 8–10 years and are replaced thereafter. The volcano slopes have been reported to be a preferred environment for its luxurious growth (Borneman and John 1997). Normally the use of fertilizers is not practiced in abaca cultivation but the recent studies have revealed that fertilizer application (NPK) to abaca plantations enhances their growth performance by positively affecting dry matter production and growth kinetics (Bande et al. 2012, 2013).

Although the abaca cultivars have been introduced to other regions like Malaysia, Central America, Indonesia, etc., they are commercially cultivated in Philippines (except the northernmost part) and Ecuador. The important productive areas of

Table 3.1 The number and distribution of some abaca manufacturing units

Manufacturing unit	Number	Location
Pulp millers	6	Laguna (1), Bicol (2), Leyte (2), and Mindanao (1)
Cordage manufacturers	6	Metro Manila (2), Laguna (1), Albay (1), Cebu (1), and Davao (1)
Fibercraft manufacturers	108	Bicol, Eastern Visayas, Western Visayas, Southern Mindanao, and Central Visayas

abaca cultivation are located in Bicol, Caraga, Southern and Western Mindanao, and Eastern Visayas (FIDA 2009). Today it is cultivated in 56 provinces of which the top five producers include Catanduanes, Northern Samar, Leyte, Davao oriental, and Surigao del Sur that account for 32.0, 10.2, 9.8, 5.8, and 5.0 % share in total production respectively. United Kingdom, Japan, China, Indonesia, and USA are the topmost importing countries of raw abaca fibers and that Germany, USA, Japan Germany, Italy, china, and Hong Kong being the major importer of processed abaca products like pulp, cordage, fibercrafts, and fabrics (FIDA 2012).

Being a renewable resource, the demand for the abaca production is increasing day by day and the reports (FIDA 2012) have confirmed that abaca is being cultivated on about 172,524 ha and the average production has increased from 66,903 to 73, 274 m. As far as the abaca industry is concerned, the major players include involving about 111,103 farmers, many strippers, classifiers, about 506/17 abaca traders/trader-exporters (licensed), 13 licensed fiber exporters involved in grading and baling process, and many manufacturing or processing units involved in the production of commercial abaca commodities as given in Table 3.1.

3.4 Harvesting of Abaca Fiber and the Recommended Varieties

Although abaca fibers are obtained from the petioles of abaca leaves, its harvesting is not simple. It requires a set of highly laborious activities involving several operations that range from separation of primary sheaths from secondary ones to extraction and to pre-processing of the fiber (to obtain raw fiber) for various industrial applications. The main operations involved in its extraction include:

1. Tuxying
2. Stripping
3. Drying

The tuxying operation involves the separation of primary sheaths from secondary ones. In this process, the petiole's outer layer (fiber-bearing layer) is removed in the form of strips or tuxies, which are then freed at one end and pulled off. The stripping operation or cleaning operation involves the scraping of the pulpy material from outer fibrous layer of the petiole for extracting the fiber strands. The stripping is done either by hand or by use of machines. In the Philippines, generally hand-stripping is

Table 3.2 Various recommended grades of abaca fiber

Hand stripped and spindle-stripped abaca	Decorticated abaca
Excellent: S2, S3, S–S2, S–1	AD-1, AD-2, AD-3
Good: I, G, H	
Fair: JK, M1	
Residual: Y, OT	

Table 3.3 The important applications of various recommended grades of abaca fiber

Grades	Industrial and other applications
S2, S3, I, G, JK, M1, Y	Cordage products like ropes, twines, etc.
S2, I, G	Tea bags, sausage skin, base paper, filter paper, etc.
G, JK, M1, Y, OT	Currency paper, cigarette paper, charts, file folders, parchment paper, envelops, book binders, time cards, etc.
S2, I, G, JK	X-ray negative, vacuum filter, lens wiper, diapers, medical gas masks, gowns, bed sheets, etc.
All grades + wastes	Stationery, lamp shades, paper sheets, bags, albums, and photo frames, dividers table clock, flowers, etc.
S2, G	Fibercrafts like handbags, placemats, hammocks, carpets, rugs, doormats, fishing nets, wall papers, etc.
S2, S3, I, G, H	Handwoven fabrics like Pinukpok, Sinamay, Dagmay, etc.
Bacbac and Lupis	Baskets
S2, Bacbac	Furniture
JK, M1, Y, OT	Wire insulators, cables, automobile composites and components
OT + wastes	Fiberboards like tiles (roof and floor), blocks, reinforcing fiber concrete
Abaca plant	Musafel (fuel)

practiced while in Central America (Costa Rica), machine-decortication is being done in which the stalks are cut into 0.6–2 m long strips followed by their crushing and scraping inside the machines to yield fibers. In the drying operation, the extracted raw fibers are dried by hanging them in the sun (sun-drying) or by advanced mechanical drying as employed in Central America. After drying of the raw fiber, it is then graded on the basis of fiber quality. The excellent or high-quality fibers are separated from the rest and are combed to detangle and removal of other impurities. Moreover, the further processing of the extracted fibers depends on their quality-related parameters and hence different grades are utilized for different set of industrial activities.

The quality of abaca fiber is determined by many parameters like extraction procedure, strength, fiber length, color, and texture. Based on the cleaning or stripping process the abaca fiber has been classified into various grades as given in Table 3.2. In addition to these mentioned grades, the dried thin strips (5 mm or 1/8th inch wide) of abaca leaf sheaths is called "Lupis" and the outermost light brown covering of the abaca stalk (petiole) is called "Bacbac." The different grades of abaca fibers are then put into various industrial or other uses as listed in the Table 3.3.

About 200 varieties of abaca are known to exist in Philippines of which only a few varieties are cultivated on a large scale, e.g., Bongolanon, tangongon, and Maguindanao. However, the new and better varieties are being introduced and recommended for abaca cultivation, which includes Inosa, Laylay, and Minenonga

Table 3.4 The important characteristics of some recommended abaca varieties

Characteristics	Inosa	Laylay	Minenonga
Maturation time	697 days	720 days	594 days
Stalk	Hardy (from root to tip) and deep purple brown	Dark brown upto midpoint of the petiole and limestone green towards tip	Large and vigorous, deep purple or brownish
Resistance	Drought/strong wind resistant	Susceptible to wind	Resistant to strong wind
Stripping	Difficult	Easy	Easy
Fiber recovery	1.41 %	1.29 %	1.18 %
Tensile strength	57.21 kg/g-m	56.63 kg/g-m	56.89 kg/g-m
Yield	1.27 tons/hectare	1.09 tons/hectare	1.31 tons/hectare

(Lomerio and Oloteo 2000; FIDA 2009). It has been reported that the immature (8–10 month old) stalks of abaca variety "Inosa" provide an excellent material for paper and pulp industry due to their desirable properties like low lignin/ash and high α-cellulose/holocellulose/hemicelluloses content (Moreno and Protacio 2012). Moreover, the hybrid varieties particularly Canarahon × Korokotohan (1841-series) has been found to be quite promising in terms of yield and fiber quality (Moreno 2001). The important characteristics of abaca varieties ("Inosa," "Laylay" and "Minenonga") recommended for cultivation in Philippines are listed in Table 3.4.

In addition to the above mentioned varieties, NARC (National Abaca Research Centre, Philippines) have identified and selected five new accessions for fibercraft industry and about seven accessions for paper and pulp industry. Some of which include NARC-MIO, NARC-M107, NARC-159, NARC-M168, and NARC-M179. These accessions have been selected as promising ones due to their high fiber-yielding ability, long fiber length, appropriate texture, uniform fiber strand, and higher tensile strength. Moreover, the accessions selected for pulp and paper industry were found to have higher flexibility, strong folding strength, and higher resistance to mechanical damage like tearing (qualities required for production of high-quality paper, i.e., thin, strong, and highly porous paper). As far as the chemical composition of the selected accessions is concerned, they have been found to contain higher cellulosic content (holocellulose (83.02–86.90 %), α-cellulose (52.50–64.21 %), and hemicellulose (16.23–26.20 %)) and lower ash content (0.84–1.72 %) (Moreno et al. 2005).

3.5 Applications of Abaca Fiber

As mentioned above, abaca fiber is considered as the strongest natural fiber and is obtained from leaves (petioles) which are composed of elongated and slim cells (Umali and Brewbaker 1956). Classified as a hard fiber like *coir*, sisal, and *henequin*, it is highly prized for its exceptional mechanical (tensile) strength, flexibility, underwater durability, buoyancy, and long fiber length. These properties are due to its high Runkel ratio, i.e., the ratio of two times the fiber cell wall thickness over the fiber cell lumen width. It has been found that the fiber has higher tensile strength than its synthetic counterparts like nylon and rayon and that it is rotting resistant with its specific flexural strength almost equal to glass fiber (Moreno 2001; Bledzki et al. 2008). Moreover the lustrous and colored nature of the fiber makes it a preferred natural fiber. Chemically the abaca fiber is composed of cellulose, pectin, and lignin of which the lignin content is as high as 15 % in addition to significant quantities of ketones, triglycerides, *ö*-hydroxy-fatty acids (C22–C28), monoglycerides, fatty alcohols, and esterified derivatives of p-hydroxycinnamyl acids (ferulic acid; 4-hydroxy-3-methoxycinnamic acid and p-coumaric acid; 4-hydroxycinnamic acid) containing long-chain alcohols (C20–C28). It has also been found to contain diglycerides, steroid hydrocarbons, R-hydroxy-fatty acids, sterol esters, and glycosides in minor quantities (del Río et al. 2004; del Río and Gutiérrez 2006). The excellent tensile strength and exceptional under water durability of abaca fibers has led to their usage in the production of many useful industrial and domestic products. The abaca fiber is used for making ships' ropes, fishing lines, and fishing nets. It also finds their usage in the production of power transmission ropes as well as in well-drilling cables besides being used for production of cordage for naval and marine vessels. The durability and flexibility of abaca ropes is evident from the fact that a 1 in. (2.5 cm) abaca rope requires at least 4 metric tons (8,800 lb) to get broken (Borneman and John 1997). Moreover, the high-quality fiber obtained from abaca provides an excellent material for paper and pulp industry where it is processed into a variety of paper products like bank notes, security papers, cigarette papers, and filter papers. In textile industry, it is used in the manufacturing of bags, table mats, carpets, furniture fillings, and sausage casings besides being used in the production of lightweight but strong fabrics (from inner fibers without spinning) for hats, garments, and shoes. The finest quality of abaca is Lupis and Sinamay. It has been estimated that the global consumption of abaca fiber accounts for about 80 % in the production of speciality paper products and about 14 % in cordage products while the remaining 6 % in other usages. The applications of abaca fibers can be summarized under the following headings (FIDA 2009; Moreno and Protacio 2012):

1. *Paper and pulp industry*: Filter paper, Cigarette paper, sausage skin, base paper, currency paper, envelopes, book binders, parchment paper, special art paper, adhesive tape paper, lens, vacuum cleaner bag, electrolytic condenser paper, high grade decorative paper, time cards, optical lens wiper, X-ray negative, oil filter, etc. hand-made paper like sheets, multi-purpose cards, balls, decorative items (flowers, photo frames, table clock, and lamp shades)
2. *Fabrics and fiber crafts*: bags, rugs, carpets, wallets/purses, placemats, door mats, fishing nets, special fabrics like Sinamay, dagmay, and pinukpok in addition to coasters, wallpapers and baskets, some non-woven fabrics like diapers, gowns, etc.
3. *Furnishing and household construction items*: Furniture fillings, carpets, rugs, and mats. Tiles for roofs and floor, hollow blocks, fiber boards, etc.
4. *Fuel*: Musafel
5. *Miscellaneous applications*: Insulators for wires and cables, components of automobiles (particularly in reinforced form), preparation of wigs

The modern technology involves the use of abaca-reinforced polymers to make them more applicable for various purposes. The main focus is the use of thermosetting or thermoplastic matrices like polyesters or polypropylene (Shibata et al. 2002, 2003; Ochi 2006; Teramoto et al. 2004; Bledzki et al. 2007; Hadi et al. 2011) which led to the use of abaca fibers (reinforced) in under floor protection or passenger cars. This application involves a combination of abaca-reinforced polypropylene thermoplastic and the technique has been patented by Daimler Chrysler's researchers (Bledzki et al. 2006) and the manufacturing process has been initiated by Rieter Automotive, Switzerland. The experimental analysis of abaca-reinforced polypropylene polymer at various fiber lengths employing different methodologies (mixer-injection molding, mixer-compression, and direct compression process) has also revealed that increase in fiber length leads to an increase in the tensile or flexural properties with the effective method of reinforcement being mixer-injection process. Not only abaca, but the fibers obtained from other related members like *Musa acuminate* or *Musa sapientum* have been used to reinforce polypropylene to yield a valuable composite fiber (Faria et al. 2006; Bledzki et al. 2008). It has been suggested that the increases or enhancement of the durability or tensile strength of composite fibers is due to the changes in the Melt Flow Index (MFI) which can be altered by changing the level of three important variables like abaca fiber (length and composition), maliec anhydride (concentration), and the impact modifier (Hadi et al. 2011). The use of these natural fiber-reinforced green composites offers many advantages over the synthetic counterparts like dependency on renewable raw material, low production cost, specific mechanical strength, energy-efficient manufacturing, eco-friendly (low CO_2 emissions), and more importantly biodegradability (Cao et al. 2006; Pervaiz and Sain 2003). The abaca fiber has been used to reinforce furan resin (a condensate of furfuryl alcohol produced from agricultural residues like corn cobs or rice hulls) to produce a green composite. The furan resin, being resistant to many acids, alkalis, or solvents, on reinforcing with cellulosic abaca fiber therefore provides an excellent and eco-friendly material for various industrial applications (Tumolva et al. 2009). It has been reported that the abaca fiber-reinforced PP (polypropylene) composite has high tensile strength, high flexural strength, and good acoustic resistance besides being resistant to moulds, rot or UV damage and cost-effective (Proemper 2004). Moreover, comparison of abaca-reinforced PP composite with other natural fiber-reinforced composites likes jute-PP composite and flax-PP composite has revealed its superior flexural strength and damping properties compared to other composites despite the fact that jute-reinforced PP composite showed higher tensile strength. Furthermore, the use of coupling agent (MAH-PP; maliec anhydride) has been found to significantly improve the tensile as well as flexural strength of abaca-PP composite (Bledzki et al. 2007). Similar investigations on the improvement in tensile strength and water absorption capacity of abaca-reinforced epoxy composites have also been made where the results have confirmed the efficacy of plasma treatment over conventional sodium hydroxide treatment. Plasma treatment exposure for 2.5 min has been found to result in 92.9 % improvement in tensile strength and reduction in water absorption capacity of the fiber epoxy-composite and has been attributed to increase in compatibility between abaca fiber and the epoxy matrix (Paglicawan et al. 2013). Moreover, the heat-treated abaca-reinforced starch based biodegradable resin has also been prepared whose tensile strength has been found to be comparable to glass fiber-reinforced plastics (Takagi 2011). Abaca fibers are also blended with metallic threads and polyester to put them in multiple uses (FIDA 2012).

3.6 Potential Areas of Abaca-Fiber Application

1. As per the “End-of-Life-Vehicle Regulation” by the European parliament, the natural fibers like abaca will be used in designing and manufacturing of car components which will enable their safe disposal and recyclability at the end of their life. Moreover, research is being conducted to develop needle punched abaca fabric for possible use in the production of padding and backing for automotive industry.
2. Abaca fiber has a great potential in ship building, aeronautics, and construction of high-rise buildings.
3. Compared to cordage made of synthetic fibers, the abaca fibers are biodegradable and therefore can be dumped without any environmental hazard. Moreover, the poor reflecting ability of abaca ropes makes them suitable for use in American movie-making industry as they do not reflect on exposure to klieg lights.
4. The use of abaca fibers in preparation of sausage casings has a great potential due to their inability to dissolve in boiling water besides being free from any health hazard (if eaten mistakenly)
5. Abaca fibers offer a good and easily available substitute for wood pulp, thereby reducing the pressure on the conventional sources of pulp-yielding plants. A good example is provided by Japan where the Japanese currency (¥10,000, 500, and 1,000) has been found to contain about 60 % abaca components. Similarly there are reports from China where a huge increase in demand for abaca fibers is expected to meet the requirements for recycling waste paper. Similar example is provided by the European company “the PH Glatfelter” who has produced the disposable K-cups made of special filter paper containing 100 % abaca fiber.
6. Abaca fiber also has great potential in the production of world-class furniture like sofas, tables, chairs, beds, etc.
7. The production of products like abaca soap or lotion with anti-aging or therapeutic properties will also revolutionize the cosmetic industry.
8. It also offers great potential for textile industry as blending of abaca fibers with other natural fibers like silk can be used to produce fabrics of excellent quality, e.g., the manufacturing of denim by Asiatex (The Asia Textile Mills, Inc.) in Calamba City by bending of abaca (40 %) and polyester (60 %). Other fabrics like shirts, blouses have also been developed and research is being conducted to produce fabrics of extraordinary qualities like antimicrobial and “stay cool and fresh.”
9. Abaca-reinforced composites have a good potential for use in automotive plastics.

3.7 Abaca Market Demand and Supply

The Philippines, being the world's leading producer of abaca fiber, has been reported to supply about 84 % of the global abaca requirement followed by Ecuador which supplies about 16 % fiber requirement (FIDA 2009). The abaca industry has been found to maintain a stronghold in both national/domestic and international markets since 1989 as the demand for raw abaca fibers or processed products has grown to a great extent and is expected to grow further with the advancement in technology and scientific formulations which will ultimately boost the Philippine economy. Moreover, with the availability of new international markets, the demand of abaca fibers (raw) or the processed products has increased to a great extent which is reflective of the marginal increase in its export. As per the reports, the export volume of abaca products has registered a growth rate of 121.4 % per year (Lalusin 2010). The growing concern for environment protection or forest conservation is an important reason of ever-increasing demand for natural fibers, so is the case with abaca and there is an expectation that the demand will continue to increase keeping in view the potential of the fiber and its processed products. Despite the increasing demand and higher market prize, the production of abaca has not been found to keep pace with the demand. The main reasons for this gap between demand and supply are the low yield and low fiber quality (Moreno 2001). Moreover, low-income generation from abaca farming, the laborious process of fiber extraction and availability of less human resources (who prefer jobs than traditional farming) is also responsible for its reduced productivity. Furthermore, the old typhoon damaged or disease-infected plantations (Sharman et al. 2000a, b; Villajuan-Abgona et al. 2001) add to the problem. *Banana bunchy top virus* (BBTV), *Banana bract mosaic virus* (BBrMV), *Abaca mosaic virus* (AMV), and *Cucumber mosaic virus* (CMV) are the four main viruses which have been found to infect abaca plants (Bajet and Magnaye 2002; Furuya et al. 2006; Pietersen and Thomas 2001; Pinili et al. 2011; Sharman et al. 2000a, b) of which BBTV (transmitted by banana aphid; *Pentalonia nigronervosa* Coq) has been reported to contribute to huge economic loss and resulted in destruction of many abaca plantations in Philippines (Calinisan 1939; Raymundo and Bajet 2000). Recently, the mutation breeding program has been initiated to produce virus-resistant (BBTV and BBrMV) abaca cultivars by using gamma irradiation (Cobalt 60) in two abaca cultivars Tangongon (TG) and Tinawagan Pula (TP) (Dizon et al. 2012).

3.8 Ecological Implications

The abaca-reinforced composites offer an eco-friendly material for many industrial applications with the same strength and qualities as provided by synthetic fibers or glass fibers. The excellent example is provided by the use of abaca composites in car manufacturing by Chrysler-Daimler. Moreover, the production of these fiber composites is energy-efficient as it has been found to save 60 % energy besides reducing CO_2 emissions. Moreover, abaca plantations have been used to prevent soil erosion and in promoting biodiversity rehabilitation by intercropping abaca plants in monoculture plantations or rainforests. Waste material produced from abaca plants is also used as organic fertilizers to replenish the soil fertility.

3.9 Conclusions and Future Prospectus

1. Although the cultivation of abaca plants is being currently practiced on large scale in Philippines, Ecuador, and other adjacent areas where its plantation is done in the humid regions having an altitude upto 500 m, the studies have also revealed that its cultivation could be extended upto 1,000 m latitudinal extent which is suggestive of the fact that there is a great scope for expanding the cultivation practice of abaca in other neighboring regions or regions with similar climatic conditions so that its production could be increased to the extent that the gap between the demand and supply will be minimized or nullified.
2. Abaca plants in Philippines are generally propagated from vegetative propagules or seeds in a traditional way (without any modern agricultural practice). However, the recent studies have revealed that the use of fertilizers leads to enhancement of growth in abaca thereby paving way for higher fiber yields. Moreover, FIDA (Philippines) is also providing the micropropagated plant material for successful cultivation of abaca.
3. Although about 200 varieties of abaca are known to exist, only a few varieties are cultivated on commercial scale because most of the varieties are either low-yielding or yield fiber of inferior quality. Now, NARC (National Abaca Research Centre, Philippines) and FIDA have been and are promoting research programs so that better (high yielding and good fiber quality) varieties will be introduced to overcome the problem.
4. Keeping in view the advantages of abaca fibers and the processed products over synthetic ones, there is a great expectation that there will be a continuous increase in its demand in the national and international markets. To manage the increasing demands, the most important thing is to increase the supplies but during the last few years, the trend in abaca supply or production has been found otherwise. The main reasons have been found to be the low-income generation from the abaca cultivation, burdensome fiber extraction, and the natural calamities like typhoon or disease-incidence. As far as the income generation (for farmers) and fiber extraction is concerned, the Philippine government as well as the agencies like FIDA and NARC has a role to play. For the control of disease-incidence, different conventional plant breeding approaches coupled with the modern biotechnological techniques should be employed to produce disease-resistant varieties as has been recently initiated in two abaca cultivars Tangongon (TG) and Tinawagan Pula (TP) to produce virus-resistant (BBTV and BBrMV) abaca cultivars.

5. Abaca fiber is considered as the strongest natural fiber and known for its exceptional mechanical strength, durability, and long fiber length. It is because of these properties that it has become an important raw material for various industries like paper and pulp industry, furnishing industry, textile industry, automobile industry, etc. where it is being used in the production of many industrial or domestic products like cordage products, fabrics, speciality papers, bank notes, carpets, rugs, baskets, fiber boards, insulators (for wires/cables), and automobile components. It is also used as a fuel (Musafel). As per the estimates, paper and pulp industry consumes maximum share (about 80 %) of the fiber production. With the advancement in technology, currently the production of abaca-reinforced polymers is gaining more importance due to their superiority over pure fibers and the synthetic counterparts like nylon, rayon, etc. Keeping in view the above mentioned applications of abaca fibers in various industrial or domestic activities, it has a great potential to be used as an important renewable bio-resource.
6. The production of abaca fibers or its composites is eco-friendly, energy-efficient, and biodegradable, thereby posing no major threat to the environment. Moreover, abaca plantations have been used to control soil erosion and to promote biodiversity rehabilitation. Wastes produced from abaca plant find its use as organic fertilizer to maintain the fertility of soil.

In conclusion, it can be stated that the abaca industry holds a great scope in national as well as international markets providing employment or economic benefits to a large number of people (including farmers, traders, exporters, manufacturers, etc.). The production of high-quality fibers by industrial units creates multiple job opportunities and increase in the income of farmers and laborers. Being renewable natural fiber and superior in qualities, its market demand is expected to strengthen as far as its industrial applications are concerned. Also, the use of abaca fiber composites for automotive and other industrial applications carries ecological as well as economic benefits, thereby leading to sustainable development program. As abaca is mainly grown in Philippines and other adjacent areas, both government and the private sector should coordinate and extend its support in developing the abaca markets at the domestic and international level so that its unfulfilled potential will be attained in future.

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Chapter 4
Processing and Properties of Bagasse Fibers

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_4,

Abstract Botanically, sugarcane belongs to an economically important seed plant family that includes maize, wheat, rice, and sorghum known as *Saccharum officinarum*. Bagasse, an agricultural residue not only becomes a problem from the environmental point of view, but also affects the profitability of the sugarcane industries. This chapter discusses the properties and processing methods for the extraction of the bagasse fibers from sugarcane and its current status of research. The applications of the bagasse fibers in different fields have also been discussed.

Keywords Sugarcane • Bagasse • Extraction methods • Image analysis

4.1 Introduction

Sugarcane is a tropical, perennial grass typically 3–4 m high and has approximately 5 cm in diameter and become mature stalk. The composition of mature stalk is composed of 11–16 % fiber, 12–16 % soluble sugars, 2–3 % non-sugars, and 63–73 % water. Sugarcane is the world's largest crop. There is a variation in the properties of the sugarcane stalk which generally depends on variety. Under normal field conditions it has been observed that the height of sugarcane stalk varies from 1.5 to 3 m and has diameter range from 1.8 to 5 cm. The color of the surfaces of the stalk may be green, yellow, or red and covered by a thin layer of wax (van Dillewijn 1952). The stalk (cane) generally comprises shorter segments and also some joints. The length of these joints varied from 5 to 25 cm. It is also observed that the lower joints are longer and larger in diameter. Generally it has been seen that every joints comprise of two parts, one is the node and the other is internode (Elsunni and Collier 1996). Stalk structures like the root band, bud, and the shoulder lies at the node (Clements 1980). From the point of view of internode it has been observed that there are two particular areas. The primary one is the outer layer, which is also known as the rind and is so hard and dense. The secondary is the inside layer which has soft region where the fibro vascular bundles are firmly fixed in a surrounding mass, and known as the pith. It is found that there is a wide space lies between the fibro vascular bundles in the middle part of the stalk, but at the boundary the number of bundles increases and their sizes decrease. Generally the compositions of the bundles are fiber cells bounded by lignin and hemicellulose. On aging of the cane the deposition of the lignin like compound occurs around the fibro vascular tissues (van Dillewijn 1952). Advancement of cane aging results removal of lignin and softening and weakening of bundles. The nature of the soft rind is only because of the cellulosic effect (Elsunni and Collier 1996). The fibrous strands of the fibro vascular bundles extended for long distances in the stem. The separation of fibrous strands is found to be at the secondary part (internode). At the internode the bundle grows just in parallel to the stalk. The fibro bundles are dispersed through inside of the stalk and are more ample at the region of rind, as compared to the center of the stalk. This type of the positioning of bundles not only improves the strength but also improves the rigidity of the stalk. The stalk hardness is a characteristic regarding both in the sugarcane mill and also in the pasture. The varieties of hard cane result in so many mechanical problems (van Dillewijn 1952). The hard rinds cane are very difficult to operate by manual cutters and results excessive failure of mechanical harvesting units which also ultimately results the loss of spare parts and crushing time (Barnes 1964). Similarly the varieties of hard rind also have some advantages over softer cane varieties associated with resistance to attacks by animals such as rats, pigs, and mongooses.

It has been also observed that from the point of view of biomass energy sugarcane is found to be one of the important agricultural sources. There are generally two main types of biomass produced by the sugarcane; these are cane trash and bagasse. Cane trash is the remainder after harvesting of the cane stalk while on the other hand milling of the cane results bagasse which is the fibrous residue with 45–50 % moisture content.

The use of bagasse (after combustion) is in the production of steam for power generation. Bagasse is also recognized and used for the production of bioethanol. The important application of bagasse is found in paper making. In paper making industries it is utilized as the raw material. The calorific value estimation of bagasse as a fuel also describes its value, which is influenced by its composition and also on the calorific value of the sugarcane crop mainly because of the content of sucrose present. Moisture content generally decides the calorific value of the sugarcane. A good milling process results low moisture content of sugarcane which is of about 45 % whereas poor milling results 52 % moisture content. Generally it has been observed that most of the mills produce bagasse of 48 % moisture content, and most boilers burn bagasse at around 50 % moisture. Bagasse generally composed of fiber (cellulose), which contains carbon, hydrogen, oxygen, sucrose (1–2 %), and ash originating from extraneous matter. Sugar factory produces 30 tons of wet bagasse after crushing 100 tons of sugarcane. Bagasse is generally found as a primary fuel source for sugar mills which when burned then generates sufficient electrical energy, used to fulfill all the basic needs of a sugar mill.

The most energy projects have been demonstrated and presented in many sugarcane producing countries. The power generation from sugarcane is a good option as renewable energy that increases sustainable development, increases profitability and competitiveness in the industry.

In 2010, Food and Agriculture Organization (FAO) estimates that sugarcane was cultivated in more than 90 countries in 23.8 million hectares, with a worldwide harvest of 1.69 billion tons. Brazil produces the sugarcane on a larger scale in the world. Another five main producers, in descending order of production, are India, China, Thailand, Mexico, Pakistan (Duttamajumder et al. 2011). To obtain bagasse fiber first the sugarcane is crushed in a series of mills, which consists of at least three heavy rollers. Crushing process of sugarcane results breaking of the cane stalk in small pieces, and milling will squeeze the juice out. The juice obtained from sugarcane is collected for the production of sugar. The crushed and squeezed cane stalk named as bagasse (Elsunni and Collier 1996). Collier et al. (1992) suggested that bagasse will be a good source for the pulp and paper industry ahead and compared to other crops. The annual estimated amount of bagasse production is about 80,000,000 metric tons (MT), from which 25,000,000 MT will be utilized for pulping. The value added agricultural products development not only optimizes the extraction process and process parameters on fiber properties, but also optimizes the sampling and measuring technique (Romanoschi et al. 1997). Image analysis will allow to determine physical parameters for unconventional fiber such as bagasse in an easy and inexpensive way. The research in this field will have an impact on economic development by providing alternatives to agriculturists in crop choices and providing value to the sugarcane crop. Conversion of agricultural by-products to the value added products not only provides benefit to the economy of country but also developed new markets for agricultural crops. In this chapter, various properties and extraction methods of bagasse fibers and their applications are discussed. The various applications of the bagasse fibers in nonwoven form have also been reported.

4.2 Sugarcane: A World Scenario

Sugarcane area and productivity differ widely from country to country (Table 4.1). Brazil has the highest area. On the other side, Australia has the highest productivity. Out of 121 sugarcane producing countries, 15 countries (Brazil, India, China, Thailand, Pakistan, Mexico, Cuba, Columbia, Australia, USA, Philippines, South Africa, Argentina, Myanmar, Bangladesh) present 86 % of the area and 87 % of production (Table 4.1). Out of the total white crystal sugar production, approximately 70 % comes from sugarcane and 30 % from sugar beet.

Table 4.1 Sugarcane in the world: area, production, and productivity (Source www.sugarcane-crops.com)

Country	Area (million ha)	Production (million tons)	Productivity (Tons/ha)
Brazil	5.343	386.2	72.3
India	4.608	289.6	62.8
China	1.328	92.3	65.5
Thailand	0.970	64.4	66.4
Pakistan	1.086	52.0	47.9
Mexico	0.639	45.1	70.6
Colombia	0.435	36.6	84.1
Australia	0.423	36.0	85.1
USA	0.404	31.3	77.5
Philippines	0.385	25.8	67.1
Indonesia	0.350	25.6	73.1
Cuba	0.654	22.9	35.0
South Africa	0.325	20.6	63.4
Argentina	0.295	19.2	65.2
Myanmar	0.165	7.5	45.4
Bangladesh	0.166	6.8	41.2
World	20.42	1,333.2	65.2

Fig. 4.1 Sugar cane

4.2.1 Cultivation and Production of Sugarcane

A tropical climate is necessary for the production or cultivation of sugarcane with minimum 24 in. of moisture annually. In growing regions, such as Mauritius, Dominican Republic, India, Peru, Brazil, Bolivia, Cuba, El Salvador, and Hawaii, sugarcane crop produces over 15 kg of cane per square meter of sunshine.

The cultivation of sugarcane is only possible in the tropical and subtropical areas with 6–7 months continuous supply of water through natural resources like rainfall or artificial resources like irrigation (George et al. 1917). The production of cane is only possible in the presence of plentiful sunshine and water supplies. This condition provides good irrigation facilities to the countries where less availability of water supply is the major problem such as Egypt. Fig. 4.1 shows a general picture of sugarcane crops.

Sugarcane cultivation can be done by both mechanically and manually, i.e., by hand. Hand harvesting accounts for more than half of production. The process of hand harvesting involves the field to set on fire and burns dry leaves without harming the stalks and roots. Harvesters then cut the cane manually by knives just above ground-level. The mechanical cutters cut the cane at the base of the stalk and take off the leaves, cut the cane into regular lengths and deposit it into a transporter. The structure of bagasse is shown in Fig. 4.2. From Fig. 4.2 it is observed that the bagasse mainly consists of cellulose and lignin (Fig. 4.2, b, respectively).

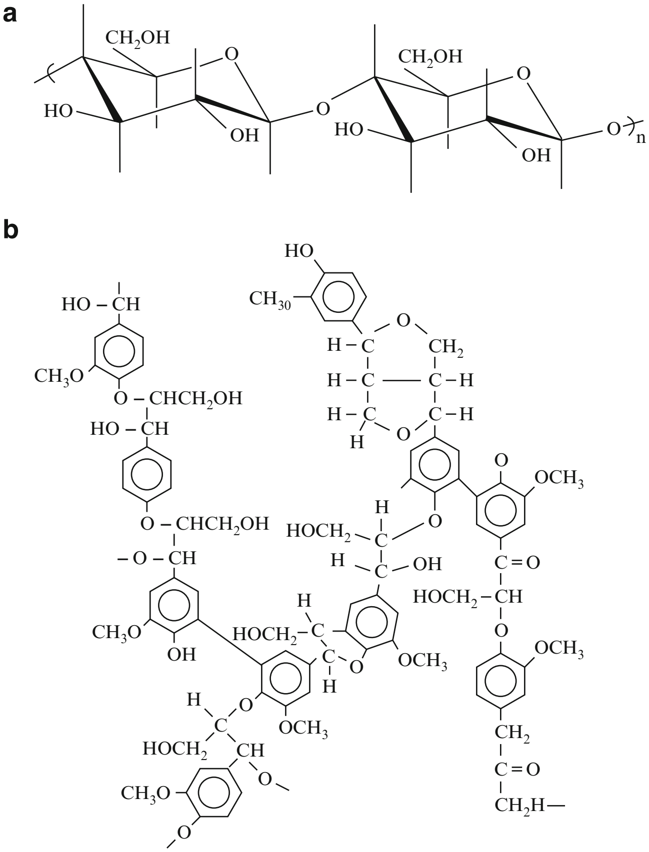

Fig. 4.2 Structure of bagasse (**a**) cellulose and (**b**) lignin. Reproduced with permission from Elsevier Ltd. (Said et al. 2009)

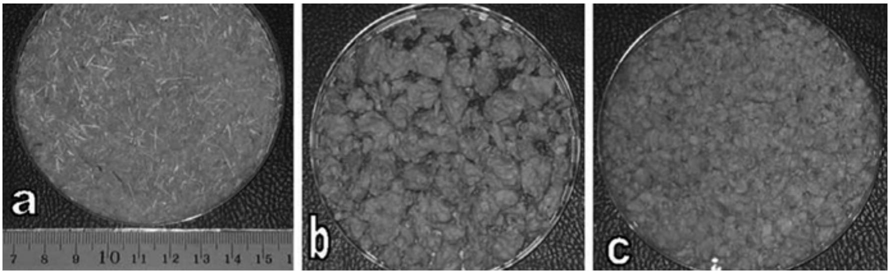

Fig. 4.3 Morphology of bagasse: (**a**) raw, (**b**) without lignin, and (**c**) grafted with fatty acid. Reproduced with permission from Elsevier Ltd. (Said et al. 2009)

Figure 4.3a showed the morphology of the washed raw bagasse obtained from the sugarcane mill. The composition of this consists of a mixture of cellulosic short fibers and fine particles. The removal of lignin (Fig. 4.3b) makes the material fairly hard, coarse cellulosic particulates. The modified bagasse fibers shown in Fig. 4.3c display fluffy soft texture.

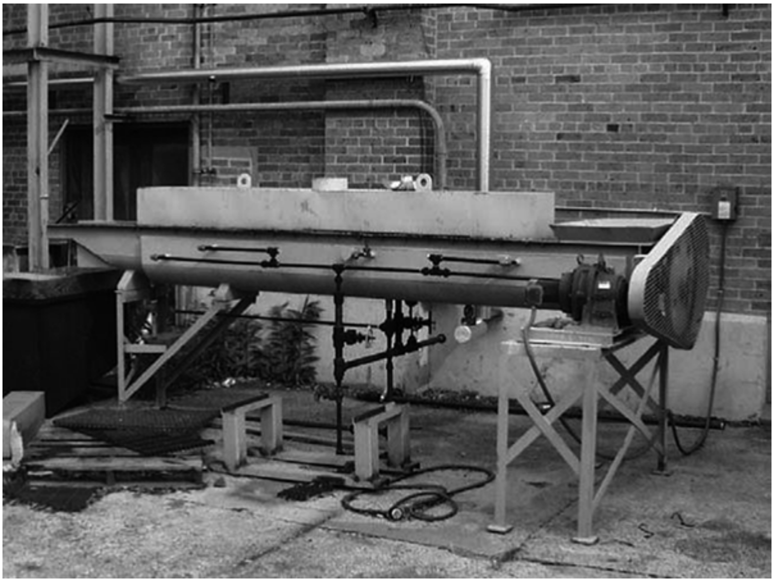

Fig. 4.4 Atmospheric extraction reactor

4.3 Processing Techniques/Extraction Methods of Bagasse Fibers from Sugarcane and Bagasse Compositions

The following extraction methods can be used to obtain bagasse fibers from sugarcane.

4.3.1 Atmospheric Extraction Process to Obtain Bagasse Fibers

There are various mechanical and chemical methods are available for the extraction of the bagasse fibers. Bagasse was put down on the surrounds of an open but sheltered in a sugar factory for duration of minimum two weeks. To satisfy uniform drying process the layer of bagasse was turned over a day. The moisture content was calculated for arbitrarily selected specimens of fibers. The results showed a uniform level of moisture less than 15 %. Small fibers and impurity were separated through a sieve process using a 2 ft by 2 ft wooden frame having a screen with 1/16 in eye dimension.

4.3.2 Chemical Extraction

It has been noticed that the most dominant factors for the extraction process are alkaline concentration, reaction time, incorporation, and presence of steam explosion. The extraction process tooks place at atmospheric pressure. For the alkaline extraction, an atmospheric process is employed. In this process an LSU designed atmospheric reactor was used (Fig. 4.4). From previous studies, it is observed that a 2.0 N NaOH solution needed for the removal of a remarkable amount of lignin. The capacity of the reactor was 200 L. Reactor first heated the solution to the boiling point at 100 °C and then gradually screened bagasse is fed to the reactor. The fiber/liquid ratios were maintained at 1:10. After approximately 90 min the whole amount of bagasse delignifies and collected at the other hand of the reactor. The extracted fibers were washed thoroughly with water and left (to dry) in a controlled environment for two days with a relative humidity of 65 % and a temperature of 71 °C (Collier and Arora 1994).

4.4 Bagasse Composition, Properties and Physical Characteristics of Bagasse Fibers

Bagasse is a fibrous residue that remains after crushing the stalks and contains short fibers (Fig. 4.5). It consists of water, fibers, and small amounts of soluble solids. Percent contribution of each of these components varies according to the variety, maturity, method of harvesting, and the efficiency of the crushing plant. Table 4.2 shows a typical bagasse composition.

Fig. 4.5 Bagasse

Table 4.2 Bagasse composition (Verma et al. 2012)

Items	Percentage
Moisture	49.0
Soluble solids	02.3
Fiber	48.7

4.4.1 Physical Properties of Bagasse Fibers

Physical properties of bagasse fibers can be evaluated by Image Analysis and is as follows:

4.4.1.1 Image Analysis

Image analysis method can be used for the determination of physical characteristics of bagasse fibers. AGFA Duoscan T1200 scanner can be used to measure the length of the fibers through a digital imprint. The images collected from the scanner were in JPEG (Joint Photographic Experts Group) format. The length of the fiber was directly measured using the Scion Image software (SIS). Fiber imprint contour of Scion Image software was used to measure the length of each individual fiber. The SIS software is used to take, display, and measure the output images. It is also used for the analysis of images. For the determination of cross-sectional area, the fibers were chopped to a length of 1 mm and stick with the cross-section using “Spot-o-gold” labels. The process involves coating of the cross-sections with 25 nm gold palladium using a Hummer II Sputter Coater. The cross-sections of the bagasse fibers were visualized by using scanning electronic microscope (SEM) with a magnification range upto 50,000 and a resolution of 10–29 nm (Chiparus 2004).

4.4.1.2 Determination of Fiber Length and Fineness

The important physical characteristic of the fibers is their fineness. For the determination of the fiber fineness instrumental methods have been developed. Generally there are two methods for measurements of fineness: direct method for the measurement of the fiber cross-section, and second is an indirect method for the measurement of the length per unit weight. It has been observed that the direct method is not the practical one. The reason for this is nonuniformity of the cross-section of natural fibers which ultimately create difficulty in the computation and measurement of the area and diameter of the fibers. So by considering this factor several methods were formed for the determination of the fineness of most commonly used fibers like cotton and wool. The first method is the British Standard Method. According to this method, fibers are chopped to suggested length and weighed. The second method is Arealometer method (ASTM D1448-97) which uses a two channel Wheatstone bridge in a tube. In this method a certain amount of cotton is dribbled in one of the channels keeping the next one empty. When it is observed that the pressure drop is standardized in both sides, then the given series of equation determines the fineness of the fibers. The SDL Fineness and Maturity Tester (Montalvo 2000) can also be used for the measurement of the fall in pressure across 4 g of cotton at high and low air flow. On other hand in the Vibroscope method (ISO 2061-95),a tension is applied to the fiber up to the completion of the fundamental frequency. As noticed earlier, these are the traditional methods and are time-consuming and also require specific training. Generally bagasse comes under the category of coarse fiber and has limited access to the testing instruments. (Elsunni and Collier 1996)

4.5 Applications of Bagasse Fibers

4.5.1 Oil Spill Sorption

The nonwoven material made from bagasse fiber is an efficient method of cleaning up oil spills. For the removal of contaminant oil from water, carbonized pith bagasse is being used as an adsorbent. The extracted fibers from bagasse and carbonized at 300 °C were found to have a high performance for sorption. The carbonized pith bagasse is packed into a polypropylene bag and used for sorption behavior. It has been observed that the pad containing carbonized pith bagasse has higher sorption capacity as compared to the commercial sorbents. This pad can be reused for eight times.

4.5.2 Agricultural End-Use

The other application of bagasse fiber nonwovens can be found to make flowerpots. This type of flowerpot made has excellent biodegradability and can be buried in a clay pots. The bagasse nonwoven pot buried in flowerbed is dissolved within only 23 days. When the nonwoven pot is put in a larger plastic pot, it is biodegraded within 50 days. The study also shows that the bagasse nonwoven pot is capable of sustaining weather and watering during seedling and retailing.

4.5.3 Animal Bedding

Animal bedding is another application of bagasse fibers which is generally used in poultry farms. The nonwoven and the bedding material (after collecting enough poultry wastes) are easy to layout and can be packed and sold as garden mulch directly. This approach not only promotes production of biodegradable and nutritional garden mulches, but also helps ease animal waste management.

4.5.4 Aquaculture

Aquaculture is also one of the useful applications of the nonwoven bagasse fibers. The bagasse fiber nonwovens can be enforced in aquaculture as bank weed control and filtration. Fish cultivation used artificial habitats that can profit the aquaculture system by giving shelter, nutrition, and improvement in water quality. Thus, availability of inexpensive artificial habitat materials can help fish farmers with profits.

4.5.5 Sugarcane Bagasse Paper

For high quality paper making, sugarcane bagasse is one of the most eco-friendly, sustainable, and renewable resources. The bagasse fiber generally used state-of-the-art technology and creates a bagasse pulp which is suitable for high quality paper making. The important application of bagasse fiber can be found in newsprint papers which are produced from 100 % bagasse fiber. High quality office and printing papers generally have a 20 % internal fiber added to ensure that the paper is suitable for all office and print applications.

Paper products fall under the following categories:

1. Paper produced from a non-forest resource (alternative fiber)
2. Paper sourced from a renewable resource (crops are constantly renewed for sugar consumption)
3. Recycled paper (as per FSC's description of papers which are considered recycled, Chiparus 2004)

4.5.6 Production of Ethanol from Sugarcane Bagasse

The second generation biofuel technology for the production of ethanol is cellulosic ethanol technology. Cellulose plants are the main source for the production of cellulosic biofuels. They have categorized it as "energy crops" rather than the crops for food production. Some of the examples are perennial grasses and trees, like switch grass and *Miscanthus*. Another source of cellulosic biomass is residues (crop) such as stems and leaves.

Generally it has been observed that the lignocellulosic biomass is the main feed stock for ethanol and includes various materials like agricultural residues such as corn stover, husks, bagasse, woody crops, waste paper and municipal and industrial wastes. Environmental issues can be resolved by using or disposal of agricultural waste residues and other wastes for the production of bioethanol. There is no interference of the lignocellulosic feedstocks with food security and are important in terms of energy security in all areas, environmentally and also agricultural development and employability.

4.5.6.1 Processes Used for the Production of Ethanol

Two different processing methods can be used for the production of ethanol from lignocellulosic biomass. These are as follows:

- *Biochemical Method*—In this method before fermentation, enzymes and other micro-organisms are used for the conversion of cellulose and hemicellulose part of the feedstocks into sugars for the production of ethanol.
- *Thermochemical Method*—In this method pyrolysis/gasification technologies are used to produce a synthesis gas ($CO + H_2$) from which a range of long carbon chain biofuels, such as synthetic diesel, can be reformed.

The main compositions of the lignocellulosic biomass are lignin, polysaccharides cellulose, and hemicellulose. It is generally seen that the use of lignocellulosic biomass becomes difficult because of the stability of the polysaccharides and it became difficult to ferment the pentose sugars by *Saccharomyces cerevisiae*. Hydrolysis of the polysaccharides must be undertaken for the conversion of lignocellulosic biomass to biofuels, or broken into simple sugars by using acid or enzymes. To overcome these problems several biotechnology-based approaches are being used which include development of strains of *Saccharomyces cerevisiae*, which is used to ferment pentose sugars. Generally the biochemical routes are used to produce ethanol from lignocellulosic biomass. The three main steps involved for the production of ethanol are pretreatment, hydrolysis of enzymes, and fermentation. In detail, first the pretreatment of Biomass is undertaken to enhance the advancement of enzymes. After pretreatment hydrolysis of biomass can be undertaken to change polysaccharides into monomer sugars, like glucose and xylose.

Simultaneous saccharification and cofermentation (SSCF) process can be used to convert pretreated biomass into ethanol. Generally it is assumed that the pretreatment is an important step used to improve the enzymatic hydrolysis of biomass. The basic step involved in this process is that it modifies the physical and chemical properties of biomass and ultimately enhances the enzyme access and efficacy leading to modification in crystallinity and degree of polymerization (cellulose). This process also increases the internal surface area and pore volume of pretreated biomass leading to facilitate substantial improvement in enzymes accessibility. Enzymatic hydrolysis step also enhances the rate and yield of monomeric sugars.

4.6 Conclusion and Future Perspective

The chapter explored sugarcane world scenario, processing techniques, and also discussed the properties of bagasse fibers. Bagasse fibers extracted from sugarcane do not require very typical or complicated technical process. For the determination of physical properties like length of fibers Scion Image Software has also been discussed in this chapter. The image method discussed in this chapter provides simple way for determination of bagasse fineness. The model used in this method can be used contrarily for evaluating the cross-sectional area when the fineness is known. The applications of bagasse fibers used in the various field were also discussed in this chapter. The other application of bagasse fiber is also found in composites making. It can be used as reinforcer in polymer matrix or concrete matrix composites. These composites have good mechanical properties and can be used in household, aircraft structures, and building structural applications.

Acknowledgement The authors are thankful and grateful to the Elsevier Ltd. for granting permissions to reproduce figures and tables to include in this chapter from their journals.

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Chapter 5
Agricultural Biomass Raw Materials: The Current State and Future Potentialities

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_5, © Springer International Publishing Switzerland 2014

Abstract Nowadays, the depletion of natural resources, growing population and raising environmental concerns have raised a tremendous interest in finding a sustainable alternative for creating new materials that are environmental friendly. Agricultural biomass is the plant residue left in the plantation field after harvesting. This lignocellulosic material possesses a composition, structure and properties that make them suitable to be used in various conventional and modern applications. This renewable plant waste is abundant, biodegradable, low cost and low density that could be a principal source for production of fibres, chemicals and other industrial products. The uses of these materials are not only limited to composite, paper and textile applications, but are also progressing immensely to many other unlimited applications such as medical, nano technology, biofuel and pharmaceutical. These expanding applications of agricultural biomass would not only help in reducing the environmental pollution but also provide an opportunity in developing renewable and sustainable material to be used in various advanced applications in the future. This would also help in generating employment and contributing to the improvement of people's livelihood. The aim of this chapter is to discuss different types of agricultural biomasses with its present applications and future potentialities.

Keywords Agricultural biomass • Properties • Fibre design • Fibre network • Applications

5.1 Introduction

The widespread concern over increasing fossil fuel prices, global warming issues, environmental pollution and green house effects have stimulated a tremendous interest in the use of renewable materials that compatible with the environment. A way of addressing this sensitive issue could be through promoting the biomass from agricultural as an important alternative source for raw materials in the composition of various products and applications.

Biomass such as agricultural crops is the largest of cellulose resource in the world. Approximately 2×10^{11} tons of lignocellulosics is produced annually compared to 1.5×10^{8} tons of synthetic polymers (Pandey et al. 2010). Biomass is a clean source of energy as it releases carbon dioxide (CO_2) as it burns but the gas released is recaptured by the growth of the same materials. This material considered as the most abundant waste after harvesting. After harvesting the fruit for food, most of the biomass is traditionally wasted for which it is normally left in the plantation field as organic fertilizer, mixed with the rejected fruits to make animal feed or is open-burnt. Utilization of these wastes could solve the disposal problem and reduce the cost of waste treatment (Goh et al. 2010).

Compared to glass fibre, biomass offers many advantages due to their unique characteristic such as low cost, low energy consumption, zero CO_2 emission, low abrasive properties, low density, biodegradability, non-toxicity and their continuous availability (Guimarães et al. 2009). However, biomass fibres also have certain drawbacks especially when considering its application in composite. They have high moisture absorption and poor compatibility with polymer matrix which is responsible for poor mechanical and thermal properties. Modification or treatment of the fibre is needed to enhance the performance of biomass in different multiple applications (Pandey et al. 2010).

In the past few decades, the development of new materials that involve natural resources as the raw material, especially as a composite material, has accelerated. Nowadays, a large number of interesting applications are emerging for these materials due to recent progress in technological advances, biomass material development, genetic engineering, and composite science technology that offer significant opportunities for an exploration and development of improved materials from renewable resources which can be used in various applications such as biocomposites, pulp and paper, construction, automotive, medical, packaging, aerospace, pharmaceutical and biomass energy production (Lau et al. 2010).

5.2 Classification of Agricultural Biomass Raw Materials

Agricultural biomass, also referred to as lignocellulosic are produced in billions of tons around the world every year. There are various types of agricultural biomass across the world that can be a potential candidate as raw material in different applications such as oil palm trunks, bagasse, coconut coir, bamboo and kenaf. Mostly, this biomass is found in the form of residual stalks from crops, leaves, roots, seeds, seed shells, etc. They can be divided into main groups depending on the part of the plant which they are extracted, i.e. bast (stem), leaf, fruit (seed) and straw as shown in Fig. 5.1. The composition of these organic fibres varies from one plant species to another. In addition, the polymer constituent composition in a single plant varies among species and even different parts of the same plant. It depends on the plant age, development growth, environment and other condition (Kumar et al. 2008). The properties of biomass vary considerably depending on the fibre diameter, structure, degree of polymerization, crystal structure and source and on the growing conditions.

Since decades ago, biomass raw materials have been historically used for ancient tools, food source, construction materials and textiles and as a source of energy. However, there has been a dramatic increase in the use of plant fibre recently for the development of environmental renewable materials especially as a reinforcing agent in polymeric composite materials in substitution of synthetic fibres like glass fibres. This situation is largely spurred by environmental awareness, ecological consideration and technological advances. Figure 5.2 depicted an example of different types of agricultural biomass raw materials that has been used in various applications.

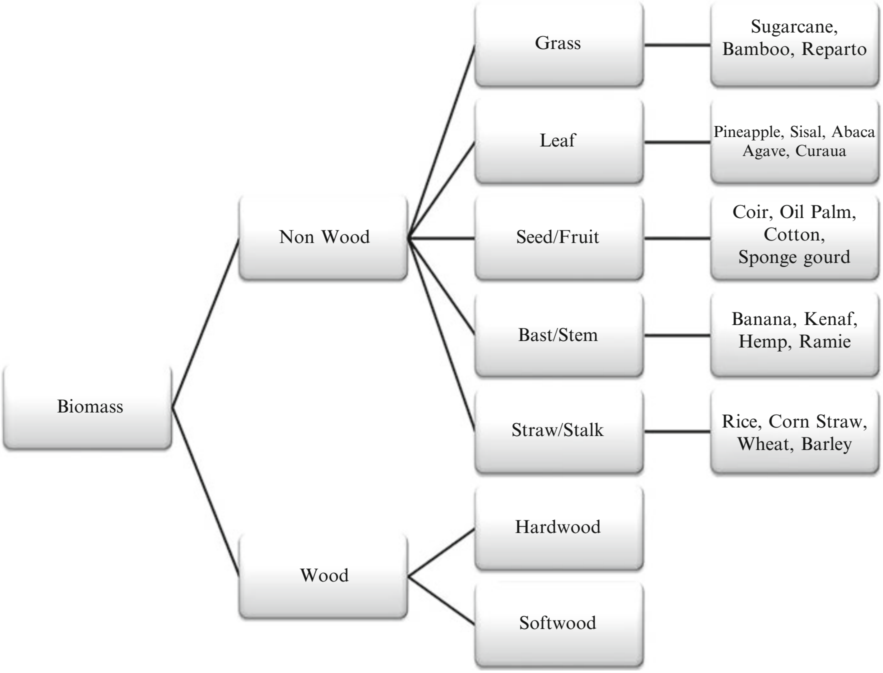


Fig. 5.1 Classification of agricultural biomass

Fig. 5.2 Various types of agricultural biomass

5.3 Agricultural Biomass Properties

The properties of biomass has been studied for decades; however the data were different among cited works because different types of biomass were used, different moisture conditions were present and different methods were employed. Researchers concluded that the overall properties of agricultural biomass are determined by large variables including its structure, chemical composition, cell dimension and microfibril angle. Furthermore these properties are also varying considerably between plant species and even in the same individual plant (John and Anandjiwala 2008).

5.3.1 *Chemical Properties*

Plant biomass is primarily composed of cellulose, hemicelluloses and lignin along with smaller amounts of pectin, protein and ash (Kumar et al. 2009). Cellulose is a semicrystalline polysaccharide made up of D-anhydroglucose ($C_6H_{11}O_5$) units linked together by β-(1-4)-glycosidic bonds. It provides strength, stiffness and structural stability of the fibre which help to maintain the structure of plants and serves as a deciding factor for mechanical properties. Hemicelluloses are branched and fully amorphous polymers. Meanwhile, lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. Lignin is associated with the hemicelluloses in plant cell wall and plays an important role in the natural decay resistance of the biomass material (Majhi et al. 2010). Table 5.1 shows the variability in cell wall composition in biomass. The table shows that content of the polymers are highly variable depending on the plant species. The composition, structure and properties of biomass depend on plant age, soil condition and other environmental factor including stress, humidity and temperature (Jawaid and Abdul Khalil 2011). The polymer chemistry of these fibres will affect their characteristics, functionalities and properties processing in different applications (Gorshkova et al. 2012).

5.3.2 *Physical Properties*

Final properties of biomass fibres are strongly influenced by its individual characteristic which played an important factor when considering this material in multidisciplinary applications. Biomass fibre properties that are related to vital variables include fibre structure, cell dimension, microfibril angle and defects (Abdul Khalil et al. 2012b). According to John and Thomas (2008), origin, sources, species and maturity of fibres determined the dimension of single cell in biomass fibres. Table 5.2 shows the physical properties of various agricultural biomasses. The properties of end product such as tensile strength, tear strength, drainage, bonding and

Table 5.1 Chemical properties of agricultural biomass

	Composition (%)				
Type of biomass	Cellulose	Hemicellulose	Lignin	Extractive	Source
Bagasse	40	30	20	10	1
Corn cobs	45	35	15	5	1
Corn stalks	35	25	35	5	1
Cotton	95	2	1	0.4	1
Oil palm empty fruit bunch	50	30	17	3	1
Flax (retted)	71	21	2	6	1
Flax (unretted)	63	12	3	13	1
Hemp	70	22	6	2	1
Jute	71	14	13	2	1
Ramie	76	17	1	6	1
Sisal	73	14	11	2	1
Wheat straw	30	50	15	5	1
Oil palm frond	56	27	20	4	2
Bamboo	73	12	10	3	2
Kenaf (whole)	53	–	21	6.4	3
Kenaf (bast)	55	29	14	5.5	3
Kenaf (core)	49	33	19	4.7	3
Rice straw	34	23	11	17	4
Switchgrass	31	29	17	17	4
Henequen	78	4	13	4	5
Istle	73	4	17	2	5
Sunn	80	10	6	3	5
Banana	50	0.77	17	–	6
Sponge gourd	66	17	15	–	6

Source: (1) Abdul Khalil et al. (2012a), (2) Jawaid and Abdul Khalil (2011), (3) Abdul Khalil et al. (2010) (4) Zhao et al. (2012), (5) Klemm et al. (2005), (6) Guimarães et al. (2009)

stress distribution are highly dependent on the fibre structural characteristic especially on fibre length, fibre width and thickness of cell wall (Rousu et al. 2002; Ververis et al. 2004; Abdul Khalil et al. 2008). Fibre aspect ratio (length/width) is important in determining the suitability of fibre for an exact application in order to reach its maximum potential (Han and Rowell 1997). Biomass fibre cell wall structure is composed predominantly of polysaccharide-rich primary (P) and secondary wall layers (S_1, S_2 and S_3) (Abdul Khalil et al. 2008). This thick multilayered and sandwich-like structure of bonded cell wall layers provide strength, toughness and collapse resistance to the structure (Smook 1992). Moreover, lumen structure influenced the bulk density of fibres and its size affects the thermal conductivity and acoustic factor of fibre in end product (Liu et al. 2012).

Table 5.2 Physical characteristics of agricultural biomass

Agricultural Biomass	Fibre Length (mm)	Fibre Diameter (μm)	Thickness of single cell wall (μm)	Width of lumen (μm)	References
Oil palm EFB	0.6–1.4	8.0–25.0	–	6.9–9.8	13, 17, 20
Coconut coir	0.3–1.0	12.0–14.0	0.06–8.0	–	1, 4, 7, 8, 19
Banana	0.1–4.2	12.0–30.0	1.2–1.5	13.4–22.4	5, 7, 8, 9, 13
Pineapple leaves	3.0–9.0	5.9–80.0	1.8–8.3	2.4 –3.0	13, 20
Jute	0.8–6.0	5.0–30.0	5.2–11.3	3.4–7.6	8, 13, 15, 21
Sisal	0.8–8.0	7.0–47.0	8.0–25.0	8.0–12.0	11, 13, 19
Flax	10.0–65.0	5.0–38.0	10.0–20.0	–	13, 20, 22
Cotton	15.0–56.0	10.0–45.0	3.6–3.8	15.7–16.4	9, 13, 14, 17
Ramie	30.0–60.4	7.0–80.0	2.8–3.0	12.8–13.0	3, 13, 16
Kenaf (bast)	1.4–11.0	4.0–36.0	1.6–12.6	5.4–11.1	2, 3, 13
Kenaf (core)	0.4–1.1	0.27–37.0	0.5–11.5	14.8–22.7	2, 13, 20
Bagasse	0.7–2.8	10.0–40.0	1.4–9.4	1.0–19.1	3, 12, 13
Bamboo	2.0–3.0	14.0–17.8	3.0–9.0	3.8–8.6	1, 10, 13, 17
Rice	0.4–1.2	8.0–15.5	2.0–5.6	1.1–8.7	12
corn	0.4–1.4	12.1–26.7	2.4–6.5	2.4–20.1	12
Sunflower	0.5–1.4	16.1–36.1	2.2–9.4	3.2–24.6	12
Rapeseed	0.6–1.3	6.2–34.1	1.5–9.3	3.1–27.9	12

Adapted from: (1) Joseph et al. (1999), (2) Rowell et al. (2000), (3) Mohanty et al. 2005, (4) Reddy and Yang (2005), (5) Wathen (2006), (6) André (2006), (7) Abdul Khalil et al. (2007), (8) Satyanarayana et al. (2007), (9) Omotoso and Ogunsile (2009), (10) Yueping et al. (2010), (11) Ahmad (2011), (12) Kiaei et al. (2011), (13) Jawaid and Abdul Khalil (2011), (14) Sadegh et al. (2011), (15) Zimniewska et al. (2011), (16) Abdul Khalil et al. (2012a), (17) Jawaid et al. (2012), (18) Kalita et al. (2013), (19) Shah (2013), (20) Moya et al. (2013), (21) Mershram and Palit (2013), and (22) Nguong et al. (2013)

5.3.3 Mechanical Properties

Table 5.3 provides an overview of mechanical properties of various biomasses. The mechanical properties of the fibre types from different sources and origin clearly show why the large variation of mechanical properties of biomass becomes a crucial concern when it comes to commercial utilization. The large variability of tensile properties is also a drawback for all natural products which is influenced by species, fibre structure and environmental conditions during plant growth. The structural parameters that have been reported by different methods have influences on the tensile properties of plant fibres—chemical composition, cellulose crystallinity, microfibril angle and stiffness of cell wall materials—and the fibre lumen size as well as the presence of defects (Vincent 2000; Alix et al. 2009).

Table 5.3 Mechanical properties of selected agricultural biomass and glass fibres

Types of biomass	Density (g/cm^3)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Source
Oil palm empty fruit bunch	0.7	3.2	248	2.5	1
Ramie	1.5	44	500	2	1
Banana	1.3	33	355	5.3	1
Cotton	1.5	12	400	3	1
Hemp	1.5	70	550	1.6	2
Coir	1.2	44	500	2	2
Sisal	1.3	38	600	2	2
Kenaf	1.1	53	930	1.6	3
Flax	1.5	58	1,339	3.2	4
Jute	1.5	60	860	2	4
Pineapple leaf	1.4	4.4	126	2.2	5
Abaca	1.5	6.2	764	2.6	6
Bamboo	0.9	35	503	1.4	7
Date leaf	0.9	11	309	2.7	7
Palm	1.0	2.7	377	13	7
Vakka	0.8	15	549	3.4	7
E-glass	2.5	2,500	70	2.5	1
S-glass	2.5	4,570	86	2.8	1

Source: (1) Jawaid and Abdul Khalil (2011), (2) Wambua et al. (2003), (3) Pandey et al. (2010), (4) Summerscales et al. (2010), (5) Arib et al. (2006), (6) Symington et al. (2009), (7) Rao and Rao (2007)

5.4 Biomass Raw Material Design and Network

5.4.1 Biomass Fibre Design

Agricultural fibres are presently a major area of research for various end product applications. The major strength of fibres can be utilized as reinforcement in biodegradable composites and as alternative raw materials for several manufacturing industry. Figure 5.3 shows that the design of fibre biomass varies according to the type of species and sizes. Each size also varies according to each specific application of particle, pulp, fibre, fibrils, micro and nano. In terms of strength per unit weight, the fibres have strength comparable to that of man-made fibres, while the modulus is very high (Chinga-Carrasco 2011a). The micro and nano-microchips invisible to the normal view were widely used in many modern applications for various purposes and is also a very important technology in the future (Chinga-Carrasco 2011b). Several modern and high-tech nano-applications were introduced because of the excellent result as for medical applications, cosmetic, pharmaceutical, aerospace and others. In addition, the successful applications have been demonstrated in military research and development, and by-products have also been explored.

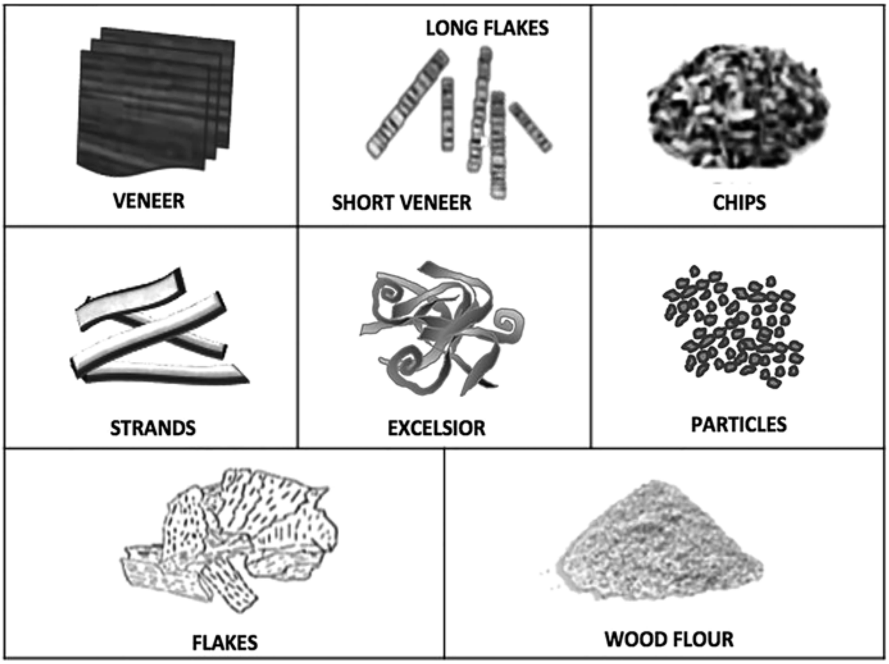


Fig. 5.3 Variations of agriculture raw materials

Agricultural biomass or lignocellulosic fibres can be described as resources comprising primarily cellulose, hemicellulose and lignin (Rowell et al. 2000). Detailed observation of the fine structure of biomass fibre is achieved by using electron microscope that provides a clearer understanding of biomass cell wall structure organization. Figure 5.4 depicted the schematic illustration of biomass fibre cell wall structure which consists of primary and secondary multilayered structure (Abdul Khalil et al. 2006). Each cell wall layer comprises different chemical composition, microfibril alignment which depends on the development and functionalities of the plant that provides mechanical support and stability to the structure. Advanced biocomposite production has dominated the world of manufacturing industry to increase value-added bamboo materials to produce innovative products such as bamboo fibre reinforced, particleboard, pulp, medium density fibre board and composites for the construction industry. The production of green composites derived from renewable sources such as palm trees, bamboo, kenaf, and others have potential to provide positive benefits to the manufacturing industry, consumers and the natural environment (Koronis et al. 2013).

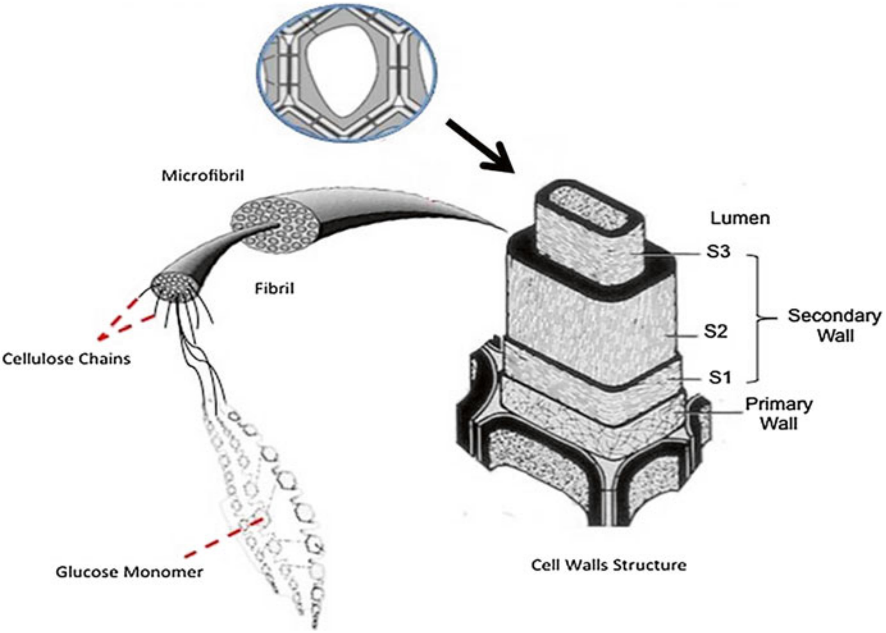


Fig. 5.4 Cell wall structure of agricultural fibre

5.4.2 Biomass Fibre Network

The use of agricultural biomass has been proven in the laboratory scale and has been commercialized as an alternative to wood material. Characteristics, properties and compatibility of the fibres are essential for biomass integration into existing industrial production for various products. Studies conducted on the relationship between structure, network, physical and mechanical properties of biomass fibres shows that they are closely related to each other. These factors have influenced the use and application of biomass fibres, as for example in pulp and paper, textile and biocomposite industry.

5.4.2.1 Biomass in Fibre Industry

Biomass fibres are usually found as short reinforcements which are used to produce mat fabrics. Discontinuous fibres (chopped) are generally used for a randomly oriented reinforcement (mat) when there is not any preferential stress direction and/or there is a low stress/strain level in the composite. The alternative to the use of short fibres is the manufacture of long yarns. Yarn is a long continuous assembly of relatively short interlocked fibres, suitable for use in the production of textile, sewing, crocheting, knitting, weaving, embroidery and rope making that are twisted with an

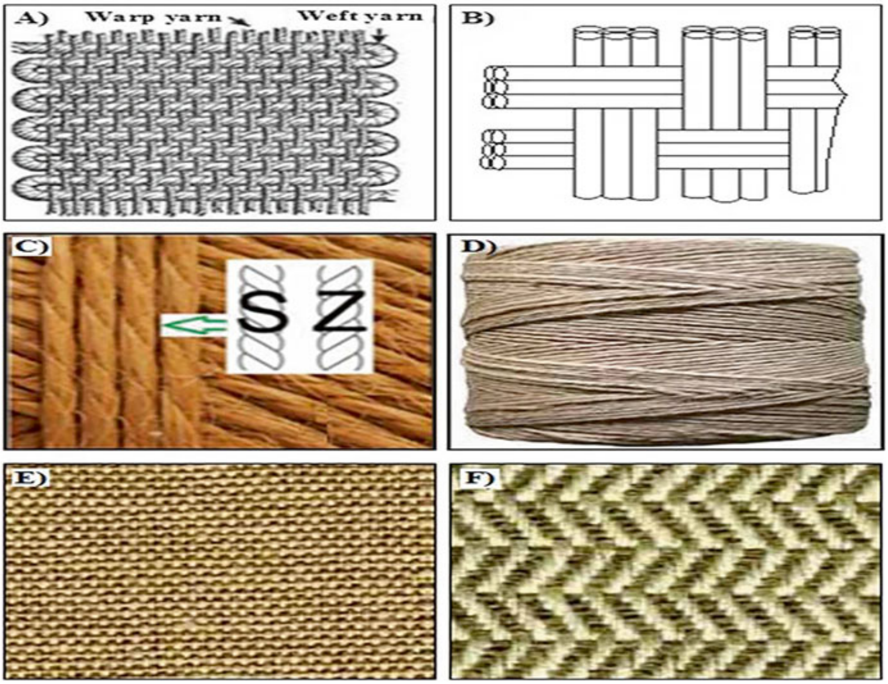


Fig. 5.5 Warp and weft in plain weaving (**a, b**); Plain woven flax yarns (**c, d**)

angle to the yarn axis in order to provide axial strength to the yarn. An important control parameter for such natural yarns is the twist level. Spun yarns are made by twisting or otherwise bonding staple fibres together to make a cohesive thread and may contain a single type of fibre or a blend of various types (Fig. 5.5). Two or more spun yarns twisted together to form a thicker twisted yarn, known as S-twist or Z-twist depending on the direction of the final twist.

The main advantage of using natural yarns is the ability to weave them into 2D and 3D fabrics with tailored yarn orientations. Weaving is a textile production method which involves interlacing a set of longer threads, twisted yarn or roving (warp) with a set of crossing threads (weft). Natural yarns differ from multifilament of synthetic fibres because they are an assembly of short fibre instead of an assembly of aligned continuous fibres. The manner in which the warp and weft threads are interlaced is known as the weave style, which are plain weave, satin weave and twill weave. Plain weave is the most basic type of textile weaves, where the warp and weft are aligned so they form a simple criss-cross pattern. Each weft thread crosses the warp threads by going over one, then under the next and so on. The next weft thread goes under the warp threads that its neighbour went over and vice versa. In balanced plain weaves the warp and weft are made of threads of the same weight (size) and the same number of ends per inch (Cicala et al. 2010).

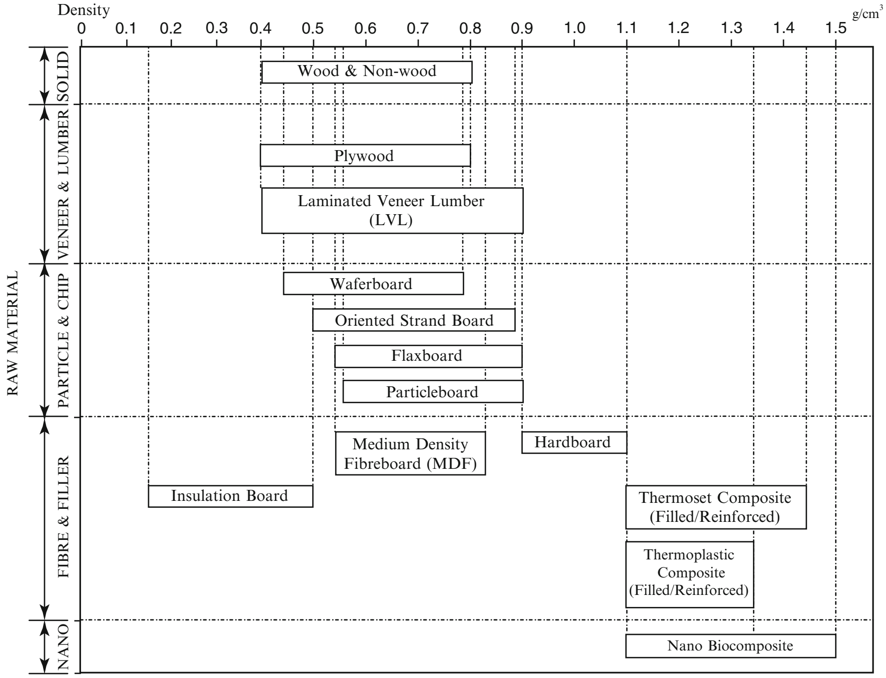


Fig. 5.6 Classification of composite based on raw material, particle size and density

5.4.2.2 Biomass in Biocomposite Industry

The composite-like structure of natural fibres are generally not single filaments as most man-made fibres, where they can have several physical forms, which depend on the degree of fibre isolation to make them competitive in terms of specific and economic properties compared to synthetic fibre. Physical and mechanical properties of biomass fibre depend on the single fibre chemical composition according to grooving, geometry of the elementary cell and extraction/processing method conditions. The earliest review by Maloney (1986) and later Abdul Khalil and Rozman (2004) has outlined a general classification system for various wood-based composites. Conventional wood-based composites (e.g. cellulosic fibreboard, hardboard, particleboard, waferboard, flaxboard, oriented strand board, oriented waferboard) and advanced polymer composites, which frequently termed as biocomposite (e.g. thermoplastic composite, thermoset composite, elastomer composite, hybrid composite, and ceramic composite) are classified by specific gravity, density, raw materials and processing methods (Fig. 5.6). Performance of the composite can be tailored to the end use of the product with each classification category. They are widely used in structural and non-structural applications for both various interior and outdoor structures.

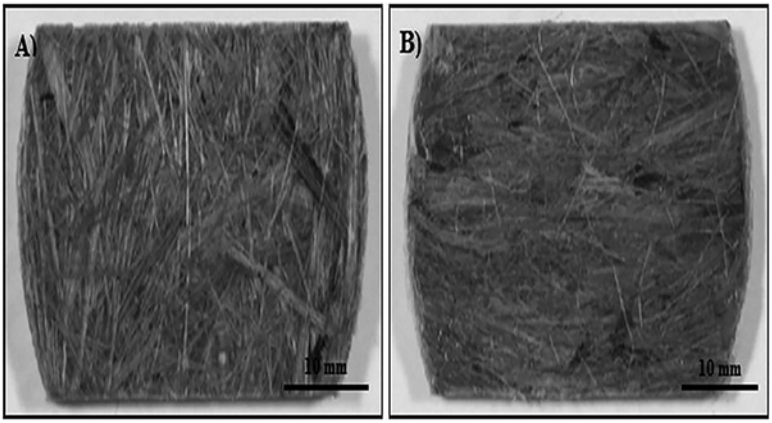


Fig. 5.7 Random kenaf fibre (**a**); Oriented kenaf fibre (**b**) (Shibata et al. 2008)

In composite manufacturing, it is crucial to know the fibre characteristics such as shape and aspect ratio as well as their distribution, orientation, alignment, volume fraction and interfacial adhesion in the polymer matrix. Some experimental studies show that fibre orientation plays a very important role in physical and mechanical properties of fibre reinforced nanocomposites (Smith et al. 2000; Shokuhfar et al. 2008; Wang et al. 2008). Rozman et al. (2013) found good mechanical strength and wettability of non-woven composite from kenaf fibre and PP fibre by using carding process and needle punching process. In other case, Shibata et al. (2008) claimed that fibre oriented kenaf reinforced composites can be produced using additional fabrication steps added into compression moulding process. Example for random and oriented kenaf fibre is shown in Fig. 5.7.

Furthermore, nanotechnology is able to manipulate and control fibre-to-fibre bonding at a microscopic level, which offers an opportunity to control nanofibrillar bonding at the nanoscale. Preparation and application of nanocomposites using nano- and microfibrils of biomass fibres are undergoing rapidly in biocomposite science (Bhat et al. 2011; Henriksson et al. 2008; Moon et al. 2006). The fibrillation of pulp fibre from biomass fibres was done to obtain nano-order unit web-like network structure, called microfibrillated cellulose. It is obtained through a mechanical treatment of pulp fibres, consisting of refining and high pressure homogenizing processes. In the range between 16 and 30 passes through refiner treatments, pulp fibres underwent a degree of fibrillation that resulted in a stepwise increase of mechanical properties, most strikingly in bending strength (Abdul Khalil and Rozman 2004; 2010). The bulk of the fibres went through a complete fibrillation that causes the increase in mechanical properties. For additional high pressure homogenization-treated pulps, composite strength increased linearly against water retention values, which characterize the cellulose's exposed surface area, and reached maximum value at many passes through the homogenizer (Kamel 2007).

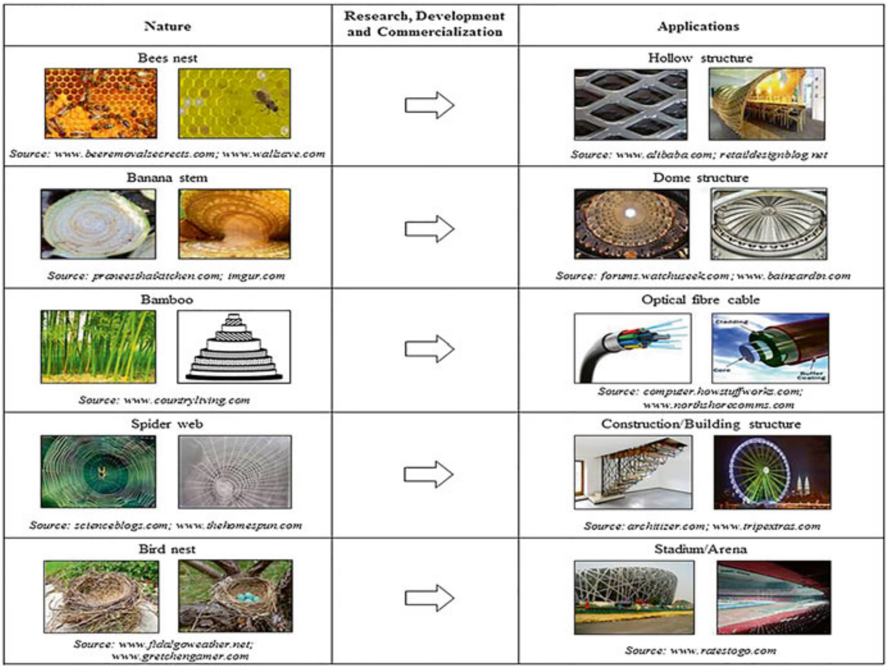


Fig. 5.8 Application of material structure inspired by nature

5.4.2.3 From Nature to Community

Without us realizing it, invention or innovation, particularly in the areas of development and construction in everyday life, is indirectly inspired by natures, which in this context are the network, structure and arrangement of biomass fibres or lignocellulosic raw materials. The architecture and fibre network which in fact may look nothing to normal eyes actually have a huge influence in terms of dimensional stability and strength for various material structures in the real world. Thus, by doing research, development and commercialization, researchers/scientists are inspired to apply the ideas in inventing some kinds of bio-inspired material structures for our daily use. For example, the structure of optical fibre cable is inspired by fibre network in bamboo structure. Other examples are bees nest, banana stem, spider web as well as bird's nest, where their fibre design and network give ideas to scientist for their new inventions (Fig. 5.8) (Amirul Hakim 2014; Baincardin 2014; Cahaya Purnama 2014; Cooper 2014; Pugh 2014a, 2014b).

5.5 Current and Future Applications of Agricultural Biomass

Biodegradable/bio-based polymeric products is based on renewable plant and agricultural biomass as a basis for sustainable portfolio with eco-efficient products that can compete in markets, which currently dominated by petroleum-based products. Through intensive research and development, the large quantities of biomass have now found applications in commercially viable bio-based products. The utilization of lignocellulosic materials from biomass for a number of value-added products is very significant through chemical, physical and biological innovations to invent such innovative and competitive products in various fields, as shown in Fig. 5.9.

5.5.1 Future Potential of Biocomposite Industry

Both upstream and downstream activities are covered in biocomposite industry. Upstream activities involve a systematic and sustainable harvesting of natural forests and plantations, whereas downstream activities include primary, secondary and

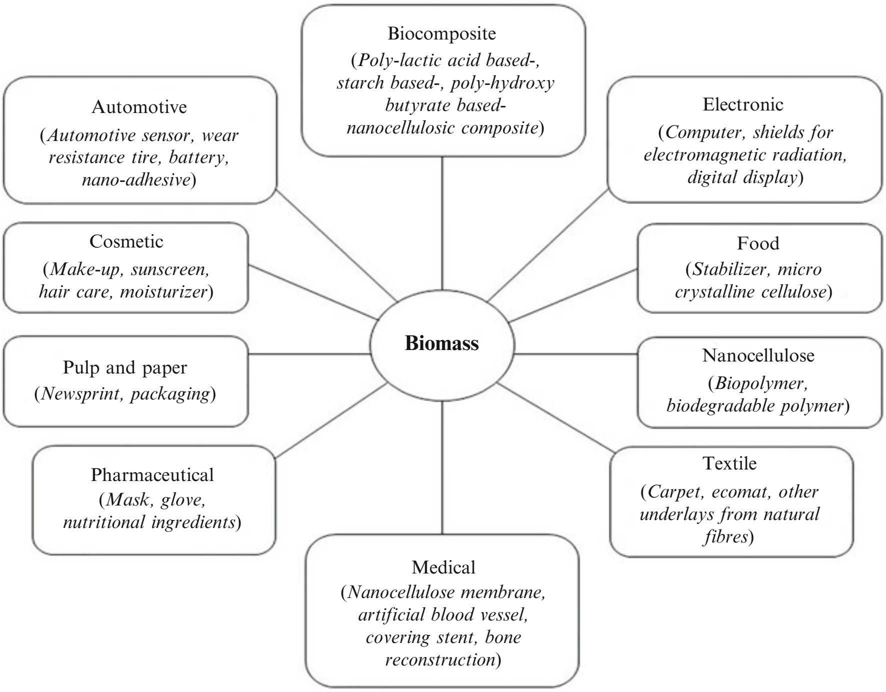


Fig. 5.9 Application and potential of biomass in various fields

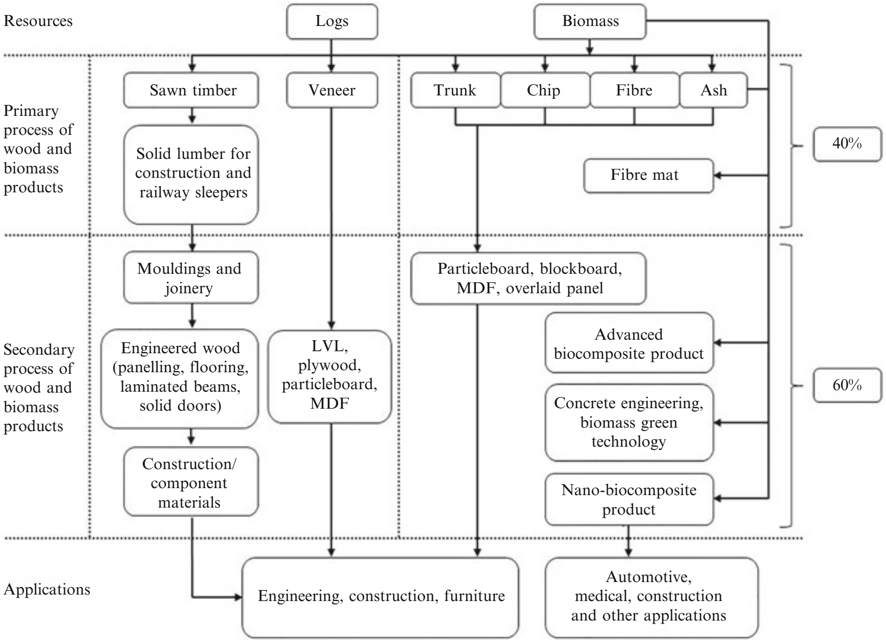


Fig. 5.10 Recommended resources and products for biocomposite (wood and non-wood) industry

tertiary level of operations, ranging from the processing of raw materials to the manufacture of semifinished and finished products. The proposed exports value percentage of the primary processing is shown in Fig. 5.10. Primary, secondary and tertiary processing activities contribute 40 % and 60 %, respectively.

5.5.2 *Value Chain of Biocomposite Industry*

Biocomposite industry is acknowledged as an important contributor to the economic growth of other industries. The biocomposite industry value chain begins from the preparation of agricultural biomass raw materials and resin production to produce consumer products (Fig. 5.11). Reduction in the supply of raw materials has caused concern and, in this context, agricultural biomass raw material is used as an alternative material for the industry to produce value-added biocomposite products. Therefore, research and development sectors are encouraged to explore the potential of natural resources for the production of new value-added products to enhance growth, competitiveness and sustainability of biocomposite industry.

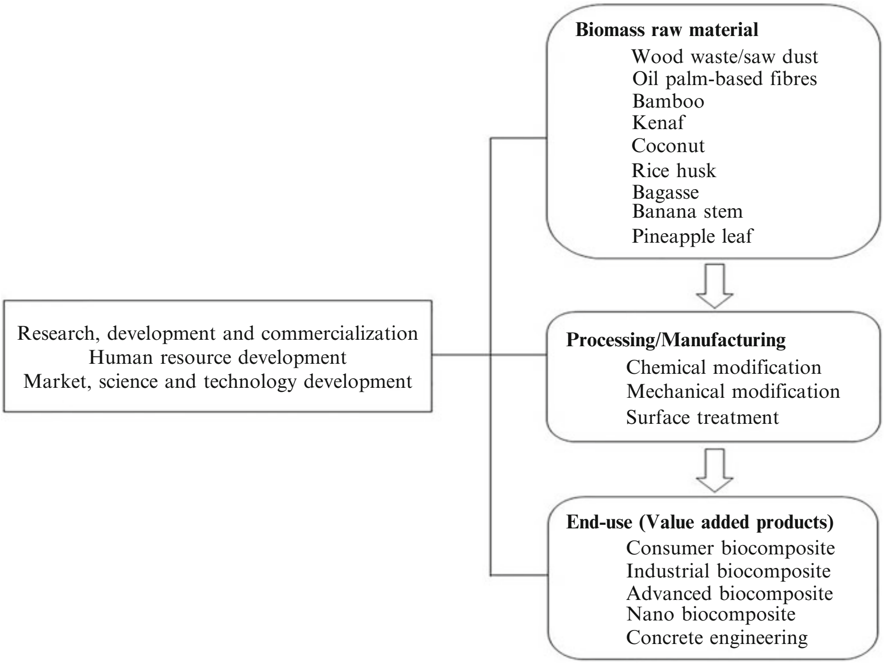


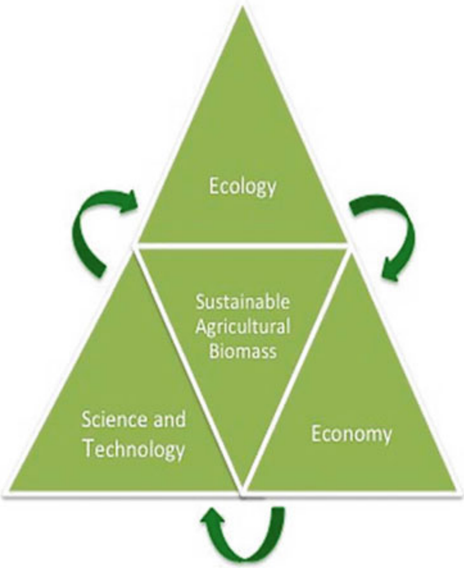
Fig. 5.11 Value chain of the biocomposite industry

5.6 Agricultural Biomass Raw Materials for Sustainable Economical Development

Wise development of agricultural biomass within prudential excellence should have some elements to ensure that the sustainability of the environment with other living thing is not affected in terms of quality and quantity. Elements of ecology, economy and technology as shown in Fig. 5.12 are determined based on the importance and the effectiveness of the product life cycle, processes and properties of raw material from excellent research by scientists.

Environmental issues often become a hot topic of the international community every year since rapid urbanization has resulted in the loss of conventional raw materials due to lack of natural resources. The world is confronted with serious environmental hazard problems such as environmental pollution, global warming, greenhouse gas emissions, ozone depletion, acid rain, extinction of habitat, flora and fauna also cause less health. The main key of all these problems is closely related to the sustainability of the world's ecology which was declining dramatically each year due to the ineffective management system of natural waste material (Kramer 2012). The industrial world has expanded exponentially over the past

Fig. 5.12 Three elements of agricultural biomass raw materials for sustainable economical development



century involving raw materials usage without emphasizing universal aspects of sustainability, but only profit oriented that may soon become a silent killer to the world ecology cycle.

All levels in the ecology of the world will receive a direct impact on development, agricultural waste resource operation that involved in different stages. This concept can be illustrated based on the increase demand by society for the product, preservation of balance of the forest, the diversity of material resources and benefits (Bovea and Vidal 2004). Previous research demonstrated that the use of composite biomass-based products in the market can sustain the ecology and economy of a country and the effect caused very less damage to ecosystems and natural resources. Society awareness can be achieved by evaluating the advantages of using agricultural biomass materials and its impact on the environment. The perspective of the product life cycle in terms of raw materials manufacturing process, marketing and disposal should also be considered. Transformation of low impact materials such as kenaf, oil palm, coconut fibre, and bagasse is necessary to diversify the market by providing alternative sources of fibre that has many advantages in mechanical properties for advanced applications. This can increase the market potential of the new manufacturing industry in developing sustainable solutions (Kar and Jacobson 2012).

Agriculture is one of the world's largest industry also a lifeblood of the economy of each country as it involves a lot of the manufacturing sector, such as food (e.g. wheat, sugar, oil), construction (e.g. buildings, automotive) and the production of products (e.g. furniture, clothing, tools packaging). Agriculture is one of the world's largest industry also a lifeblood of the economy of each country as it involves a lot of the manufacturing sector, such as food (e.g. wheat, sugar, oil),

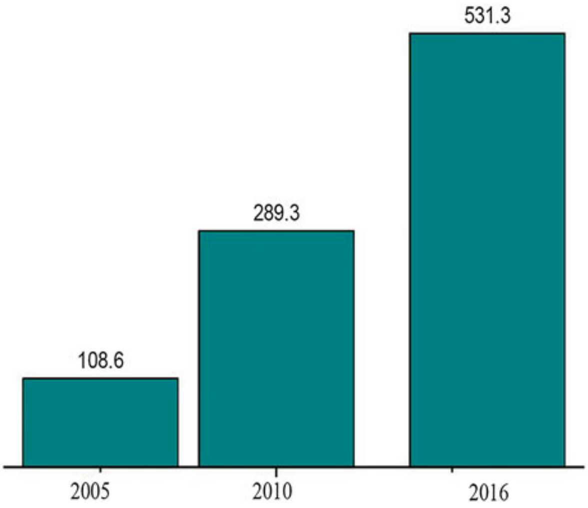


Fig. 5.13 Global growth trend and forecast (million USD) of natural fibres sector from year 2005 to 2016 (Lucintel 2011)

construction (e.g. buildings, automotive) and the production of products (e.g. furniture, clothing, tools packaging). Pawlak (2007) detected the importance of the economic transformation for country depends on how the success of the product. Economics is an important factor related to the development of the country, and the demand of natural fibres using appropriate technology to produce quality fibre reinforced for use in concrete construction is gaining high score. Among the examples of countries Japan and America who excel in a variety of advanced design and high demand in the world market successfully provide economic incentives and strengthen the country's agricultural and industrial sectors. On the other hand, the economy had jumped up along with the effectiveness of economic development based on sustainability, and product can be evaluated based on the production process of a product from base till the end by provided at minimal cost. The "waste to profit" step is very important to exploit biomass raw material in the production of value-added and innovative new products.

As shown in Fig. 5.13, the global exports trend for biomass-based manufacturing sector continues to increase every 5 years from 2005 to 2016 (Lucintel 2011). Electrical and electronic sector, pharmaceutical, textile and other significant contributors in the export value of 90 % compared to wood-based industry sector and only 10 % biocomposites. Continues scenario will be able to bring a stronger economy for the world market. Many factors such as easy planting and care, short-term crops, easy handling and minimal cost might benefit two fold compared with conventional materials (Majeed et al. 2013). For example, an oil palm biomass crop that is widely grown in ASEAN countries such as Malaysia and Indonesia can be used and converted into various products that would create an optimal supply of raw materials cycle continuously through a secure supply of quality and can prevent wastage of raw materials. Raw material costs were seen to be at the highest with carbon fibre at the price of between MYR20,000 and 50,000 per tonne, followed by fibre glass with the price starting from MYR6,000 to 10,000 per tonne, and at the lowest was oil palm fibre with the cost ranging from MYR600 to 1,000 per tonne. Advantages of agricultural waste-based manufacturing industry can have a positive impact on society and the country creates many job opportunities and is able to raise the living standards of the community (Kar and Jacobson 2012). Well-income communities while increasing consumer purchasing power and domestic sources of raw materials might be able to help reduce the loss of imports.

Over recent years, many researchers have focused on research related to agricultural waste to solve the environmental problems due to the disposal of the biomass waste material. Agricultural waste biomass have become an interesting research field and led to the creation of new solutions and materials through research and development in science and technology. The research continued to become important for producing a new generation of processes and innovative composite products with the features of a more sustainable and improved quality (Kramer 2012). Advances in science and technology enable the world's manufacturing industry to manipulate matter at the policy level to improve the overall properties of alternative materials to replace conventional materials. Technology-based research with a focus on biomass species variety with high potentialities can be grown to be applied in various industries for energy, pulp and paper, textiles, composites, cosmetic, construction, nanotechnology and pharmaceutical. This activity can make a huge impact not only on the product and the community, but to the transformation of technology development (Lane and Fagg 2010).

5.7 Conclusions

Agricultural biomass raw materials are highly potential candidates either as replacement or as complement to synthetic fibre in various applications due to their comparable properties. This integrated biomass technology is not only devoted in minimizing the environmental impact but in maximizing the performance and functionality of fibres, sustainability of resources and profitability. The growing enthusiasm to fully exploit agricultural biomass as material for green product also benefiting towards people as its generating many posts and opportunities. Agricultural biomass as a fascinating material brings the possibility to gain plenty of interest application in multidisciplinary fields. Until now, there have been a vast amount of well-established applications of agricultural biomass especially in construction, automotive, etc. However, the potential applicability of this raw material is unlimited and rapidly expanding due to their variety of unique characteristic which offered many properties that meet different requirements.

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Chapter 6
Kapok Fiber: Structure and Properties

Yian Zheng and Aiqin Wang

Contents

Abstract Due to the development of sustainable technology, green renewable resources have attracted increasing interests in recent years. Kapok fiber belongs to a typical cellulosic fiber, which is obtained from the seed hairs of kapok trees (*Ceiba pentandra*). Kapok fiber possesses the features of thin cell wall, large lumen, low density, and hydrophobic–oleophilic properties. This chapter focuses on the structure and properties of kapok fiber.

Keywords Kapok fiber • Structure • Properties

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_6, © Springer International Publishing Switzerland 2014

6.1 Introduction

Kapok fibers are obtained from the fruits of kapok trees (*Ceiba pentandra*) which belong to the family of Bombacaceae and are growing in Asia, Africa, and South America. Their color is yellowish or light brown with a silk like luster. Kapok fiber is odorless, fluffy, nontoxic, nonallergic, and resistant to rot. Traditionally, 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. As a kind of natural biodegradable fibers, kapok fiber is now receiving more attention in scientific researches.

6.2 Structure of Kapok Fiber

As a kind of natural fiber, kapok fiber shows the highest hollowness and the lowest specific mass that any microchemical fiber is incomparable. Kapok fibers consist of natural microtubules with fine tube structure (ca. 8–10 μm in diameter and ca. 0.8–1.0 μm in wall thickness) (Chung et al. 2008), and the hollow ratio can reach 97 %. One end of the fiber that tapers to one point is closed, and the other end is bulbous shape and may be closed tightly (Xiao et al. 2005). As a single-cell fiber, cotton fiber looks like ribbons, rolled in a helicoidal manner around the axis, while kapok fiber is not convoluted. Figure 6.1 shows the SEM micrographs of longitudinal and cross-sectional view of kapok fiber. A longitudinal view of kapok fiber shows smooth cylindrical surface, while a cross section reveals a wide open lumen (Mwaikambo and Bisanda 1999). Kapok fiber shows a unique hollow structure, and this feature is expected to enlarge its specific surface area, endowing the fiber with outstanding moisture transfer property and making it an ideal environment-friendly natural thermal fiber (Feng et al. 2006).

From the fine structure of the walls of kapok fiber, five layers, i.e., cuticle (S), primary wall (W1), secondary wall (W2), tertiary wall (W3), and inner skin (IS), have been clearly observed in lateral and longitudinal cross sections. The W1 is characterized by an interlaced fibril-like network (Xiao et al. 2006), while the fibrils of W2 and W3 are arranged angled or parallel to the fiber axis. The thickness of W1 is about 200 nm, and this thickness seems the same for W2 and W3 (ca. 500 nm). The cuticle S is the protective layer of kapok fiber and shows the highest packing density. In addition, the fibrils of W1 and W3 are closely packed and accordingly, the structure of them is more compact than that of W2. However, the structure of IS is relatively loose, and the fibrils are easily escaped from IS and then dispersed in the lumen. Between the adjacent layers, a transition layer with the low packing density is present. In transitional layers, the interactions between the fibrils are weaker than those in the individual layers. As for different walls, the variety in the fibril size from protofibrils to fibrils is observed for the smallest structural units. The smallest fibril size is found to be 3.2–5.0 nm in different walls (Shi et al. 2010).

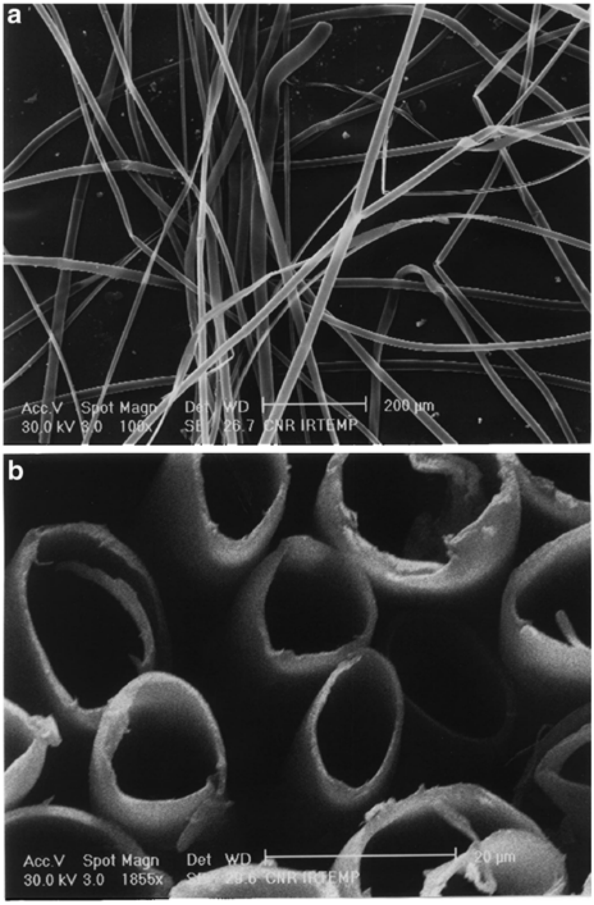

Fig. 6.1 SEM micrographs of longitudinal (**a**) and cross-sectional (**b**) view of kapok fiber (Mwaikambo and Bisanda 1999) (Copyright 1999, reproduced with permission from Elsevier)

The main components of kapok fiber are cellulose, lignin, and xylan (Fengel and Przyklenk 1986; Gao et al. 2012). The outer cell wall layer contains less lignin and more of the minor polysaccharides mannan and galactan and more proteins than the main part. There is a high mineral content in the outer layer which obviously influences the surface properties of the kapok fiber. Kapok fiber includes a high ratio of syringyl/guaiacyl units (4–6) and a high level of acetyl groups (13.0 %) as compared with normal plant cell walls (about 2–4 %) (Chung et al. 2008). The bulk density of the kapok fiber is 0.30 g/cm^3, the crystallization degree is 35.90 %, and the specific birefringence is 0.017 (Xiao et al. 2005). The kapok fiber shows the well-resolved spectrum of cellulose I, and the crystallinity is lower than cotton fiber (Cao et al. 2010).

To enhance the intrinsic properties or alter the surface characteristics, natural kapok fiber is usually pretreated including (1) chemical treatment, such as alkali/acid treatment, solvent treatment, oxidation treatment and acetyl treatment, and

(2) physical treatment, such as ultrasonic treatment and radiation treatment, by which the surface impurities can be removed and the interfacial properties will be improved.

Solvent treatment is a popular method to change the surface property of kapok fiber. Previous studies have shown that the kapok fiber has lost their silky luster after solvent treatment. By comparing the spectra of untreated and solvent-treated kapok fiber, the increase in absorption bands at 3,410 and 2,914 cm^{-1} can be observed, and this information is an indication of the removal of plant wax from the surface of kapok fiber. Except for the above absorption bands, there is no significant variation in other bands for water-treated and chloroform-treated kapok fiber. But for NaOH-treated fiber, the absorption bands at 1,740 and 1,245 cm^{-1} show a remarkable reduction in their intensities. This is ascribed to the fact that the alkali treatment can remove all the esters linked with aromatic ring of lignin, resulting in a significant de-esterification of kapok fiber. For $NaClO_2$-treated kapok fiber, the absorption bands around 1,602 and 1,504 cm^{-1} nearly disappear, owing to the cleavage of the aromatic ring in lignin (Wang et al. 2012a).

Furthermore, for untreated, water-treated, HCl-treated, NaOH-treated, $NaClO_2$-treated, and chloroform-treated fiber, the crystallinity index is determined to be 35.34 %, 33.93 %, 22.17 %, 32.00 %, 26.97 %, and 27.17 %, respectively. This result implies that the crystalline region of lignocellulose in kapok fiber shows no remarkable change for water-treated kapok fiber, while HCl, $NaClO_2$, and chloroform treatment will change the aggregate structure and expand the proportion of amorphous region of kapok fiber. But for NaOH-treated kapok fiber, there appears no remarkable reduction in the crystallinity when compared to $NaClO_2$ treatment, even though a significant de-esterification occurs for kapok fiber during this process (Wang et al. 2012a).

Liu and Wang (2011) investigated the effect of mercerization on microstructure of kapok/cotton yarns, with the findings that the chemical compositions of fiber showed no appreciable changes after mercerization treatment, but this treatment could decrease the crystallinity of kapok/cotton yarns, transforming partial cellulose I to cellulose II. Chen and Xu (2012) found that the ultrasonic treatment with water had little influences on the morphological structure and chemical component of the kapok/cotton-blended yarns, except for some loss of kapok flocks. Via the combination process of chlorite–periodate oxidation, kapok fiber was found to harbor a certain amount of polysaccharides, together with lowered lignin content. Although a distorted hollow shape and rough surface were observed, the characteristic fine hollow shape was still maintained in all of the chemically oxidized kapok fiber (Chung et al. 2008). To provide the functions or facilitate further modification, some polymerizable monomers had been grafted onto the kapok fiber by Co^{60} γ-ray radiation-induced graft copolymerization, such as styrene, glycidylmethacrylate (GMA), and acrylic acid (AA) (Cho et al. 2007; Kang et al. 2007).

6.3 Properties of Kapok Fiber

6.3.1 Spinning Property

Kapok fiber is known as the soft gold in plants for its finest and lightest quality, highest hollowness, and most warm nature. Due to their wide lumen filled with air, their smooth surface, and low strength, kapok fibers are considered unfit for textile fabrics in the early years (Fengel and Wenzkowski 1986). With the development of technology, the spinning of 100 % kapok fibers beyond lap formation stage is not possible, but kapok yarn property and weavability could be improved through sizing or blended spinning (Yang and Jin 2008). To resolve the problem of pure kapok yarn such as low strength, much hairiness, poor wear resistance, and difficult to weave, sizing experiment of 27.8 tex pure kapok yarns was carried out in order to improve yarn performance and meet the requirements of weaving. According to the characteristics of kapok yarns, a mixed size composed of acid-modified starch and poly(vinyl alcohol) (PVA) was selected to size kapok yarns. The results show that low solid content helps size penetration and facilitates yarn strength and elongation improvement (Yang 2010). Furthermore, the spinning of kapok fiber blended with cotton fiber is largely successful. With an increase in kapok content in the blend, the yarn regularity and tenacity decrease, while the yarn extensibility increases. It is considered that kapok fiber can be blended with cotton for spinning yarn, but the content of kapok fiber should not be more than 50 %, or the blended yarn property and weaving processing will be effected (Dauda and Kolawole 2003; Yang et al. 2013). Also, the total cost of production of the yarns decreases significantly as the kapok content increases in the blend.

6.3.2 Dyeing Property

Owing to large hollow structure and waxy surface, kapok fiber shows the hydrophobic–oleophilic characteristics. The higher surface tension (7.2×10^{-4} N cm^{-1} at 20 °C against air) will drive out the water droplets, leading the surface of kapok fiber cannot get wet with the water droplets (Chung et al. 2008), making this fiber show poor affinity to hydrophilic coloring agents or dyes. For kapok fiber, the dyeing efficiency is relatively low, and the dyeing property of kapok fiber is worse than that of cotton fiber (Lou 2011). Pretreatment of kapok fiber is thus important to enhance the dyeing property of this fiber, but up to now, no mature processing or pretreatment techniques have been established except for the mercerization. Compared with cotton fiber, the alkali resistance of kapok fiber is rather poor, and accordingly, mild alkali treatment conditions are generally expected for kapok fiber in dyeing and finishing processes.

6.3.3 Mechanical Properties

According to the tested data of four types of kapok fibers, the average breaking strength and breakage elongation of kapok fibers are 1.44–1.71 cN and 1.83 %–4.23 %, respectively. By comparing with cotton fiber, kapok fiber has the lower tensile elongation, similar breaking tenacity and initial modulus, while easily fragile due to the fineness and softness of kapok fiber (Xu et al. 2009). Comparing kapok fiber with cotton and some synthetic fibers, the bending rigidity of a single kapok fiber is lower. However, its relative bending rigidity is much higher (Xu et al. 2011). As reported, the average bending rigidity of a single kapok fiber is found to be 0.823×10^{-5} $\mathrm{cN \cdot cm^2}$, whereas its relative bending rigidity is determined to be 21.06×10^{-4} $\mathrm{cN \cdot cm^2 \cdot tex^{-2}}$. The compression test is an indirect evaluating method of kapok fiber hollowness and manufacturing technology of kapok products, with the finding that the compression elasticity of dry kapok fibrous assemblies is better than that of wet kapok fibrous assemblies (Fang et al. 2012). For the kapok-/cotton-blended yarns, the mercerization treatment will produce some impressive influences on their mechanical properties. When NaOH concentration increases from 180 to 250 g/L, the strengths of kapok-/cotton-blended yarns increase and elongations at breaking decline, and up to 280 g/L, the strengths of kapok-/cotton-blended yarns exhibit a dramatic drop and elongations at breaking present a gradual increase with an increase in kapok fiber content (Liu and Wang 2011).

6.3.4 Hydrophobic–Oleophilic Property

Kapok fiber contains the pectin and wax substances that contribute to its hydrophobic–oleophilic characteristic. On the glass slide coated with kapok extract, the diesel drop and water drop will show a different spreading radius and contact angle. The diesel drop can spread out rapidly, and in contrast, the water drop cannot spread out on the glass slide. As a result, a large spreading radius and small contact angle are observed for diesel drop, whereas a large contact angle is visualized for water drop, demonstrating that the oil is a wetting liquid for kapok fiber and the water is a non-wetting liquid for kapok fiber (Lim and Huang 2007). The static and dynamic contact angle of kapok fibers with different kinds of liquids such as vegetable oil, used oil, and engine oil is also investigated. It is found that kapok fiber is an excellent oleophilic and hydrophobic fiber with the contact angle of kapok fiber to water of 139.55°, but is less than 60° to various kinds of oil. The contact angle of kapok to water is constant as time flies. All the oil liquids on the kapok fibers have the quick spread rates, and the spread curves are similar though the spread rates varied with viscosity and surface tension of the liquids (Sun et al. 2011). This hydrophobic–oleophilic characteristic can be tuned by solvent treatments. Our study reveals that for untreated and $NaClO_2$-treated kapok fiber, different wetting phenomenon can be observed using water drops, with a large contact angle of 116° and a large spreading

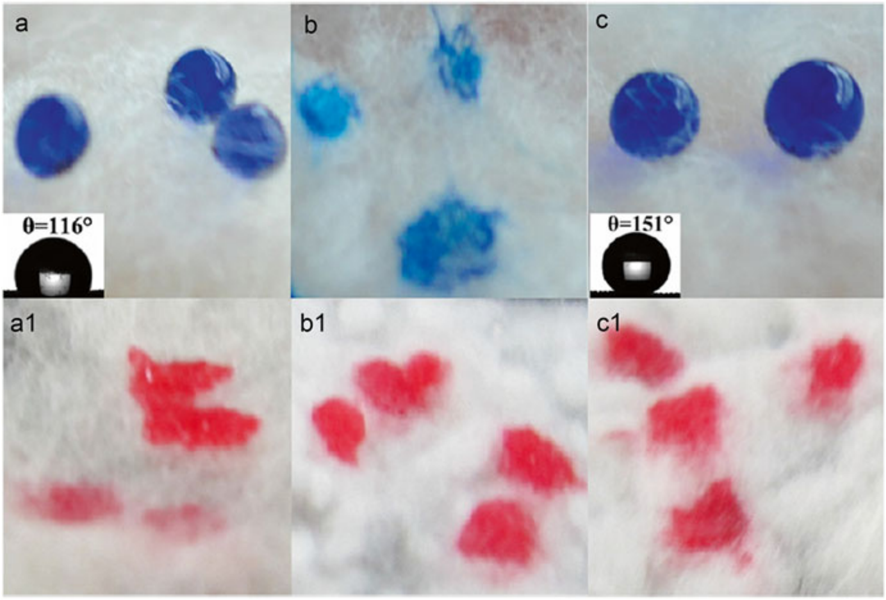

Fig. 6.2 Pictures of water droplet (dyed with methylene blue) on (**a**) raw, (**b**) treated, and (**c**) superhydrophobic kapok fiber surface; oil droplet (dyed with oil red O) on (**a1**) raw, (**b1**) treated, and (**c1**) superhydrophobic kapok fiber surface (Wang et al. 2012b) (Copyright 2012, reproduced with permission from Elsevier)

radius for untreated and $NaClO_2$-treated kapok fiber, respectively (Fig. 6.2) (Wang et al. 2012b). Here, another observation should also be mentioned. Before and after collecting the oils from water, the kapok fiber may float steadily on the water surface due to its light density and hydrophobic–oleophilic properties, a useful characteristic for oil spills cleanup. In addition to the thin hydrophobic plant wax layer covered on the surface of kapok fiber, the hydrophobic–oleophilic characteristic is also related to its micro–nano-binary structure (Zhang et al. 2013).

6.3.5 Adsorption Property

The water is a non-wetting liquid for kapok fiber due to the formation of large contact angle (>90°) between water and kapok fiber. Therefore, the water is not accessible to the large lumen of kapok fiber. Then, the kapok fiber should experience a chemical or physical pretreatment to be hydrophilic for further application as the adsorbent for removing different kinds of pollutants from aqueous solution. Wang et al. (2012b) found that after $NaClO_2$ treatment, the water drop can form a large spreading radius on the corresponding fiber surface, suggesting that by $NaClO_2$ treatment, the surface of kapok fiber has been transformed from intrinsic hydrophobic–oleophilic to hydrophilic. In addition, $NaClO_2$ treatment can lead to the de-esterification of kapok fiber, thus reducing the aggregate structure and expanding the proportion of amorphous region in kapok fiber (Wang et al. 2012a). In this case, Liu et al. (2012a) investigated the adsorption behaviors of a cationic dye methylene blue from aqueous solution using $NaClO_2$-treated kapok fiber as the adsorbent. In order to alter the hydrophobicity to hydrophilicity, a series of chemical modifications on the kapok fibers via the combination processes of chlorite–periodate oxidation have also been carried out (Chung et al. 2008). When treated with $NaClO_2$ for lignin degradation and $NaIO_4$ for sugar degradation, the chemically oxidized kapok fibers retained their hollow tube shape and evidenced elevated ability to adsorb heavy metal ions, with the adsorption rates of 93.55 %, 91.83 %, 89.75 %, and 92.85 % for Pb, Cu, Cd, and Zn ions, respectively. This enhanced adsorption of heavy metal ions onto the chemically oxidized kapok fibers can be attributed to the generation of -COOH groups during the oxidation process. When the kapok fiber is washed with dichloromethane to remove the botanic wax and further treated with NaOH solution, the resultant fiber can be modified with diethylenetriamine pentaacetic acid (DTPA). The resultant kapok-DTPA shows a fast adsorption for the metal ions with the adsorption equilibrium being reached within 2 min for Pb^{2+} and Cd^{2+}, and 5 min for Cu^{2+}. Maximum adsorption capacities of kapok-DTPA are 310.6 mg/g for Pb^{2+}, 163.7 mg/g for Cd^{2+}, and 101.0 mg/g for Cu^{2+}, respectively (Duan et al. 2013).

6.3.6 Microbiological Properties

Because of high lignin content, kapok fiber is not easily attacked by ordinary cellulolytic bacteria (Nilsson and Björdal 2008) and shows better antibacterial property (Han 2010). Liu et al. (2007) investigated the anti-moth, anti-mite, and antibacterial properties of kapok battings. The results of anti-moth test showed that the mean value of weight loss of kapok batting was smaller than reference sample obviously, and the damage grade of surface of kapok batting was 2A. In the anti-mite test, the mite expelling rate was 87.54 %, which proved the anti-mite property of kapok batting. For antibacterial test, kapok batting was confirmed to possess both the bactericidal effect and bacteriostatic effect on *Escherichia coli*. But in contrast, it did not have these effects on *Staphylococcus aureus*.

6.4 Conclusions and Future Perspective

As the “low-carbon” concept prevails, abundant kapok fiber has received increasing attention as an eco-friendly textile material for its intrinsic superiorities such as finest and lightest quality, highest hollowness, and most warm nature. With the focus on this green cellulosic fiber, more studies will be carried out to expand the application fields for kapok fiber by combining its higher hollowness and hydrophobic–oleophilic characteristics.

Acknowledgment We are grateful for the support of the National Natural Science Foundation of China (No. 21107116).

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Chapter 7
Production of Natural Fiber Obtained from the Leaves of Pineapple Plants (*Ananas comosus*) Cultivated in Costa Rica

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Contents

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_7, © Springer International Publishing Switzerland 2014

Abstract *Ananas comosus* crops, particularly the MD-2 variety, have demonstrated to adapt well to the environmental conditions of Costa Rica. However, one of the main issues that the management of this crop involves is how to deal with residues or post-harvest wastes. The objective of this study is to develop a machine for small-scale production of natural fiber from pineapple leaves, adaptable to rural conditions in Costa Rica. The proposed machine is of the scrapping type, in which the leaf is introduced and the machine eliminates the tissue covering the leaf fiber. The study showed that the machine has the capacity to process an average of 4.9 kg dried fiber/hour, with an average cost of US$0.49/kg of dried fiber. The study also found that the machine's capacity varies for plant leaves from the first or the second crop, giving better performance with the leaves from the second crop. The fiber produced with the machine showed a greenish coloration created by the combination of white, green, and yellow colors which were measured by the Color Systems CIE Lab. Once extracted, the fiber may be bleached with water, hydrogen peroxide 5 %, or chlorine 1 %, of which the most effective is chlorine 1 %, since it gives the highest color change to pineapple fiber.

Keywords *Ananas comosus* • Natural fiber • Fiber production • Production costs • Fiber bleaching

7.1 Introduction

Ananas comosus is commonly found in tropical regions, in any type of soil as long as it has good drainage and its pH ranges between 5.5 and 6.0 (Collins 1947; Ziska et al. 1991). The productivity level of this plant is higher in regions having average daily temperatures above 25 °C (Bertsch 2005), where up to two yearly crops are obtained (Acuña 2006). In Costa Rica, this species was planted for the first time in 1970 (Canapep 2012). According to estimations, there is at present 40,000 ha planted (GFA Consulting Group 2010), mostly of the variety MD-2, which has demonstrated better adaptation to environmental conditions (Acuña 2006; Blanco et al. 2011).

However, one of the major limitations of this culture is the large amount of post-crop wastes. Araya (1998) showed that close to 220 tons of wastes/ha/rotation are produced in an *A. comosus* plantation. Due to lack of processing technology or of commercial products, pineapple wastes have not received adequate management in Costa Rica (Moya et al. 2013a, b). A glyphosate herbicide is applied to plantations after the harvest. A week later, the plantation is burnt, which is an agricultural practice considered unfriendly to the environment (Acuña 2006; MAG 2010).

Another inconvenience for the utilization of wastes is that the planted areas are segregated and they belong to small and medium producers, which makes harvesting and management of the wastes more difficult (Araya 1998).

A possible use that may be given to pineapple wastes, particularly to the leaves, is to produce natural fibers to make ropes and textiles, among others. Studies developed by Paul et al. (1998) and Banik et al. (2011) determined that *A. comosus* has high potential for textile production since only 3.5 % of the fiber is covered by a hydrophobic waxy layer, which makes processing easier since the need for mechanical treatments or substances to eliminate the fiber's waxy layer is reduced. Furthermore, *A. comosus* fiber has been found to have suitable properties for mixing with cotton, jute, ramie, and other artificial fibers (Sinha 1982; Banik et al. 2011) and to manufacture interior components of cars (Banik et al. 2011; Holbery and Houston 2006; Neves-Monteiro et al. 2009). Kannojiya et al. (2013) analyzed the importance of pineapple fiber in commercial products in the textile industry.

Although Costa Rica lacks the technology to process *A. comosus* leaves, it does have the experience and technology to process and produce other types of fibers, such as *Furcraea cabuya* (cabuya). Although machines to obtain fiber have been manufactured in some countries in Asia (Banik et al. 2011, Kengkhetkit and Amornsakchai 2012), the conditions of the economy, human resources, and productivity of the plantations in Costa Rica are different from those of Asia. In Costa Rica, for example, manpower costs are higher than in Asian countries; the density of plantations is also higher (70,000 plants/ha, whereas in Asia it is only 40,000 plants/ha).

For this reason, the present work proposes the development of a productive system to industrialize and produce natural fibers from the leaves of *A. comosus*, given their morphologic characteristics. In addition, the production and economic evaluation of the proposal for industrialization is presented, as well as color characterization of the pineapple fiber and three different fiber bleaching methods.

7.2 Material and Methods

7.2.1 Proposal for Industrialization

A prototype model for the industrialization of *A. comosus* fiber was developed, based on the following principles: (1) it should be adaptable to the *A. comosus* leaf morphology; (2) the scale of production should be no more than 4 kg dried fiber/hour; (3) it should be portable, handled by three people, and transportable in a less than 2,000 cc engine pick up; and (4) it can be operated by staff with low training.

7.2.2 Testing Sites of the Model

The prototype machine was tested in four *A. comosus* plantations of the variety MD-2, two located in the North region and two in the South Pacific. All of the plantations had the same density with 70,000 plants/ha. In each region, the machine was tested with plants from the first crop (11 months old) and from the second crop (18 months old).

Table 7.1 Bleaching treatments applied to fiber extracted from the leaves of *A. comosus*

Bleaching type	Description
Water	The fiber was placed under running water at room temperature until it lost the green coloration given by the chlorophyll
Hydrogen peroxide 5 %	The fiber was put into a recipient with 250 ml of a hydrogen peroxide 5 % solution during 5 min. Then the fiber was washed under running water at room temperature
Hypochlorite 1 %	The fiber was introduced into a recipient with 250 ml of a hydrogen peroxide 1 % solution during 5 min. Next, it was washed under running water until the hypochlorite smell was lost

7.2.3 Industrialization Tests

These tests were taken in two parts: In the first test, 11 plants per crop type in each region (11 plants × 2 crop types × 2 regions) were evaluated to determine the leaf's morphological characteristics, the amount of leaves, and their weight in relation to the total weight of the plant (expressed in percentage). In the second test, fiber production was carried out ten times with intervals of 15 min, with the purpose of finding the costs and the level of production of the prototype machine.

7.2.4 Morphological Parameters of the Leaf and Bleaching

All plants (11 in each site) were randomly selected in the plantation. The plants were manually extracted and the roots were eliminated. Posteriorly, the leaves of the base of the plants (small stalk) were separated and each part was weighed. Each leaf was measured lengthwise and then all leaves were put together to determine their weight. Following that, fiber was extracted using the prototype machine and three fiber bleaching treatments (Table 7.1) were applied. Next, the fiber was dried using the drying system developed by Moya and Solano (2012).

7.2.5 Fiber and Waste Moisture Content Determination

After the leaf fiber was obtained, ten fiber samples in green condition weighing approximately 100 g were randomly selected. Then the samples were taken to the laboratory where they were put to dry into an oven at 103 °C for 24 h to determine the moisture content (Eq. 7.1). The moisture content of the waste from fiber extraction was also determined by means of Eq. 7.1.

$$\text{Moisture content}\left(\%\right)=\frac{\text{Green weight}\left(\text{g}\right)-\text{Dry weight}\left(\text{g}\right)}{\text{Green weight}\left(\text{g}\right)}\times 100 \tag{7.1}$$

7.2.6 Fiber Color and Color Change

Fiber color was tested during three stages of fiber production. These were as follows: (1) after the fiber came out of the scrapping machine, when the fiber was in green condition; (2) after the application of the three bleaching treatments; and (3) after fiber drying. Color was measured with a Hunter Lab spectrophotometer, miniScan XE Plus model, to obtain parameters L^*, a^*, and b^*. Since colorimeter diameter in its measuring area is 1 cm, fiber rolls of the appropriate thickness were prepared in order to fit the hole totally. Color change (ΔE^*) was determined with the difference between the color of the fiber obtained with the prototype machine and the color after treatment (with water, peroxide, or hypochlorite). The value of ΔE^* for color of the fiber obtained with the prototype machine and fiber color after drying was also obtained. To determine ΔE^*, the ASTM D 2244 (ASTM 2012) standard was used. This standard defines ΔE^* as the net color variation after a period and is obtained by means of Eq. 7.2.

$$\Delta E^* = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \tag{7.2}$$

where ΔE^*: pineapple fiber color change; ΔL: L^* fiber color after scrapping–L^* after washing or after fiber drying; Δa: a^* fiber color after scrapping–a^* after washing or after fiber drying; Δb: b^* fiber color after scrapping–a^* after washing or after fiber drying.

7.2.7 Costs and Production Tests

Machine processing tests were performed to measure the time taken by the machine to scrap the leaf. The following costs were also evaluated: (1) initial investment costs (fixed), considering depreciation of the scrapping machine; (2) material expenses, without including the leaves of *A. comosus* as a cost since they are presently considered as waste (only the fuel for the scrapping machine was taken into account); and (3) manpower costs, which included three workers to whom the corresponding salary according to the legislation in Costa Rica was paid. All costs were reported in US dollars.

7.2.8 Information Processing

The lengths of the leaves of the first and second crops were applied a frequency distribution. The distributions were later compared using the Kolmogorov–Smirnov test to determine the degree of similarity between the leaf length distribution of the plants from the first and from the second crops. Meanwhile, the weight data obtained from the different plant elements were first compared among themselves to evaluate whether there were differences between the plants of each crop and were later used to generate the weight percentages based on the total weight. Also, a projection was made of the possible weight per hectare to be obtained from the different elements of the plant.

7.2.9 Data Analysis

Regarding the performance of the machine, firstly, its productivity was determined based on the time evaluations carried out for fiber production in the four plantations evaluated. The data obtained showed the amount of plants and leaves consumed per hour and their equivalents in green and dried fiber. The production costs for each kilogram of dried fiber were also calculated. Regarding fiber color, a variance analysis was applied to $L*$, $a*$, $b*$, and $\Delta E*$ parameters obtained from the three bleaching treatments used, in order to determine whether there were any differences between the values of green fiber and thus detect differences between the fiber from the first and the fiber from the second crop. Next, the values of the three treatments in the bleaching and drying stages were compared; the ANOVA tests and the Tukey test with 0.01 significance were applied in order to find which treatments varied. SAS 8.1 (SAS Institute Inc., Cary, NC) and STATISTICA 9.1 Windows programs were used for both the analysis and for the Kolmogorov–Smirnov test.

7.3 Results and Discussion

7.3.1 Production and Morphological Characterization of **A. comosus** *Leaves*

First, differences were found in the amount of leaves of the plants from the first and the second crops. The first crop plants presented an average of 69 leaves, whereas the second crop plants had 105 leaves. Regarding the length of the leaves, a variation of 30–130 cm was found in the first crop plants and of 30–140 cm in the second crop plants (Fig. 7.1). Distribution by leaf length showed that (1) for longitudinal classes between 50 and 100 cm, the first crop plants' production is statistically higher than the production of the second crop plants; (2) however, the percentage of leaves in classes between 30–40 and 100–140 cm in plants of the first crop is statistically lower than the percentage shown by the second crop plant leaves for the same classes, and (3) classes from 20 to 30 cm and 40 to 50 cm and the 140 cm superior class did not show statistical differences in the frequencies or percentages of leaves between the plants from the first crop and from the second crop (Fig. 7.1). The differences found between the plants from both crops are similar to those mentioned by Pérez et al (2011) and Aragón et al (2012)with regard to P3R5 and MD-2 varieties.

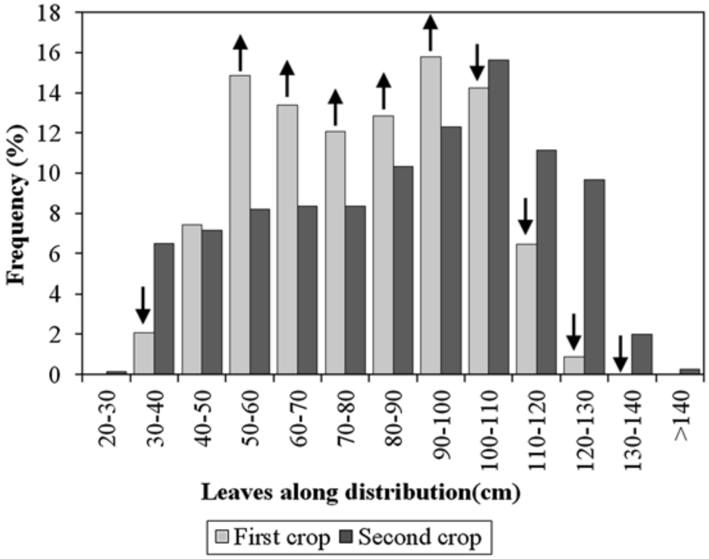

Fig. 7.1 Frequency distribution of the length of leaves of *A. comosus* evaluated for the first and the second crops coming from two plantations with different origins (the *arrows* indicate a statistical variation between the first and the second crops)

Table 7.2 Weight distribution of *A. comosus* coming from the first and the second crops

	First			Second			Average	
Parameter	Per plant (kg)	Per hectare (kg)	Percentage	Per plant (kg)	Per hectare (kg)	Percentage	Per plant (kg)	Per hectare (kg)
Total weight	3.91	382,720	100.0	5.67	35,3145	100.0	4.79	36,7932
Base weight	0.89	123,370	22.8	1.57	109,900	27.7	1.27	107,022
Leaf weight	2.90	238,060	74.2	4.10	264,355	72.3	3.50	266,207
Fiber weight	0.056	6,175	1.7	0.095	6,175	1.8	0.076	6,175
Waste	3.85	376,545	98.3	5.58	346,970	98.2	4.71	361,757

The justification these authors give is that the first crop plants are young and their leaves are not completely developed. Therefore, leaves with lengths less than 100 cm from the first crop are fewer than the leaves of the same length of the second crop. Meanwhile, the second crop plants are mature and their leaves are more developed (Pérez et al 2011; Aragón et al 2012), therefore concentrating in classes above 100 cm long.

Weight evaluation of the different parts of the *A. comosus* plant (Table 7.2) showed that the values varied for the first and second crop plants. Total plant weight, base weight, and leaf weight of the second crop plants were significantly higher than the weight of plant parts of the first crop (Table 7.2). However, a great similarity between both crops was found in the evaluation of the distribution of the weight

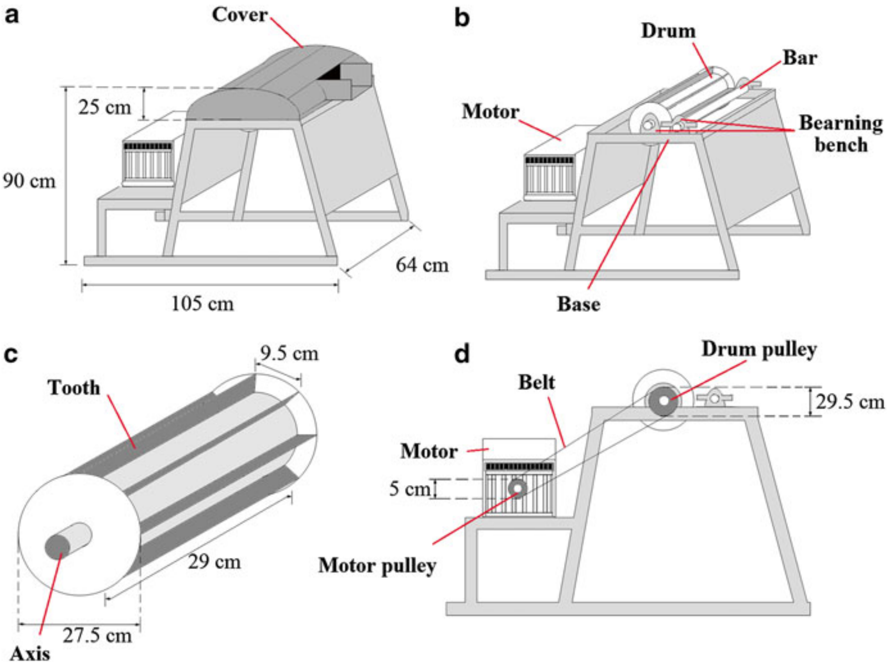

Fig. 7.2 Proposed scrapping machine model for *A. comosus* leaves from the first and the second crops from two different plantations. (**a**) General dimensions (**b**) structural parts (**c**) Drum dimensions and part and (**d**) Motor and broadcast of force

percentages of the different parts of the pineapple plants; the weight of the bases of the plants did not exceed 28 % of the total plant weight (Table 7.2), while the leaves presented the highest weight (over 70 % of the total weight), which makes evident leaf dominance in *A. comosus* morphology. These percentages coincide with those reported by Pérez et al. (2011) for the P3R5 variety and D'Eeckenbrugge et al. (2011) and Aragón et al (2012) for the MD-2 variety. They determined that the weight of the base of the plant (stalk) is not above 30 % of the total plant weight. As for most Bromeliaceaes, *A. comosus*'s growth depends on the development of the small stalk and abundant rose-shaped leaves to satisfy photosynthesis requirements, necessary for fruit production (Bartholomew et al 2003).

7.3.2 Proposed Leaf Scrapping Machine

The model was adapted to process *A. comosus* leaves from the first and second crops, which present different quantities of leaves (an average of 69 leaves in plants of the first crop and 105 leaves in plants of the second crop), as well as leaf lengths varying from 30 to 140 cm (Fig. 7.1). The machine's dimensions are 105 cm long, 64 cm wide, and 90 cm high (Fig. 7.2a), with an approximate weight of 50 kg. It is easily

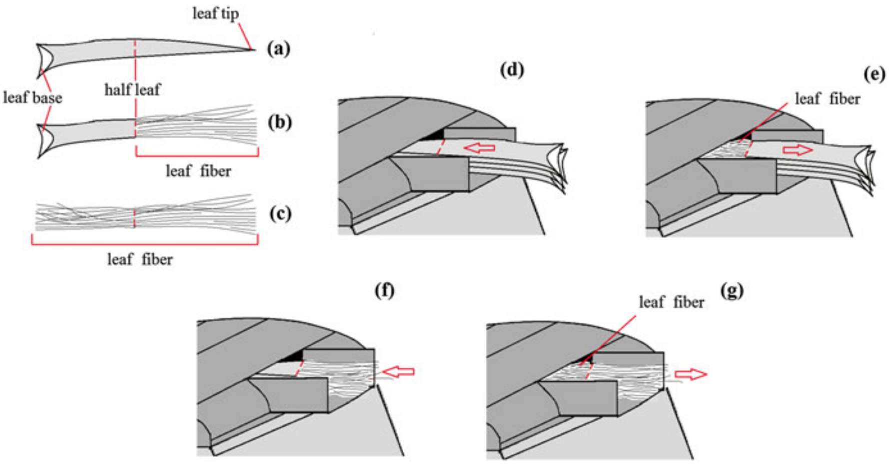

Fig. 7.3 Operation system of the proposed machine for shredding *A. comosus* leaves. (**a**) pineapple leaves before shredding, (**b**) first step of shredding (**c**) pineapple leaves after shredding or fiber obtained, (**d**) introduction of leaf tips (**e**) taken out backwards of leaf tips (**f**) introduction of leaf base and (**g**) and taken out backwards of leaf base or fiber exposure

transportable by a pickup car. A wooden cover for the machine was designed in order to avoid the risk of accidents when the machine's drum is working (Fig. 7.2a).

The scrapping machine has a drum (27.5 cm in diameter and 29 cm long) on a 4.5 cm diameter axis at the base of the machine. The axis is placed on two bearing benches (Fig. 7.2b). The drum has nine metallic teeth separated 9.5 cm from one another (Fig. 7.2c). The drum is rotated by a four-stroke petrol Honda engine, GX-120 model, with a cylinder capacity of 118 cc. The axis rotates at a minimum speed of 1,400 rpm and a maximum speed of 3,600 rpm, with a power of 4 HP. The transmission of the movement of the engine's main axis is performed by a system of pulleys and a belt. The main engine's axis has a 5 cm diameter pulley, and onto the axis crossing the drum, there is a 29.5 cm diameter pulley connected by a B-55 belt (Fig. 7.2d).

The machine was put to work by introducing 4–6 pineapple leaves tip first (Fig. 7.3a). The worker must hold the leaves from the base. Once half the length of the leaf has been introduced (Fig. 7.3d), it must be taken out backwards (Fig. 7.3e). At this stage, the leaf fiber is separated from the parenchymal tissue (Fig. 7.3b). Later, the worker holds the leaves by the already shredded extreme (Fig. 7.3f) and introduces them their bases first until reaching the exposed fiber (Fig. 7.3g). Then, the leaves are taken out with the fiber completely extracted (Fig. 7.3c).

7.3.3 *Fiber Characterization*

The study found that an average of 0.076 fiber kg/plant is extracted from the two types of crops, which is equivalent to 2.6 % of the total weight of the leaves before scrapping and to 1.75 % of the plant's total weight. The plant from the first crop produces less fiber quantity than the plant from the second crop (Table 7.2). Plants from the second crop produced 59 % more fiber compared with the plants from the first crop. Projecting these values per crop unit (hectares) shows that an average 6,175 fiber kg/ha (Table 7.2) may be extracted. The inconvenience is, however, that a great amount of the plant is waste material, an average of 361,757 waste kg/ha (98.2 % of the plant weight). Nevertheless, it is important to point out that evaluations showed that 89.20 % of the waste material is moisture, which means that 322,687 kg (89.2 %) of waste correspond to water.

The values found for fiber are due to the fact that the central part of the pineapple leaf consists of bundles immersed into parenchymal tissue and the leaf surface is made of epidermal tissue (Bismarck et al., 2005, Moya et al. 2013a, b). Due to this anatomical characteristic of the leaf, a great amount of water is stored in the parenchymal tissue, thus increasing weight due to moisture, which results in low fiber percentage (D'Eeckenbrugge et al. 2011; Aragón et al 2012).

According to the evaluations of moisture content of both extracted fiber and waste, extracted fiber presented an average moisture content of 74.24 %, whereas waste moisture content amounted to 89.20 %. In the case of fiber, the percentage found coincides with studies carried out by D'Eeckenbrugge et al. (2011), Aragón et al (2012), and Moya and Solano (2012), who reported moisture contents in *A. comosus* leaves of the variety MD-2 ranging from 70 to 75 %. Regarding ash quantity, the value is 4.75 % for leaf fiber, which is significantly higher than the value of 1.1 % reported by Mukherjee and Satyanarayana (1986). On the other hand, the ash content of leaf waste was 10.37 %. High ash content, as is the case of the wastes, has a negative effect on some possible uses; if the waste is used as fuel for heating, the resulting ashes have to be constantly eliminated.

With regard to fiber color evaluation, the average values presented by the fiber coming out of the machine or green condition were L^* of 56.02, a^* of −10.81, and b^* of 35.23. This is a combination of white, green, and yellow shades, which results in a greenish clear coloration of the fiber. No differences in color parameters of fiber in green condition were found between plants coming from the first or second crops (Fig. 7.4); therefore, color could be treated without distinction of crop.

Evaluation of the three bleaching treatments (water, hydrogen peroxide 5 %, and chlorine 1 %) for both the bleaching and drying stages showed that parameter L^* (luminosity) increased for all treatments (Fig. 7.4a), which means that the fiber became clearer; however, differences were found among the bleaching treatments. The fiber in green condition bleached with chlorine 1 % showed a significantly higher value for L^*, followed by water treatment, and lastly by hydrogen peroxide 5 % (Fig. 7.4a). After the fiber drying, the L^* value decreased with chlorine 1 % treatment; the fiber bleached with the latter treatment shows no statistical differences with water treatment. When the fiber is treated with hydrogen peroxide 5 %, the L^* value after drying is significantly higher than for the fiber treated with water or chlorine 1 % (Fig. 7.4a).

Parameter a^* for fiber color increased its value in both the bleaching and drying stages (Fig. 7.4b), which means that the reddish shade of the fiber was intensified. Chlorine 1 % bleaching was the only treatment showing positive a^* values

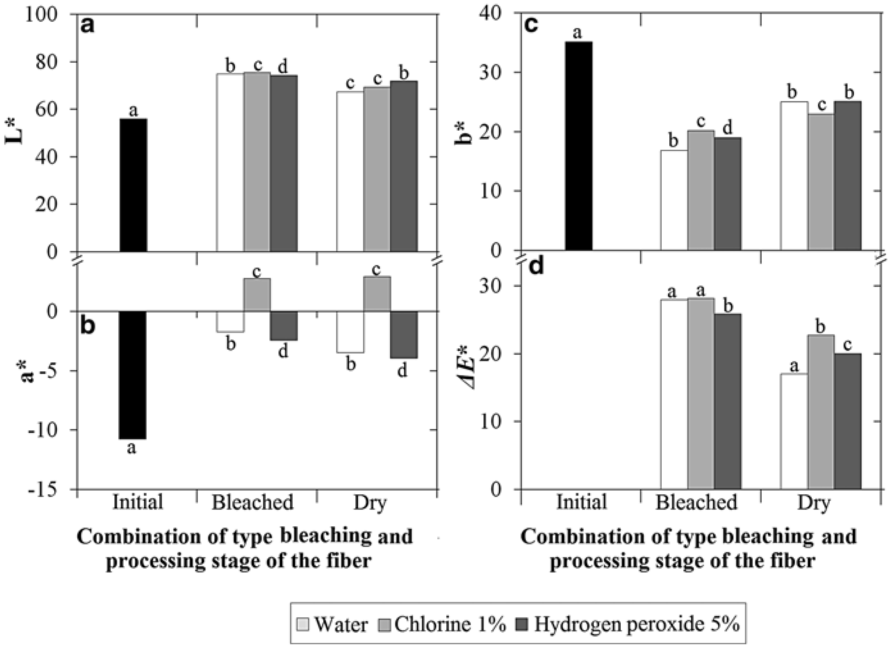

Fig. 7.4 Variations of the *L** (**a**), *a** (**b**), *b** (**c**), and Δ*E** (**d**) color parameters after the application of the three treatments for fiber bleaching and after the drying process of natural fiber obtained from *A. comosus* leaves from the first and the second crops

(Fig. 7.4b) unlike hydrogen peroxide 5 % treatment, which showed the lowest increments of *a** in both stages (bleaching and drying). Lastly, water treatment also showed an increment in the value of *a** (Fig. 7.4b).

Parameter *b** decreased significantly with the bleaching and drying process (Fig. 7.4c), which means that the yellow shades of the fiber diminished. Also, differences were found in this parameter between the bleaching and drying process. For bleaching, water treatment showed the highest reduction of parameter *b**, followed by hydrogen peroxide 5 %, and next by chlorine 1 % with the lowest reduction. After fiber drying, the behavior of the parameter varied, since bleaching with water and hydrogen peroxide 5 % showed no differences (in the b* value) between both treatments, although the values were significantly lower than for bleaching with chlorine 1 % (Fig. 7.4c).

With regard to color change (Δ*E**), it varied from 18 to 33. The highest color changes were found in the bleaching process with water and chlorine 1 %, among which there were no differences; these values were significantly higher than for bleaching with hydrogen peroxide 5 %. For dried fiber, chlorine 1 % was the bleaching treatment showing the highest value of Δ*E** and therefore the most effective, followed by hydrogen peroxide 5 %, and lastly by water.

Table 7.3 Production performance of the proposed machine for fiber production from *A. comosus* leaves from the first and the second crops from plantations with different origins

	Type of crop		
Aspect	First crop	Second crop	Average
Amount of plants/hour	101	125	113
Production in leaves (kg/h)	118	238	178
Wet fiber production (kg/h)	12.5	21.9	17.2
Dry fiber production (kg/h)	3.5	6.4	4.9

7.3.4 Production Performance

Table 7.3 presents the results of the productivity tests for the prototype scrapping machine for *A. comosus* leaves. The tests found that the prototype machine has an average processing capacity of 113 *A. comosus* plants/hour, with a slightly superior capacity in the case of the second crop plantations than in the first crop plantations (Table 7.3). Such difference may be explained by the higher amount of leaves present in the second crop plants (105) compared with the quantity of leaves in the first crop plants (an average of 69).

As for productivity, it is possible to process an average of 178 pineapple leaves kg/hour, with the second crop plantations showing again the highest productivity. This level of productivity allows the production of an average of 17.2 fiber kg (in green condition) per hour. This is the equivalent of an average dry fiber final weight of 4.9 kg/h.

Evaluation of performance of other types of machines (Banik et al 2011; Das et al 2010) shows that this model presents lower performance than that of systems developed in Asia, which have a more advanced technology for this kind of processing. Banik et al (2011), for example, report equipment capable of producing 25 fiber kg/hour; Das et al (2010) also report that high-performance technical equipment for industrial production can process 1,500 green fiber kg/day. In these cases, however, the machines, although more powerful, are more expensive.

7.3.5 Production Costs

Cost evaluation for dry fiber production from *A. comosus* leaves is presented in Table 7.4. A slight increase of the production costs was found in the first crop plants compared with the plants from the second crop, which was due to the difference in productivity between both crops (Table 7.4). However, a similarity was found in the distribution of costs; fuel was the rubric which had most influence on the cost of the product, accounting for an average 70.1 % of the total cost, followed by manpower costs, with 29 % of total cost. Three workers were considered in the manpower rubric: one to operate the machine, the second to hand the leaves to the machine operator, and the third to collect and arrange plants for transportation or for drying.

Finally, the lowest cost was depreciation of the equipment with 0.9 % of the production costs. The cost of the equipment was of US$3,000 with a lifetime of 12

Table 7.4 Production costs of the proposed machine to obtain fiber from *A. comosus* leaves from the first and the second crop plantations from different origins

		Type of crop		
Type of cost	Cost (US$/kg of dried fiber)	First crop	Second crop	Average
Manpower	Operators (3)	0.184	0.100	0.142
Materials	Gasoline	0.373	0.314	0.343
Investment	Depreciation of the machine	0.005	0.003	0.004
Total	Production cost	0.561	0.416	0.489

years which means that for plantations of 70,000 plants/ha, this rubric has little influence on the total cost. Costs of raw material or drying were not considered since the first comes from wastes and air-drying was used.

7.4 Conclusions

The quantity of leaves as well as the distribution by leaf length of *A. comosus* plants from the first and the second crops was different. The plants from the first crop produced less quantity of leaves per plant, therefore less quantity of leaves and less fiber per area unit (hectare). With respect to the scrapping machine prototype, productivity tests showed that the average processing capacity was 113 *A. comosus* plants/hour, slightly higher in the second crop than in the first crop, for the reason that the second crop plant had more leaves, thus allowing production of 4.9 kg/h of dried fiber. The fiber produced had an average 74 % moisture content and presented a greenish shade, which can be bleached with water, hydrogen peroxide 5 %, or chlorine 1 %, the most effective being chlorine 1 %, which gives the highest color change for pineapple fiber.

Lastly, a slight increase in production costs of the first crop plants was found compared with the second crop, due to the difference in the level of productivity of each type of crop. However, the distribution of costs was similar for both crops, since fuel accounted for 70.1 % of the total cost, followed by manpower with 29 %, and lastly by depreciation of the equipment with the lowest cost at 0.9 %. In addition, the average cost to produce 1 kg of dry fiber was US$0.49.

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Chapter 8
Indian Date Leaf FRP Composites: Mechanical and Dielectric Properties

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Contents

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_8, © Springer International Publishing Switzerland 2014

Abstract Natural fibers and their composites play a vital role in the fabrication of various components in automobile and structural components because of their superior specific performance. In order to satisfy day-to-day requirements in various sectors, new eco-friendly materials are introduced which are reinforced with renewable, cheap, and easily available natural fibers. A new leaf fiber, i.e., Indian date leaf (IDL), is introduced in this work and extracted by “pure splitting method” (PSM). Initially, the fiber is characterized for its density and tensile behavior. Surface morphology of the fiber is also examined by using JEOL JSM scanning electron microscope (SEM). Using IDL and IDL CT fibers as reinforcement in the polyester matrix, the composites are fabricated by wet lay-up technique. The fabricated composite specimens are tested to determine mechanical and dielectric properties as per ASTM procedures. Chemically treated IDL fiber exhibited 25.69 %, 4.6 % more tensile strength and modulus than untreated ones, and the stress vs. strain curves are drawn for all tested specimens. The specific tensile strength of chemically treated IDL FRP composites is 1.38 times higher than untreated IDL FRP composites whereas specific tensile modulus of IDL FRP composites is 1.04 times higher than treated IDL FRP composites at maximum fiber volume fraction. Chemically treated IDL FRP composites exhibited flexural strength, modulus of 63.47 MPa, 5 GPa under flexural loading, which is higher than untreated FRP composites. IDL FRP composites’ impact strength is 18.94 kJ/m^2 at maximum fiber volume fraction. The dielectric strength is clearly decreasing with increase in fiber content, which gives an opportunity for a designer in selecting suitable lightweight material with reasonable insulation. A clear rougher surface at all portions on the surface of chemically treated IDL fibers is visualized from SEM image.

Keywords Indian date leaf fiber • Mechanical properties • Dielectric strength • Scanning electron microscopy (SEM)

8.1 Introduction

Natural fibers, the name itself implies that they are created by nature. The renewable nature of fibers and high specific performance when they are reinforced into the matrix invited the attention of several researchers from the past few decades. Several people made numerous efforts for investigating the performance of fiber and its composites under mechanical, thermal, and electrical loadings at various fiber contents. Some of the imperative results related to various natural fiber reinforced composites using various fibers and matrices have been reviewed and are highlighted. In order to understand the behavior of IDL FRP composites, focus is made to compare the obtained results from the present work with the results which are available in literature on leaf fibers like sisal and pineapple polymer composites.

The pineapple fiber length of 6 mm was found to be optimum in pineapple leaf fiber reinforced LDPE composites when the mechanical properties and process ability characteristics were considered (George et al. 1995). Cardanol derivative of toluene diisocyanate-treated sisal fiber reinforced composites had shown best mechanical performance dimensional stability when compared with the composites reinforced with sisal fiber under same aging conditions (Joseph et al. 1995).

Sisal fiber reinforced polystyrene composites had exhibited marginal increase in tensile strength at 10 mm fiber length, and benzoylation-treated sisal fiber reinforced composites have shown considerable improvement in tensile properties (Manikandan Nair et al. 1996). After conducting the study on pineapple leaf FRP composites, it was found that the mechanical properties were optimum at a fiber length of 30 mm (Uma Devi et al. 1997). With enhancement in fiber volume in matrix, the tensile strength of henequen fiber reinforced HDPE composites decreases for different processing temperatures, whereas the flexural strength and modulus were increased (Herrera-Franco et al. 1997).

An improvement in the mechanical performance of the composites was observed with the reinforcement of wood fiber in LDPE matrix along with titanate coupling agents (Liao et al. 1997). In order to assess the improved mechanical performance of the FRP composites, acetylated coir/oil palm fibers were reinforced in case 1, whereas in case 2, silane/titanate coupling agents were used (Hill and Abdul Khalil 2000). A comparison of mechanical properties was made among the composites reinforced with abaca (short) and glass fiber prepared by melt mixing and injection molding (Mitsuhiro et al. 2002).

An increase in tensile strength and modulus was observed up to an MAPP concentration of 35 % weight (Luo et al. 2002). The natural rubber composites were reinforced with bamboo fiber, and their mechanical performance was assessed after the silane coupling agents were added (Ismail et al. 2002). Big blue stem fiber reinforced composites had shown higher strength than wood and are comparable (Julson et al. 2004). A new experiment was conducted and composites were made, i.e., the use of polyester matrix, modified with coupling agent; flame retardant system; and blend of both as matrices and sisal fibers were reinforced to determine their mechanical properties (Fonseca et al. 2004).

Two investigations on flax and jute fiber reinforced composites were made. In the first case, various maleated PP coupling agents were used in agro-fiber PP composites. In the second case, oxidized PE, MAPP, and newly introduced MaPE coupling agents were used in the composites. The tensile and impact behavior of the composites in both the cases were studied (Keener et al. 2004). The effect of hybridization on the mechanical properties of randomly oriented banana/sisal hybrid FRP composites was investigated with the reinforcement of banana and sisal fibers at various volume fractions (Idicula et al. 2005). With the enhancement in NaOH concentration, the mass loss in Phormium tenax fibers was investigated. The composites consisting of epoxy matrix and treated and untreated fibers are tested under flexural load (Roger et al. 2007).

The glass, sisal, and coconut fibers reinforced polyester composites were tested for their mechanical properties after they were exposed in salt spray chamber (Nicolai et al. 2008). The resin transfer-molded banana FRP composites had shown maximum tensile, flexural, and impact properties at 40 % fiber content and had fiber of 30 mm in length (Sreekumar et al. 2008). The soaking time and molarity of

Fig. 8.1 Indian date tree or Indian date palm tree

chemical on the properties of turmeric FRP composites under tensile loading was investigated (Srinivasababu et al. 2010). The composites manufactured with the reinforcement of vakka and jowar fibers had tested for their mechanical and dielectric performance at various fiber volume fractions in the composites (Murali Mohan Rao et al. 2010; Ratna Prasad and Mohana Rao 2011).

Leaf fibers are obtained from mesophyll of leaves, e.g., sisal, Indian date, etc. In the present work, an attempt is made to introduce a new fiber, IDL. Indian date is called Eetha chettu in Telugu, shown in Fig. 8.1. This belongs to the Arecaceae family, binomially called “Phoenix dactylifera L.” Palm trees are grown extensively in coastal areas, specifically in Gorigapudi village, Guntur Dt., Andhra Pradesh, India. The leaves of the ID palm trees are about 0.5 in. to 1 ft. in length.

8.2 Materials and Methods

8.2.1 Pure Splitting Method

Initially, ID leaves are washed with huge quantity of water and are dried for a period of 150 days at ambient conditions (Fig. 8.2). The dried leaves are again cleaned using soft cloth to remove fine particulates. A splitter with a needle of 0.5 mm

Fig. 8.2 ID leaves (150 days dried under ambient conditions)

diameter is used for extracting filaments from the leaves. The extracted fiber is placed in an oven at 70 °C to take away moisture before fabricating the composites, as shown in Fig. 8.3.

8.2.2 *Chemical Treatment*

Many experiments were conducted based on the literature review. Finally, the leaves are treated in NaOH solution at the concentration of 0.25 M, and the soaking time is 12 h. Now onwards, the chemically treated fibers are called as IDL CT.

8.2.3 *Fiber Characterization*

The extracted and chemically treated IDL fiber is examined under JEOL JSM-5350A SEM to understand the morphology of the fiber. Single fiber tensile test (SFTT) is also conducted on specimens as per ASTM C 1557-03$^{\epsilon 1}$. An SFTT specimen is carefully fixed in a wing-type fixture, and the tensile test is conducted on PC

Fig. 8.3 Extracted IDL fiber by PSM

2000 Electronic Tensometer which has a load cell of 20 kg. The density of the fiber is determined by the ASTM D 3800-99 Procedure A-Buoyancy (Archimedes) method and pycnometry procedure. Fiber density determined by both methods is nearly equal, but the Archimedes method is used in the present work.

8.2.4 Fabrication and Testing of Composites

Unidirectional tensile, flexural, impact, and dielectric fiber reinforced polyester composite test specimens are fabricated by wet lay-up technique (Srinivasababu et al. 2010). All the fabricated composite specimens are conditioned as per ASTM D 618-05 Procedure A in an environmental chamber, supplied by the Narang Scientific Works Pvt. Ltd., New Delhi. The physical dimensions of all the specimens are measured as per ASTM D 5947-06 Test Method A. The tensile and flexural tests are conducted on specimens as per ASTM D 5083-02 and ASTM D 790-07, respectively, on Electronic Tensometer supplied by Kudale Instruments Pvt. Ltd., Pune. The Charpy impact test is conducted on specimens using Computerized Izod/Charpy Impact Tester, supplied by the International Equipments as per ASTM D

6110-08. The dielectric test is performed on composites using the Dielectric Strength Tester according to ASTM D149-97a step-by-step test, supplied by Rectifiers & Electronics, New Delhi.

8.3 Results and Discussion

8.3.1 Physical and Mechanical Properties of Fiber

The density of the average of five samples of untreated and chemically treated IDL fiber is determined, and its value is 1,016 kg/m^3 and 1,065 kg/m^3, respectively. The density of pineapple leaf fiber is 1.526 9 g/cm^3 (Uma Devi et al. 1997).

SFTT is conducted on untreated and chemically treated IDL fibers, and the tensile strength and modulus are determined; graphs are drawn against specimen number (Figs. 8.4 and 8.5). Utmost care is taken to avoid slippage of test specimens during the test. The NaOH treated fibers (IDL CT) have shown more tensile strength and modulus than IDL fibers. The tensile strength, modulus of sisal (100–300 μm diameter), and pineapple leaf fibers was 400–700 MPa, 170 MPa and 9–20 GPa, and 6.21 GPa, respectively (Joseph et al. 1995; Uma Devi et al. 1997).

8.3.2 Fiber Morphology

Figures 8.5 and 8.6 represent the SEM images of untreated and treated fibers. A clear rougher surface with channels is visualized from treated IDL fiber (Fig. 8.7). These void channels help in filling of matrix and thereby bonding among treated fiber and matrix.

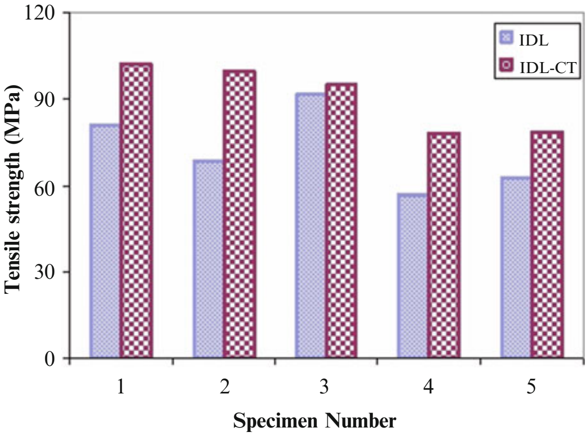


Fig. 8.4 Tensile strength of untreated and treated IDL fiber

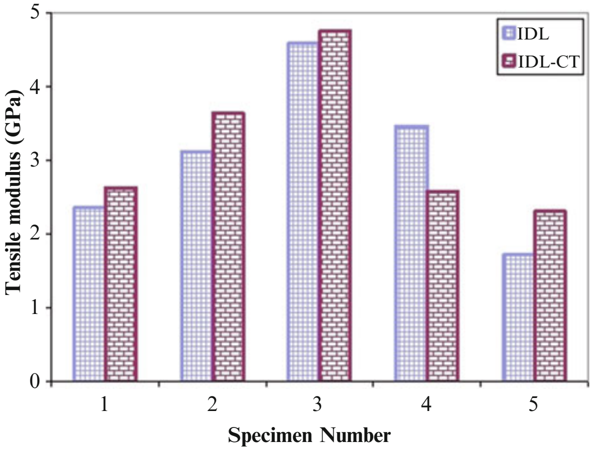


Fig. 8.5 Tensile modulus of untreated and treated IDL fiber

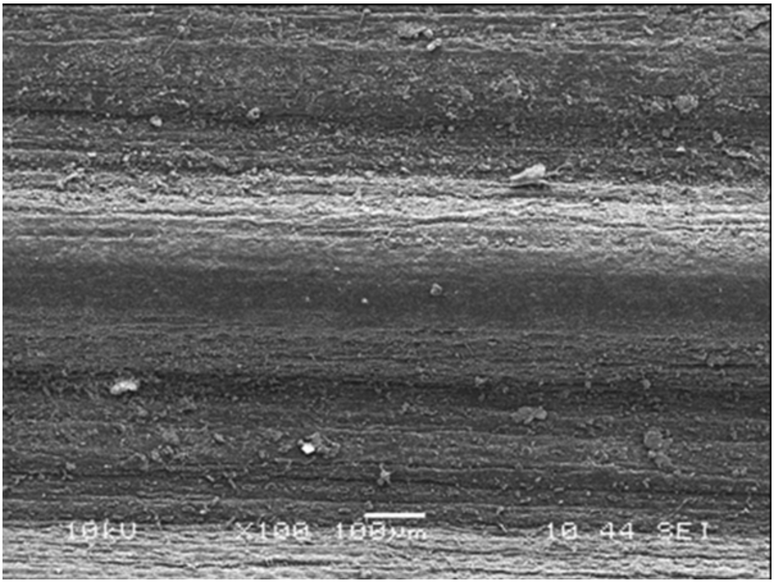


Fig. 8.6 SEM image of Indian date leaf fiber

The benzoylation treatment on sisal fiber resulted in decrease in diameter, and alkali-soluble fractions like waxy layer and lignin were removed from the fiber (Manikandan Nair et al. 1996). It was further noticed that the benzoylation treatment gives rise to many fine holes on the fiber surface which will enhance mechanical bond between the fiber and matrix.

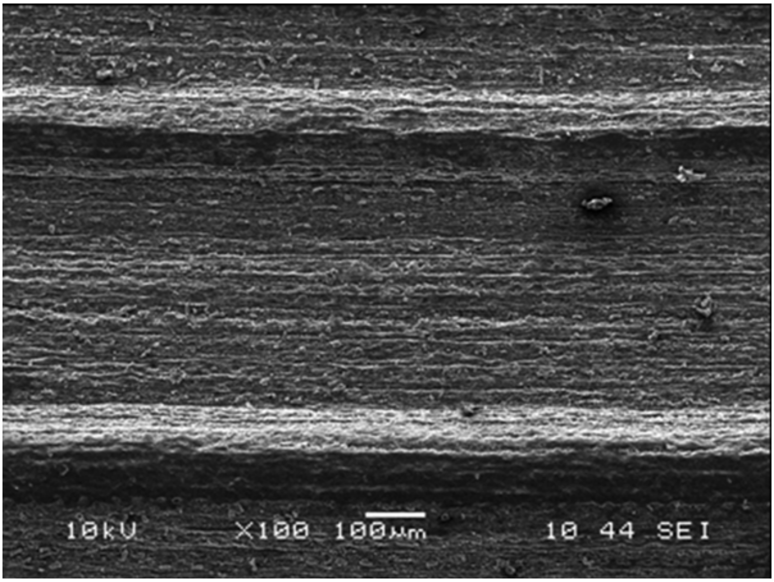
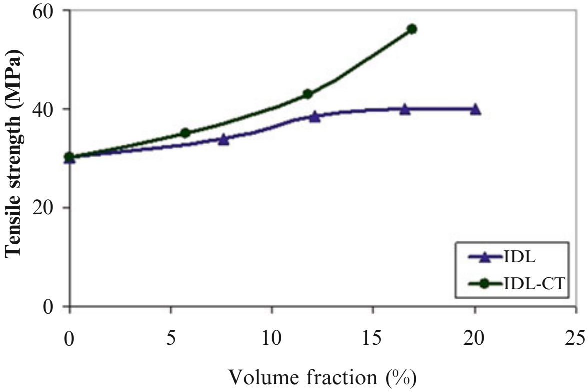


Fig. 8.7 SEM image of chemically treated Indian date leaf fiber

Fig. 8.8 Effect of fiber volume fraction on tensile strength of untreated and treated IDL FRP composites



8.3.3 Tensile Properties

With increase in fiber content, the tensile strength of untreated and treated IDL fiber reinforced polyester (FRP) composites is increased. IDL CT FRP composites have shown 39.65 % more tensile strength than IDL FRP composites at maximum fiber volume fraction which is shown in Fig. 8.8. The specific tensile strength of the composites is also determined and is graphically represented in Fig. 8.9 against fiber volume fraction.

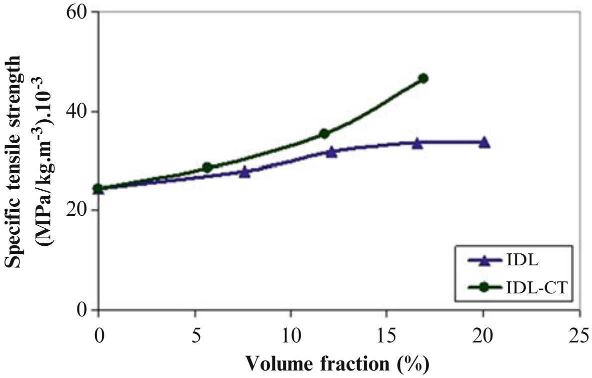


Fig. 8.9 Effect of fiber volume fraction on specific tensile strength of untreated and treated IDL FRP composites

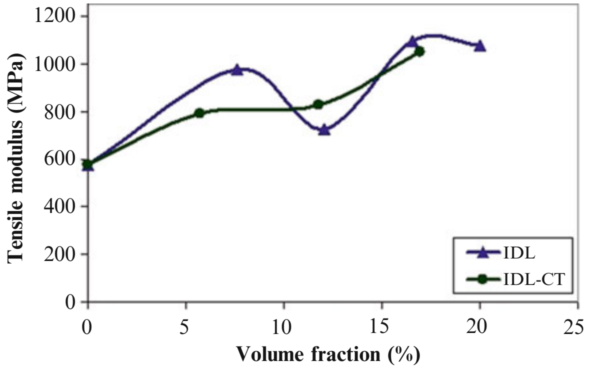
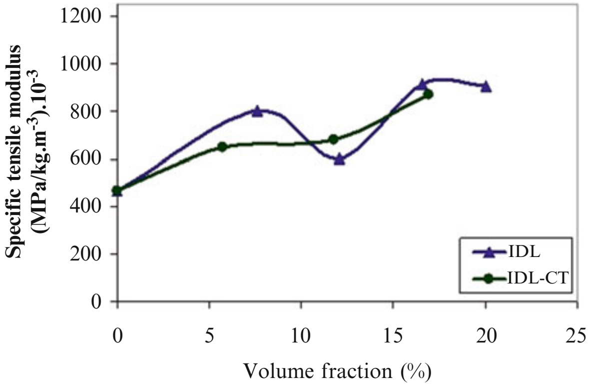


Fig. 8.10 Effect of fiber volume fraction on tensile modulus of untreated and treated IDL FRP composites

The IDL FRP composites under tensile load have exhibited relatively more elongation than load at 12.08 % fiber volume fraction; thereby, tensile modulus is decreased (Fig. 8.10). An increase in trend of tensile modulus is observed at all volume fractions in case of IDL CT FRP composites. Chemical treatment to IDL fibers resulted in good locking between fibers and matrices, evidenced from the experimental results. Though IDL CT FRP composites have taken more load at all fiber volume fractions, they exhibited more elongation, thereby resulting in nearer tensile modulus of the IDL FRP composites. Similar trend was observed in the case of PALF FRP composites reinforced with 2 % NaOH treated fibers for 1 h and has shown enhancement in tensile strength and modulus than untreated FRP composites, and its values are 55.4 MPa and 1.46 GPa, respectively (Uma Devi et al. 1997). The specific tensile modulus of IDL and IDL CT FRP composites is 906.44 and 871.72 (MPa/kg.m^{-3}).10^{-3} respectively at maximum fiber volume fraction and is shown in Fig. 8.11.

The tensile strength and modulus of 22.5 MPa and 1,095–1,100 MPa, respectively, were observed in PALF fiber reinforced LDPE composites where the fibers were longitudinally oriented at 30 % fiber content (George et al. 1995). From the experimental results, it is obvious that the IDL CT FRP composites showed superior performance than pineapple leaf fiber reinforced LDPE composites at maximum fiber content, and its value is 56.03 MPa, whereas tensile modulus of untreated and

Fig. 8.11 Effect of fiber volume fraction on specific tensile modulus of untreated and treated IDL FRP composites



treated IDL FRP composites exhibited similar trend to that of PALF-LDPE composites.

The influence of benzoylation treatment on tensile properties was reported in 1996. The bond between fiber and matrix was evidenced from the experimental results of the composites reinforced with treated fibers, in polystyrene matrix (Manikandan Nair et al. 1996). In the present work, NaOH-treated IDL FRP composites at 16.92 % fiber content exhibited 1.16 times more tensile strength than the composites (at 30 % fiber content) made of polystyrene matrix, benzoylate-treated sisal fiber.

PALF (30 mm fiber length) FRP composites have exhibited tensile strength of 63.3 MPa and are 1.13 times higher than IDL long FRP composites experimentally studied in this research (Uma Devi et al. 1997). Due to fiber entanglements that occurred above optimum size of the fibers, which was resulted in decrease in the tensile strength in PALF FRP composites when they were reinforced with 30 mm fiber length.

8.3.4 Flexural Properties

The IDL FRP composites under flexural loading beyond 15.55 % fiber volume fraction exhibited decreasing trend of flexural strength due to the lack of bond between the fibers and matrices. Figure 8.12 represents flexural strength against fiber volume fraction, where IDL CT FRP composite flexural strength is increasing with increase in volume fraction of the fiber. All the IDL CT FRP composites failed due to bending only at the outer surface of the specimen. Though the IDL CT fiber volume fraction is 8.48 % less when compared with IDL fiber, the flexural strength of IDL CT FRP composites is 17.38 % more when compared with untreated fiber reinforced composites at maximum fiber volume fraction. From the Fig. 8.13, it is observed that the specific flexural strength of IDL CT FRP composites is 13.41 times higher than IDL FRP composites at maximum fiber volume fraction.

The flexural modulus of IDL CT FRP composites crossed its value after 15.5 % fiber volume fraction when compared with IDL fiber reinforced composites, as

Fig. 8.12 Effect of fiber volume fraction on flexural strength of untreated and treated IDL FRP composites

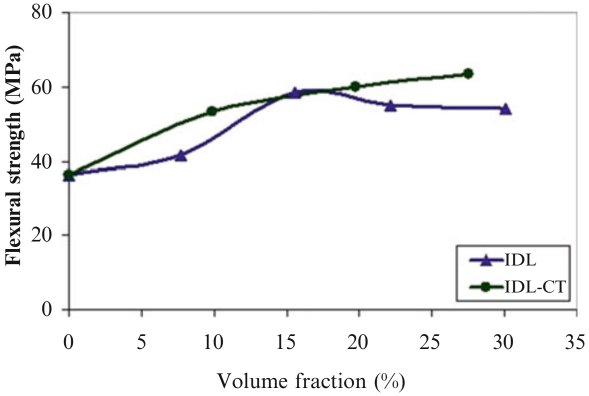


Fig. 8.13 Effect of fiber volume fraction on specific flexural strength of IDL FRP composites

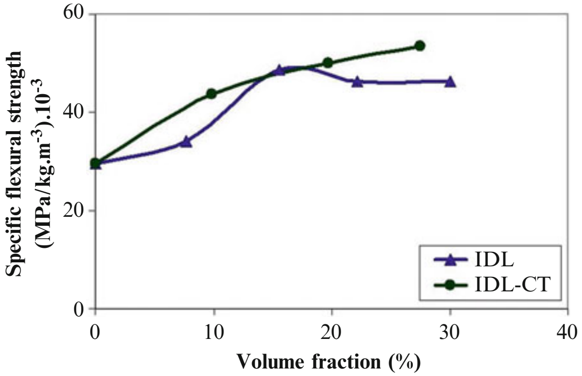
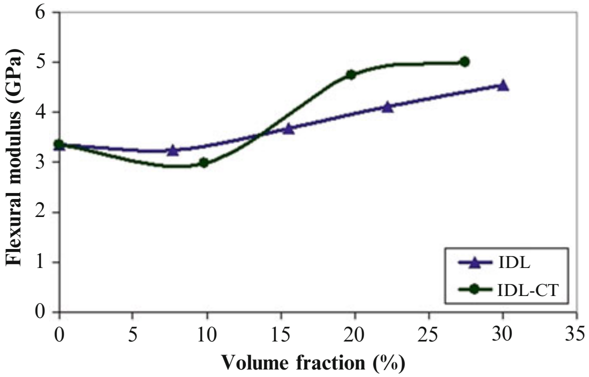


Fig. 8.14 Effect of fiber volume fraction on flexural modulus of untreated and treated IDL FRP composites



evidenced from Fig. 8.14. The determined flexural properties from the experimental results show the flexural modulus of treated and untreated FRP composites is increasing with increasing fiber content. In PALF fiber reinforced composites, the flexural properties at 30 % fiber content are very good, and its specific stiffness is 0.25 m × 10^6

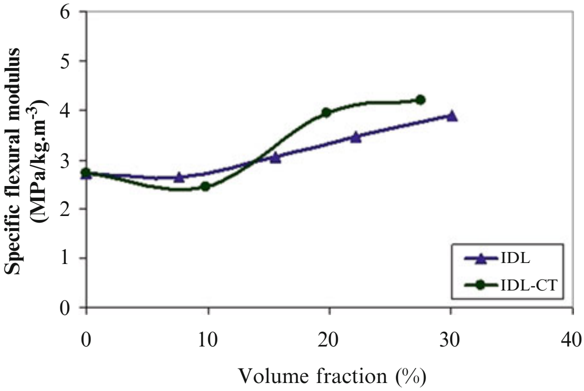


Fig. 8.15 Effect of fiber volume fraction on specific flexural modulus of untreated and treated IDL FRP composites

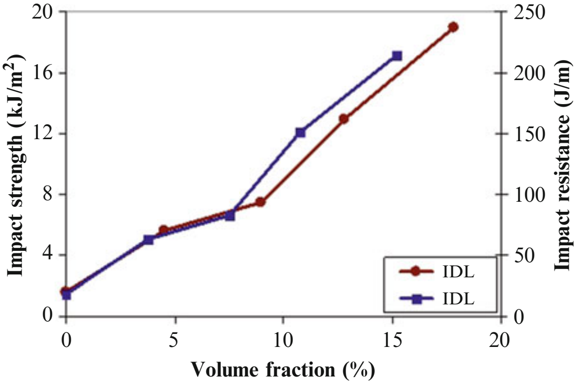


Fig. 8.16 Effect of fiber volume fraction on impact resistance and strength of IDL FRP composites

(Uma Devi et al. 1997). The specific flexural modulus of IDL CT FRP composites have shown very good performance when compared with the composites reinforced with untreated IDL fibers, which is evident from Fig. 8.15.

8.3.5 Impact Properties

The energy-absorbing mechanisms built in the composite include (Uma Devi et al. 1997):

1. Utilization of the energy required to de-bond the fibers and pull them completely out of the matrix
2. Use of a weak interface between the fiber and the matrix

Impact resistance and strength are determined from the Charpy impact test conducted on IDL FRP composite specimens, and the results are graphically plotted in Fig. 8.16. Complete break of specimens is observed at all the fiber volume fractions.

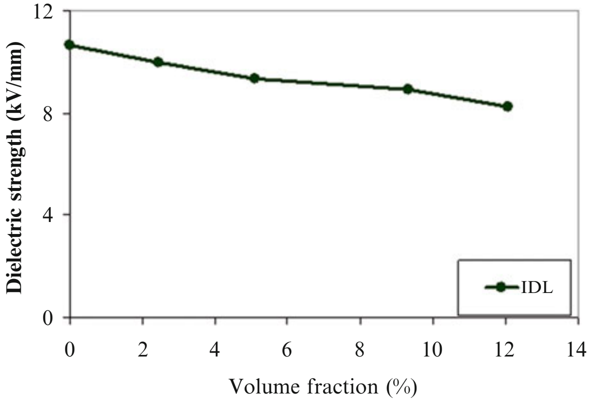


Fig. 8.17 Effect of fiber volume fraction on dielectric strength of IDL FRP composites

An impact strength 18.94 kJ/m^2 is obtained for IDL FRP composites at maximum fiber volume fraction. The impact strength of the IDL FRP composites is increasing with increase in fiber volume fraction. PALF FRP composites had exhibited similar kind of behavior, where the impact strength of the composites was found to increase linearly with the weight fraction of the fiber.

8.3.6 Dielectric Properties

The dielectric strength of IDL FRP composites is decreasing with fiber content. Hence, the designer will get an opportunity in selecting lightweight material having reasonable amount of insulation at various fiber volume fractions (Fig. 8.17).

The peculiar behavior exhibited by vakka fiber reinforced polyester composites introduced by K. M. M. Rao is noticeable (Ratna Prasad and Mohana Rao 2011). Hence, this kind of materials may be used for the purpose of insulation in electrical appliances.

8.4 Conclusions

Pure splitting method is successfully used to extract the IDL fibers. The tensile strength of chemically treated IDL FRP composites is higher than IDL FRP composites whereas modulus of IDL FRP composites is more than treated fiber composites at maximum fiber volume fraction. The tensile modulus of IDL FRP composites at 16.56 % fiber volume fraction is 1,097.53 MPa which is more when compared with untreated and IDL CT fiber reinforced polyester composites at all the volume fractions of the fiber.

The treated IDL FRP composites under flexural loading resulted in good performance than untreated IDL FRP composites. IDL FRP composites have shown reasonably good impact resistance at all fiber volume fractions. The reasonable dielectric strength at various fiber contents invites the designer to select lightweight insulating material.

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Chapter 9
Sugarcane Straw and Bagasse

Rida Rehman and Alvina Gul Kazi

Contents

Abstract For centuries now, sugarcane is being cultivated and is acting as a source of sugar production. This production is the source of many breeding programs all around the world. The sugarcane straw usually considered as trash is normally burned or is left in the soil depending on the harvesting system. There is an immense amount of straw being wasted yearly. Besides utilizing the straw for energy production or its requirement, there are a lot of other agronomic benefits that enhance the possibility of the straw blanket placed/left on the ground including protection of soil avoiding erosion, increasing organic ratio of content of carbon in the soil, inhibition of growth of weed, recycling of nutrients in textile fiber, and soil water reduction. Although consumption of sugarcane is very popular worldwide, certain factors are to be kept in mind regarding postharvest storage of

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_9, © Springer International Publishing Switzerland 2014

stalk that involves enzymatic browning. This chapter focuses on ways sugarcane straw can be utilized as a primary source for the production of products having great agronomic value. Balancing the pros of keeping sugarcane fields with a percentage of straw, which significantly outnumber the cons, economists are keen to find out beneficial properties and economic aspects of keeping straw on the ground rather than using it all as possible energy source. The most challenging factor is to maintain the straw quality rendering it useful.

Keywords Sugarcane straw • Soil • Agronomic benefits • Energy • Carbon content

9.1 Introduction

For many centuries, sugarcane has been cultivated. Many breeding programs, all over the world, are driven by production of sugar that resulted in the so-called noble varieties of sugarcane being commercially used at present. Initially, a high value specialty, sugar has now gained laurel of being one of the cheapest calorie food due to immense and rigorous reduction in the cost of its production. Sugarcane is known to be a food crop of high yield. It has also been demonstrated as a splendid feedstock for energy because of its high content of primary content per mg of cane. For whole sugarcane (140 kg of straw included; dry basis), higher heating value (HHV) is 7.4 GJ mg^{-1} of stalks of cane (which include moisture content up to 70 %), based on average quality of Brazilian cane. The amount of primary energy produced by energy products such as ethanol and bagasse is nearly 2.2 GJ mg^{-1} or less than 30 % (Leal 2007). Bagasse is the fibrous residue obtained from extraction of juice on industrial scale. Bagasse is consumed in the boiler mills in order to fulfill the energy demand of the mill. In the preharvest, the fibers in the leaves and tops of sugarcane known as straw or trash are normally burned. In the case of nonmechanized harvesting operations, i.e., manual harvesting, the cost of harvesting sugarcane is reduced by practices, which include burning of sugarcane in order to facilitate harvesting and transportation.

Due to certain agronomic, economic, and environmental reasons, mechanical operations have taken over the manual harvesting of sugarcane with dry leaves maintenance (straw) on the ground, in a system named as green cane management in Brazil.

9.2 Green Management of Sugarcane

It includes the large amount deposition of litter from/of plants on the soil after every harvest, which ranges from 10 to 20 mg of the dry matter per ha with the ratio of carbon to nitrogen to be close to 100. The whole process of sugarcane production is influenced by mulch formation. This includes management of fertilizer, yield, weed control, erosion of soil, and dynamics of soil organic matter. The effect of soil on the sugarcane straw has been analyzed with focus on the growth of root and its turnover (Leal 2007), dynamics of soil nitrogen (Ball-Coelho et al. 1993), temperature of soil and its water content (Dourado-Neto et al. 1999), erosion of soil (Sparovek and Schnug 2001), bulk density of the soil (Tominaga et al. 2002), soil aggregate stability (Graham et al. 2002), and carbon stocks of the soil (Cerri et al. 2011). For the improvement of overall balance of energy, there is an increase in the quantity of lignocellulosic material left on the ground that could be recovered partially and in turn used for energy purpose in the mills thus improving the overall energy balance. There is still required increased knowledge on the quantification of agricultural impacts, straw availability after the harvest, the rates at which the decomposition is occurring, amount spent over the collection, and, consequently, what amount should be left on the ground in order to optimize sugarcane sustainability in cultivation and processing. The primary focus of this chapter is the impact of soil on the straw, bagasse supplement, and the provision of economic and environmental benefits along with problems in the agricultural areas.

9.3 Traits of Sugarcane Straw

9.3.1 Straw Quality and Availability

The first and foremost investigating issue is the residual amount on standing crops as well as the amount left on the ground after harvesting of green cane. A wide variation is observed in the documented data and the available information does not allow complete comparison due to lack of knowledge on a number of essential issues like methodology followed, varieties of sugarcane studied, moisture content of yield and straw, etc.

Hassuani et al. (2005) summarized the results of a seven-year project covering many aspects of availability of sugarcane straw, its quality, routes of recovery and related cost, agronomic impact, impact on the environment, and use for power generation in advanced systems (biomass integrated gasification/gas turbine). Hassuani et al. reported three varieties of sugarcane in three (3) different ages, i.e., first harvest, third harvest, and fifth harvest. The straw amount varied from 10 to 18 mg ha^{-1}; dry basis and the ration of straw (db) to stalk (wet basis) lied in the range of 11–17 %. The literature showed that the yield of straw ranged from 7.4 to 24.3 mg ha^{-1} (db), whereas the straw to stalk ratio was between 9.7 and 29.5 %. The average was 14.1 mg ha^{-1} and 18.2 %, respectively (Hassuani et al. 2005). In potential assessments, it is normally accepted that the straw to stalk ratio lies between 14 and 18 %, which clearly reveals that the total amount of straw available is highly dependent on the sugarcane yield.

With regard to the characteristics of straw, the main focus is on two of the most promising uses of straw, i.e., fuel for generation of power and provision of feedstock for the biofuel of second generation. As far as fuel for power generation is concerned, it is mandatory to gather all the information about the proximate and ultimate analyses including the ultimate analysis of the mineral content as the comparison with bagasse is of extreme importance since bagasse can be burned in the same type of equipment, either separated or mixed. The studies further reveal that analyses for three main straw components were carried out: green leaves, dry leaves, and tops. This separation was generated because it had the tendency to display characteristics with marked differences and their role in the final composition of the recovered straw, which depends on the methods used for its collection and the procedures used in harvesting, for instance, whether or not the tops should be removed by the harvester. Several field experiments were conducted in which the average participation was 31, 62, and 7 % for green leaves, dry leaves, and tops, respectively (dry basis) (Leal et al. 2013).

Similar results were presented by straw and bagasse except for the content of moisture, i.e., in terms of combustion chamber design; the bagasse-fired boiler could be used for straw burning. Other than that, the higher content of chlorine, especially in the tops, could cause corrosion in the boilers. The highlighting differences between the components of bagasse and straw are as follows:

1. Increased content of potassium in straw (mainly in the tops) that can be the reason of the deposits found on hot surfaces, ash slags, and corrosion.
2. Levels of magnesium and calcium in the straw. Even though they are in higher concentration when compared with bagasse, still it is expected that they do not cause any problem in the boilers (Leal et al. 2013).

9.3.2 Recovery of Straw and Its Final Use

Even though a large potential of energy is associated with straw of sugarcane, so far, very minute efforts have been made in order to establish a suitable route from collection to harness such potential. Similar to the corn stover in the USA (Atchison and Hettenhaus 2004), for sugarcane straw to become an energy source for large biorefineries, innovations are required between the field and delivery to the processors in the areas of collection, storage, and transportation. As the attention is directed toward the cane harvesting mostly, it is not very clear which way to opt for the collection of straw for energy applications on industrial level. A set of field tests were performed in 1990s by the former Copersucar Technology Center (CTC) in order to evaluate some unburned cane harvesting routes proposed in the recovery of straw. Initially, five routes for collection purposes were evaluated with main intent of use of straw for generation of electricity (Hassuani et al. 2005). As a result of the poor harvester performance, when dealing with yield higher than 70 mg ha^{-1}, the routes that were based on whole harvesting of stalks were thrown away and discarded and the other three were subjected to further analyses which are briefly explained below:

Route 1: harvesting of unburned chopped cane with removal of straw in the harvester. This is the conventional cleaning—harvester's primary and extractor fans on. Chopped cane is transported to the mill of sugarcane. Straw is baled and transported.

Route 2: harvesting of unburned chopped cane without removal of straw in the harvester (harvester's extractor fans turned off). Cane stalks along with the straw are transferred to trucks and then transported to the mill. In the dry cleaning station of the mill, stalks and straw are separated.

Route 3: harvesting of unburned chopped cane with partial cleaning (harvester's primary extractor fan operates at reduced speed and secondary extractor is turned off). A certain amount of straw is left on the ground, while the remaining is transported to the mill with cane stalks. At the mill, stalks and straw are separated in a dry cleaning station (Leal et al. 2013).

The main reason behind the dry cleaning station is to allow and enhance the separation of mineral (soil) impurities and vegetal (straw) from stalks of cane at the mill. Once these are separated, straw can act as a complementary fuel to bagasse or as feedstock in other applications. These collection routes investigated by CTC led to extremely different percentages of recovery efficiencies. For instance, in Route 2, 95 % of the total available straw can be collected, but, instead, only 66 % can undergo separation in the mill, whereas the rest of the 29 % would be squelched and crushed with the stalks to eventually compose the bagasse. Even though the efficiencies of Routes 1 and 3 are lower, in accordance with the analysis performed by CTC, both of these present lower cost. The cost is dependent upon the impact in the field of sugarcane caused by straw removal such as loss of productivity in agricultural sector due to compaction of soil and the loss of herbicide to the blanket of straw, among others (Leal et al. 2013).

In another study, the six different recovery routes were assessed (Michelazzo 2005). A model was generated to estimate the recovery cost of straw stimulating the capacity of field, consumption of fuel, repair and maintenance, depreciation, and required labor for the operation in field and transport. Results revealed the lowest recovery costs while handling together, cane billets and straw, followed by handling of chopped straw in bulk, the round bale, the giant bale, and lastly the pellet and briquette system.

The routes indicated by these studies are based on the combined stalk handling of the straw from the cane. This is an effective alternative in which mills may eventually find more than one appropriate route, along with the knowledge of recovery level of straw may not be uniform over cane field (Braunbeck and Neto 2010). CGEE presented an analysis report after investigating three conditions of storage. It concluded that "the densification method was one of the leading factors for final cost of biomass." Based on the recovery costs identified by CTC, the cost of final biomass including straw storing operations was calculated to be in the range between 17.9 and 39.2 $/mg, depending on the route of recovery and storage methods (Braunbeck and Neto 2010). Even though it is indicated in these studies that the route that is based on the handling of stalks of cane and straw combined should turn out to be an alternative toward cost-effectiveness, mills may eventually find appropriate to utilize more than one route, also keeping in mind that the level of recovery of straw may not be uniform all over the field of cane. Improvements in the technologies used for straw recovery and incorporation of other biomass aspects can result in the expected reduction in costs. According to a research, for instance, estimation was made that the total cost on delivery of switch grass was estimated to be 80.46 mg. This was calculated using balancing technology. Nearly 8.5 % of energy input of the feedstock is required (Atchison and Hettenhaus 2004). Mature technology reduces the total delivery. Cost would be reduced to 71.16 $/mg with input of required feedstock to be 7.8 % for corn stover. Investigations have also been done on finding innovative methods for collection. Hess et al. (2009) described designs showing advanced uniform format that would enable lignocellulosic biomass trading and supply to biorefineries in a market of commodity type similar to that of grain. Apart from cost, the methods of recovery and storage must also consider its impacts on quality of biomass for its intended use. Studies estimate that nearly 40–50 % of straw is available in the field to be utilized as an additional fuel to bagasse. Estimation showed that the total electricity surplus from mills of sugarcane can reach up to 468–670 MJ mg^{-1} of cane (Seabra and Macedo 2011; Dias et al. 2011). Certain challenges with the combustion and handling of straw in large amounts in boilers of bagasse at industrial level are being faced and are still subjected to investigation. Alternative technologies are based on the straw conversion into biofuels and chemicals via biochemical and thermochemical ways. For the longer term, they are expected to become available on commercial scale. In BIG/GT-CC (biomass integrated gasification/gas turbine-combined cycles), systems may also get adapted to substantial generation of power at the mills. According to a study, surplus of electricity would reach up to 1,048 MJ mg^{-1} of cane. This analysis was made when 103 kg of straw (dry mass) per milligram of cane was used along with the bagasse in sugarcane mills with installed BIG/GT-CC system. Regarding biofuel production, the biochemical conversion of residues of sugarcane could affect the yield possibly by increasing it from 124 to 132 L mg^{-1} in case of ethanol. Further assumption is made that recovery is almost 40–50 % of straw (Dias et al. 2011; Seabra et al. 2010). If thermochemical state conversion is considered, a reduction to 116 L mg^{-1} value can be observed for ethanol and 115 MJ mg^{-1} canes for production of electricity. These rates result in 4 L of more production of higher alcohols per mg of cane (Seabra and Macedo 2011). These yields are characteristics of biomass so that the industrial performance may be affected by recovery route of straw (Seabra et al. 2010). A compromise is therefore required to be considered between the methods of collection and use of biomass of straw.

9.4 Agronomic Issues

9.4.1 Erosion of Soil

Effective soil erosion control is dependent upon decreasing the impact of drops of rain and the velocity of water running over the surface of soil (Andraski et al. 1985; Timm et al. 2002). This involves soil surface protection by utilizing mulch or cover crop to prevent soil striking, directly by the rain. This is done by avoiding the practices that compact the soil, thus causing reduction in the infiltration (Hillel 2007).

Many studies have been done in order to understand the protection of soil provided by the straw blanket spread on the ground especially for corn stover. According to one study, it was assessed that even after the removal of corn stover from the soil, it still provides adequate protection against the erosion of soil, considering implicitly the impact on recycling of nutrients and taking into consideration the local yield and tillage practices (Graham et al. 2007). A study revealed that 20–30 % of the corn stover could be removed to still provide the adequate cover for protection (Wilhelm et al. 2004). In another study which preceded the previous one, an estimation was done which stated that the amount of stover that is required for keeping the soil erosion to a level that is acceptable was dependent highly on the crop management and practices of tilling that ranged from 1 to 8 mg ha^{-1} (Wilhelm et al. 2007). Environmental protection agency (EPA) considers that 100 % of corn stover could be removed when no tillage is used and there is a decrease in the amount to 35 % when conservationist agricultural practices are used. In practices of conventional tillage, no residue is removed from the soil (EPA 2010). Sheehan et al. (2004) built a life cycle model stimulating corn stover collection in the state of Iowa for the production and use of a fuel mixture consisting of 85 % ethanol and 15 % gasoline, by volume. The individual impact on dynamics of soil carbon, erosion of soil, agronomic aspects of collection of stover and transport, and conversion of bioethanol was separately modeled. For the conditions in Iowa corn field, the average minimum amount of the residues that could be left on the field was 4.9 and 2.5 mg ha^{-1} for the typical operation of tilling and no-till operation, assuming that the corn is continuously grown.

Erosion of soil in case of sugarcane is generally limited as compared to conventional agricultural crops such as soybeans and corn, since the canopy closes rapidly, thus providing cover to the soil, and disturbance of soil is limited to the replanting period (once every 5 or 6 years). However, losses in the soil for sugarcane may dramatically vary depending on many factors like the annual rainfall, the management and system of harvesting, etc (Sheehan et al. 2004).

A recent study considered effects of no tillage techniques and also conservation of soil practices like contoured seeding, ripping and furrowing, use of absorption terraces, unburned harvesting, and others (De Maria and Dechen 1998). Other studies revealed that during an experiment of over eleven years, there was no significant effect of production of sugarcane on the soil horizon thickness or physiochemical composition of the soil (Macedo 2005). The increase in mechanical harvesting (without straw burning) reduces erosion of soil due to mulching effect of straw (Macedo 2005).

In a study conducted by Andrade et al., quantification of economic and technical impacts on nutrient and soil losses through erosion in the sugarcane cultivation in Brazil was carried out. The greatest losses of nutrients of soil as well as the erosion occurred in areas of burned sugarcane. Taking into consideration the average of five cuts, burned sugarcane lost 56.45 % of K, 48.82 % of soil, and 60.78 % of P more than the unburned sugarcane (mechanical harvesting). On the average, the nutrient replacement cost for burned cane is 16.96 $/ha which was higher than the unburned cane. The unburned sugarcane had lower cost of production as compared to the burned sugarcane and higher average economic return with respect to the burned sugarcane (Leal et al. 2013).

Erosion rates are also influenced by management of straw on the ground. Burned or buried straw as well as the straw on the surface results in soil erosion rates of 20.2, 13.8, and 6.5 mg $ha^{-1}a^{-1}$ and runoff of 8, 5.8, and 2.5 % of rainfall, respectively (Macedo 2005).

9.4.2 Impact of Water

The effectiveness of vegetative mulches against evaporation may be limited unless they are thick to a sufficient diameter because their high porosity permits rapid diffusion and air currents. The initial rate of evaporation under mulch is reduced so water is saved if rainfall is frequent. But, in case of extended periods of dry spells, mulch may keep the surface of soil moist and hence prolong the first stage of evaporation, thus producing no net saving of water (Hillel 2007). With the cane harvest via mechanical ways without burning, the addition of straw on the surface of soil is responsible for the reduction in the soil evaporation, increase in the content of water for plant transpiration, and hence improvement of the efficiency of water usage (Ball-Coelho et al. 1993; Chapman et al. 2001).

Since the surface of soil is completely covered with sugarcane for 60–90 days after emergence of shoot, mulching mostly affects evaporation/transpiration during the first 90 days. Peculiar to this, requirement of water for sugarcane is more significant during the first period of the cycle, i.e., tillering, sprouting, and establishment, whereas during the vegetative growth period, there is a decrease in water demand becoming negligible during maturation period (Leal et al. 2013). Chapman et al. (2001) confirmed this pattern with field trials when the loss of water was similar for both green (unburned) and burned canes in late growth, while the loss of water from soil in early growth under green cane was only 32 % of that from burned cane.

Many studies were conducted with the aim to quantify and correlate the benefits of mulch on crop yield. Ball-Coelho et al. (1993) measured higher water content of soil in the mulched plots in the Goiana experiment in Brazil, which was apparently related to higher soil micropore space, due to activity of higher plants and fungi in the presence of layer of litter. The yield of harvestable cane of first ratoon crop was 17 mg ha^{-1}, with the 70 % content of moisture, greater in mulch than in the treatment of burned cane. This response of yield is attributed to increased water retention of soil and reduced growth of weed under the mulch.

Tominaga et al. (2002) also measured higher content of soil water in sugarcane without burning of straw, compared to plots burned before harvest and bare soil control plots. The simulation of production of stalk of sugarcane in South Africa using APSIM model indicated that the higher production observed in unburned management was related to the higher content of soil water (Thorburn et al. 2007).

According to a study, the use of sugarcane straw around 0.1 m thick cover spread on interrow spaces is the most practical way to increase the effectiveness of irrigation by reduction in the loss via evaporation from the surface of soil by capillary rise. The straw maintained the moisture at a higher level for a relatively longer time compared to uncovered soil surface (Shrivastava and Solomon 2011). The conclusion drawn from this study is that maintenance is responsible for increase in yield by 10 % for systems under irrigation. In another study, water loss in terms of percentage was quantified in the upper layer of soil (0–0.2 m). It was determined that without the treatment of straw, the loss of water was 0.45 mm/day, while with the treatment of straw, it was 0.21 mm/day (Peres et al. 2010).

Another interesting aspect is the use of vertical mulch – a modification of subsoiling, in which organic materials, such as straw and filter cake, or inorganic materials, such as gypsum and sand, are inserted in the slot created by the subsoiler (Garcia 2005). Howell and Pheen (1983) tested the benefits of vertical mulch in irrigation studies concluding that it was responsible for intake of water resulting in 25 % increase in cotton yield in California. In the fields of sugarcane, the use of vertical mulching is responsible for increase in the effective rooting depth, hence improved intake of water, greater hydraulic flow, and increased capacity of available moisture (Meyer et al. 1992).

Among all the aspects raised, the increased infiltration and lower evaporation in the presence of straw mulch, compared to bare soil, is an advantage regarding production of stalk, mainly in areas where irrigation is not being practiced thus there is high deficit of water in the period of vegetation growth.

9.4.3 Soil Stocks of Carbon

The trend of carbon sequesteration is observed when straw of sugarcane in not burned and merely left on the ground. In the management of straw, experiments were conducted in Australia; the content of carbon in the soil was found to be 20 % higher when depth was considered to be 0–0.1 m. This was studied, 2 years after the green cane management beginning, in unburned areas and compared with the burned areas (Wood 1991). In a long-term experiment of nearly 55 years, burned sugarcane and unburned sugarcane in the southeastern part of Brazil were compared, and carbon concentration of 22.34 g kg^{-1} in the cane with straw maintenance and nearly 13.13 g kg^{-1} in burned cane in 0.2 m soil depth was reported (Canellas et al. 2003).

Razafimbelo et al. (2006) explained that the increase in soil stocks of carbon in the 0–0.1 m layer after six years of management of green cane is almost 15 %, compared to the management with burned cane. A study was conducted in Australia's adjacent burned areas in 1996 which revealed that for 4 years there was no change in the carbon stocks. Compared to that, a steady increase in carbon concentration was observed in unburned plots (Vallis et al. 1996). Another experiment conducted in the southeastern part of Brazil reported that in 12 years, due to maintenance of straw on the field, an average of 0.32 mg $ha^{-1}a^{-1}$ was accumulated in the first 0.2 m depth of an Oxisol. During the first 4 years increase from 1.2 to 1.9 mg $ha^{-1}a^{-1}$ was reported for the 0–0.4 m layer. After 8 years of up-gradation to mechanical harvest along with crop maintenance on the fields, nearly a 30 % increase in carbon stocks was signified (Galdos and Cerri 2009). The conclusion drawn from these observations deduced the results that since the adoption of proper green cane management system, potential increase in soil stocks for carbon can be expected. In the related experiments conducted in Australia and Brazil, involving the measurement of carbon concentration in burned and unburned areas, there was no significant difference in the given treatments after 12 months (Blair et al. 1998). An analysis on the management and carbon concentration in Australia described that higher concentration in soil carbon was observed to be higher in areas of green cane after 4–6 years. As far as areas that have been recently converted to this management are concerned, no significant increase in carbon concentration has been observed for 1–2 years (Robertson 2003).

In a long-term experiment carried out in South Africa for 60 years, it was noted that between burned and unburned areas, carbon concentration in the 0–0.1 m layer of soil was higher in the latter but no marked difference was observed in the 0.1–0.2 and 0.2–0.3 m layers (Graham et al. 2001). Carbon stock in these areas was as high as 70 mg ha^{-1} in the first 0.2 m (Six et al. 2002). In Brazil, a review related to litter impact on soil was conducted which involved the evaluation from 12 sites. The estimate showed a mean annual rate of carbon accumulation of 1.5 mg ha^{-1} a^{-1} (Cerri et al. 2011). From the above findings, a conclusion can be drawn that the system of sugarcane harvest without burning accumulates stores more carbon in the soil when compared with the system which involves burning. But this accumulation is variable and dependent upon the texture of the soil, for instance, rate of mean annual carbon accumulation was approx. three times greater than the sandy soil (Leal et al. 2013).

The soil texture and carbon stock and concentration correlation is well established, especially considering clay content and clay along with slit content (Silver et al. 2000; Hao and Kravchenko 2007). Climatic conditions also impart an effect on the soil carbon accumulation (Blair et al. 1998). Other than that, nitrogen fertilizer management (Graham et al. 2001) and the level of soil disturbance during the replanting operation have also been shown to aid in this accumulation. It has been noted that soils have a finite capacity to act as a carbon sink. This leads to the reaching equilibrium with respect to the management (Six et al. 2002). When carbon stock experiment was carried out with corn cultivation and corn stover, the amount of soil carbon stocks varied depending on the system that was used (Wilhelm et al. 2007). Above all, sugarcane ground maintenance tends to increase carbon stocks in mid and/or long terms. However, when carrying out experiment for understanding the optimal straw amount for carbon stock maintaining or increasing purposes, conditions such as local soil, climate, and crop management need to be taken into account.

9.5 Additional Impingement

The experiment conducted in the southeastern part of Brazil revealed that macrofauna of soil is affected by litter layer maintenance in management of unburned sugarcane in both quality and diversity. A comparison was carried out of macrofauna between adjacent areas with a history of long-term preharvest burning; but harvested without burning for a time span of 4 years and a native forest; sugarcane cropped area for 50 years with burning preharvesting. This comparison showed that a significant reduction was observed in the number of individuals per hectare along with diversification by sugarcane burned for 50 years. Approximately 75 % of individuals comprised sugarcane parasites such as Coleoptera larvae in the system of burned sugarcane (Leal et al. 2013). A significant rise, as compared to the native forest, in the levels of numbers of individuals was observed after 4 years of harvesting without burning. Ants and earthworms are the most benefited individuals from the change due to burning. It maintains a litter layer in the soil. After conducting a long-term straw maintenance, an increase of up to 3–4 times in the population of earthworm was observed, compared to the burned sites, in the Australian field experiments (Wood 1991). Commination and incorporation of litter are the few services that were provided by invertebrates of soil. Along with this, some other services include structural porosity building and maintenance, soil aggregation through burrowing, activities involving casting and nesting, and microbial activities and communities (Leal et al. 2013).

It has been studied that significant straw amount on the ground can help in the creation of ideal microclimate, in the system of unburned cane harvest, mainly involving humidity and temperature, for weed and pest development and also infestation by diseases. An increased importance is given to pests, weeds, and other diseases in the fields of sugarcane. This is due to damage caused by tillers, leaves, stalks, stalk base, and root systems. In addition, several other larger infestations also occur in older sugarcane generally (Hassuani et al. 2005).

A large number of insect species are involved in the sugarcane pest infestations. This infestation is dependent on time of the year as well as the region which can lead to serious economic damage. Sugarcane also provides sheltering for a large number of insect species such as arthropods and other microorganisms that are important in biological control of pests or involved in assistance of soil decomposition of organic substances (Hassuani et al. 2005). An increase in the insect species of froghopper, *Mahanarva fimbriolata* and *Diatraea saccharalis* (Lepidoptera: Pyralidae), is associated with the harvesting of unburned cane. This gives rise to a technical challenge that needs to be solved in areas of sugarcane without burning. The sugarcane borer, *D. saccharalis*, infestation shows variable results independent of harvesting method. A serious problem is indicated by froghopper, *M. fimbriolata*, in harvesting of unburned cane demanding control method adoption. The entomopathogenic fungus *Metarhizium anisopliae* indicated a high control in the efficiency at a reduced cost with no harmful effect on the environment. As far as weed infestation is concerned, chemical as well as biological changes may be caused by mulch in the soil. This may lead to weed suppression of *Brachiaria plantaginea, Digitaria horizontalis, Panicum maximum*, and *Brachiaria decumbens*. There are several species that are not affected by straw presence. Allelopathic compounds are released and this release is attributed by effect of mulch on the control of weed. Other effects attributed by mulch include physical effects including filtering and light wavelength and maintenance of temperature with minor fluctuations (Leal et al. 2013). Some of the weed infestation may be controlled by mulch straw left on the ground, whereas it is not enough for controlling others.

9.6 Final Remarks

One third of the total primary energy is contributed by straw in sugarcane as a crop. Sugarcane also possesses some characteristics which are very similar to widely used bagasse. This makes it a very good fuel to bagasse supplement. It can contribute to surplus power generation in the mills. For the second generation production of biofuels, straw can be efficiently used. An excellent opportunity is provided in Brazil in order to increase the fast implementation of management system of green cane to increase sugarcane energy performance, sustainability of the production of ethanol, as well as the economics. But its use is incipient, still. This is due to lack in the long-term experience with collection and use of straw along with the uncertainties in the processing, storage, and collection costs (Leal et al. 2013).

The benefits imparted by agronomic characteristics are pretty clear, but the quantification is difficult although their magnitude is analyzed in different situations. The minimum amount for the assurance of ground protection against erosion has not been estimated. A significant difference is contributed between burned cane, which is in bare soil and unburned cane, with straw mulch on the ground in the water and soil losses. Literature revealed a consistent increase concerning the content of soil carbon in the management of green cane with all straw left in the fields in comparison with burned systems of cane. A wide variation has also been shown in the results as it depends on climate and soil characteristics as well as the history of land use.

It has been noted that straw blanket imparts positive as well as negative impacts on the biota. Positive effects on macrofauna in the soil mainly include ants and worms, whereas the negative one includes increase in population of pests. The effect of inhibition of weed by straw mulch has also been confirmed by several authors for some of the species and has been found neutral for others. This data helped in gathering information about the magnitude of different impacts imparted by straw mulch left on the ground after harvesting the unburned sugarcane. This helped in assessment of optimum straw that should be left in the field to take advantage of the agronomic and industrial benefits. There are many variables that affect various benefits that were included in the evaluation. These variables include soil and climate characteristics, local topography, varieties of sugarcane and agricultural practices, etc.

At this time it is not possible to define proper amount of straw that should be left on the ground.

Best approach would be initial concentration on the erosion of soil and dynamics of soil carbon. These are associated with both economic and environmental benefits. Economic benefits include fertility of soil, yield of the crop, and cost of the production, whereas preservation of natural resource, crop sustainability, and sequestration of carbon are involved in the environmental benefits. Finally, it is significant to pin point the viability of integration of technologies of second generation in future. This involves conventional distillery of sugarcane which increases the yield of biofuel per unit area cropped and the efficiency of energy. This requires the use of straw fraction that results from unburned harvesting of cane.

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Chapter 10
Studies on Okra Bast Fibre-Reinforced Phenol Formaldehyde Resin Composites

G.M. Arifuzzaman Khan, Md. Ahsanul Haque, and Md. Shamsul Alam

Contents

Abstract Bast fibres are mainly composed of lignocellulosic materials. It is extracted from the outer cell layers of the stems of different plants species. In ancient times, bast fibres were used for making various products like rope, bags, mats and coarse textile materials to mitigate daily demands. However, such trendy usages of bast fibres were decreased behind the invention of cheap synthetic fibre. Although synthetic fibres have good strength and longibility, they are causing serious environmental pollution for their nonbiodegradable nature. To achieve the 'sustainable development', the usages of bast fibres are explored again. Diversified use of bast fibres as reinforcements of polymer matrix composites becomes popular due to its satisfactory engineering properties. The plant kingdom has a vast source of bast fibres. Few of them are utilized for reinforcing polymer composites and many species remain unexplored. Okra (*Abelmoschus esculentus*) bast fibre has no commercial value currently. It is considered as agricultural waste product after collecting

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_10,

vegetable. In fact, its chemical composition is almost similar to other commercial bast fibres, such as α-cellulose (60–70 %), hemicelluloses (15–20 %), lignin (5–10 %) and pectins (3–5 %) along with trace amount of water-soluble materials. The fibre exhibited high breaking tenacity (40–60 MPa) and high breaking elongation (3–5 %). In this chapter, okra bast fibre is introduced as a reinforcement material for fabrication of phenol formaldehyde resin composites. Manufacturing techniques and effect of fibre modification on their mechanical, thermal and biodegradation properties are discussed.

Keywords Okra bast fibre • Thermosetting phenol formaldehyde resin • Interface modification • Composite fabrication • Properties of composite

10.1 Introduction

Environmental awareness is encouraging scientific research to produce cheaper, environment-friendly and more sustainable packaging as well as construction materials. Natural fibre-reinforced thermoplastic composites are strong, stiff, light weight and recyclable and have the potential to meet this requirement. Because of their low cost, low density and excellent mechanical properties, natural fibres such as sisal, jute, hemp, flax, banana, PALF, coir and palm are promising reinforcement with thermoplastic composites (Sreekumar et al. 2011; Kabir et al. 2012; Virk et al. 2012). Among the 2,000 fibre-containing plants species, fewer have economical value. Jute and hemp were extensively used from past days (Mwaikambo and Ansell 1999; Mondal and Khan 2008). But high production cost with large cultivation area limits its use. Okra bast fibre (OBF) is a lignocellulosic fibre which is obtained from okra plant that grows everywhere abundantly in the world. Nowadays, it is rejected as agricultural waste products. However, due to the favourable mechanical properties of OBF, it has been transferred successfully to thermoplastic composite materials so far (Fig. 10.1).

OBF comes from the species ‘esculentus’, in the family ‘malvaceae’. It is cultivated throughout the tropical and warm temperate regions of the world for its fibrous fruits or pods containing round, white seeds. The fruits are harvested when immature and eaten as a vegetable. The vegetable can be collected from plant up to the period of 3–6 months. The plant was then subject for direct combustion. This operation causes not only environmental pollution but also waste valuable fibre components. The chemical composition of OBF is α-cellulose (60–70 %), hemicelluloses (15–20 %), lignin (5–10 %) and pectins (3–5 %) along with trace amount of water-soluble materials (Khan et al. 2009). Though it contains higher percent of cellulose, it may have potentiality to make good-quality composite with thermoplastic/thermoset resins. Fortunati et al. (2013) prepared OBF–PVA composites and studied its degradation properties. The fibres possess good mechanical properties and biodegradable characteristics. But such properties are not sufficient as engineering or commodity plastics. Besides, like other vegetable fibres, OBF possesses few

Fig. 10.1 Okra plants

weak points such as hydrophilic nature and degradation after prolong exposure to sunlight and is much prone to creasing, possibly due to high degree of orientation of cellulose in the fibre.

Thermoset resins are promising materials for natural fibre composite industries because they are insoluble and infusible and have high-density networks. A number of studies have been reported on thermoset-plastics-natural fibre composites. Injection and extrusion moulding processes for fabrication of short fibre/thermoplastic composites are proficient and economic (Sun et al. 2010; Paulo et al. 2007). In extrusion moulding process, fibres are well distributed into a matrix which is most desirable for enhanced composite properties. Besides, fibre content, fibre diameter, fibre length, void content, fibre orientation and fibre–matrix bonding are very important parameters for natural fibre-reinforced thermoplastic/thermoset-plastic composites (Joseph et al. 1993; Alam et al. 2010). Kalaprasad et al. (1996) found high mechanical strength, modulus and thermal resistance of sisal/glass hybrid fibre-reinforced low density polyethylene (LDPE) composites by varying fibre length and fibre distribution. Void possesses in composites reduced mechanical properties. Again, weak interface between fibre and matrix increases the probability of void content in composite as a result decreases the flexural strength, the off axis strength and the compression strength. Improvement of interfacial strength gives substantial improvement in tensile strength and modulus of short fibre composites. Since the chemical nature of fibre and matrices is different, strong interfacial adhesion is compulsorily required for an effective transfer of stress. Ray et al. (2001) reported that alkali-treated jute improves interfacial bonding of jute/vinylester composites.

Mild alkaline treatment creates rough surface topography of fibre by removing both intercellular and adhering impurities. On the other hand, fibrillation took place (breakdown the fibre bundle into smaller fibres) when fibre was treated in strong alkaline condition. As a result, the effective surface area of fibre increases which help it for easy wetting in matrix resin. Therefore, by increasing the fibre aspect ratio through alkali treatment, it can be possible to get better fibre–matrix interface adhesion and increase of mechanical properties (Weyenberg et al. 2006). This chapter deals with the fabrication process of OBF–PFR composites and their mechanical, thermal and biodegradation studies.

10.2 Functionalization of Okra Bast Fibre

Interface modification of natural fibre–polymer matrix composites is a common duty before composite fabrication because the chemical nature of fibre and polymer matrix is different, i.e. natural fibre possesses hydrophilic nature, whereas polymer matrix possesses the hydrophobic nature. A number of researchers and manufacturers tried to improve compatibility between polymer matrix and natural fibres by various techniques such as using compatibilizer, by matrix modification, by applying hybrid filler and by chemical treatments of filler. Among them chemical surface treatments of natural fibre have been reported to significantly improve the interface bonding of fibre–matrix including bleaching, alkaline treatment, silane treatment, acetylation, grafting with vinyl monomers, isocyanate and different coupling agents (Khan et al. 2009; Rosa et al. 2011). Alkali treatment enriches cellulose content of OBF around 75–80 % due to extraction of pectin and water extractives during treatments along with hemicelluloses from the fibre surface. The fibre became less dense and less rigid which provides the fibrils more capability of rearranging themselves along the direction of tensile deformation. The observations have also been reported for mercerized coir, flax, sisal and bamboo fibre (Varma et al. 1984; Sreenivasan et al. 1996; Sreekumar et al. 2011; Sharma et al. 1995; Das and Chakraborty 2006). Alkali treatment creates micropore on fibre and finally developed rough surface topography. Similar phenomenon happened when fibres were treated with $NaClO_2$ (bleaching). Fibre turns into whitened, more floppy and fibrillated after this treatment. Cellulose percentage as well as crystallinity also increases due to removal of huge amount of lignin and impurities. However, surface coating is developed when the bleached fibre was modified by vinyl monomers. Sometimes fibrillated fibre becomes defibrillated. Modified fibre behaves like compatible reinforcing fibre with several hydrophobic polymer matrices for producing high-performance composites (Khan and Alam 2013).

The percent of elements present in OBF can be determined by an Elemental Analyzer. The main elements in untreated, alkali-treated and bleached OBF are C, H and O which are mainly for cellulose, lignin and hemicelluloses (Table 10.1). The modified fibre by acrylonitrile (AN) monomer shows trace amount of N. It may come from the CN group of acrylonitrile monomer. It is seen that the percentage of C, O and H in all types of fibre is almost the same. Hence, the fibre is not degraded upon the chemical treatments (Fig. 10.2).

Table 10.1 Physical properties of okra bast fibre

Characteristics of OBF		Untreated	Alkali treated	Bleached	AN grafted
Diameter (μm)		218.3 ± 27.3	188.3 ± 54.2	153.5 ± 41.2	165.3 ± 46.1
Density (g/cm^3)		1.15	1.40	1.40	1.32
Composition	α-Cellulose (%)	60–70	75–80	75–82	–
	Hemicellulose (%)	15–20	5–8	7–10	–
	Lignin (%)	5–10	3–6	1–2	–
	Pectin and wax (%)	3–5	1	1–2	–
	Moisture (%)	4–6	6–7	6–7	1–3
	C (%)	44.33	44.64	43.91	44.81
	H (%)	5.63	6.19	5.75	5.50
	O (%)	50.04	49.17	50.34	48.24
	N (%)	–	–	–	1.58
Crystallinity index (%)		55	62	60	59
Tensile strength (MPa) (Rosa et al. 2011)		52.6 ± 23	60.1 ± 28.7	82.6 ± 47.2	120.4 ± 51
Young's modulus (GPa) (Rosa et al. 2011)		1.7 ± 0.7	4.5 ± 1.6	3.2 ± 1.5	5.1 ± 0.9
Elongation at break (%)		6.2 ± 2.4	7.3 ± 2.8	7.1 ± 3.1	8.4 ± 4.0

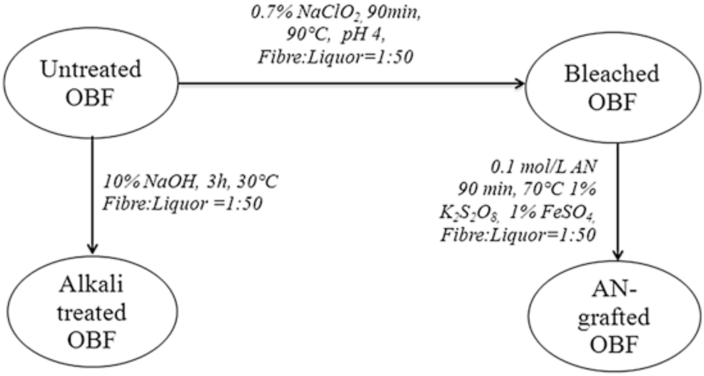

Fig. 10.2 Methods of chemical treatment of okra bast fibre

The effects of chemical treatment of OBF on the physical properties are given in Table 10.1. The quality of OBF mainly depends on its physical properties, for example, fineness, moisture regain and densities (Majumdar 2002). OBF is a multicellular fibre. The unit cell of OBF is formed with plenty of cellulose molecules. These are attached with each other in longitudinal direction to produce long continuous filaments. The filaments are sometime attached with neighbouring filaments with intermolecular hydrogen bonding or any other loosely attached bond to form a mesh-like structure. But attachments by week bonding between the cellulosic filaments are not sufficient to form high stiff fibre. The cementing materials (lignin and hemicelluloses) give stiffness by staying in between the gaps of the cellulosic filaments.

Table 10.1 reveals that the fineness of the fibre increases after chemical treatments especially in the case of alkali and bleaching treatments. Hemicelluloses are composed by β-cellulose and γ-cellulose carbohydrates. These both types of carbohydrates are soluble in alkali. So, it is supposed that hemicelluloses of the fibre are partially or completely washed out in alkaline medium. On the other hand, bleaching operation is frequently performed in textile industries to remove lignin from cellulosic yarn. A part of hemicelluloses is also removed during bleaching. Splitting of the cementing materials trends to be lesser diameter as well as mesh size. Mukherjee et al. (1993) also reported the reduction of fineness value due to the removal of lignin on bleaching. Further modification through AN-grafting has given surface coating onto OBF. Thus, the fibre diameter is increased slightly. The densities of untreated, alkali-treated, bleached and AN-grafted fibres are 1.15, 1.40, 1.40 and 1.32 g/cm^3, respectively, showing that the surface treatments have significant effect on fibre density (Aquino et al. 2007; Bledzki and Gassan 1999).

Hydrophilic nature of cellulosic fibres is a great barrier to achieve strong adhesion with hydrophobic polymer. The presence of hydroxyl (–OH) groups in OBF cellulose is the main cause of moisture absorption of natural fibre which tends to poor wettability. To achieve better wetting of fibre in matrix, those hydrophilic hydroxyl (–OH) groups of cellulose should be blocked by suitable modification. The surface chemical treatment of OBF significantly decreased moisture absorption, concomitantly increasing the wettability between fibres and polymer. As seen in Table 10.1, untreated OBF contains 4–6 % of moisture, while both alkali-treated and bleached fibres contain larger amount of moisture (6–7 %). Due to the removal of hemicellulose, pectin, waxes and fats, fibre becomes floppy, i.e. it contains more pores. Therefore, moisture can easily diffuse in these pores, and hence increases moisture content. On the other hand, moisture affinity is significantly decreased when OBF is modified by AN monomer.

The tensile strength and modulus of untreated and treated OBF are determined from the average of ten fibres of each modification; the values are shown in Table 10.1. Alkali-treated and bleached fibres have shown an appreciable reduction in tensile strength. This decrease may be attributed to considerable delignification and break down of fibre took place during the chemical treatments. The elongation at break in these fibres does not vary much. The AN-grafted OBF brings about a considerable improvement in tensile strength (TS) and tensile modulus (TM). This may be attributed to the fact that AN-grafted OBF may create orderly arrangement of fibrils by surface coating via cross-linking reaction (Rout et al. 1999).

10.3 Okra Bast Fibre-Reinforced Phenol Formaldehyde Resin Composites

10.3.1 Thermosetting Phenol Formaldehyde Resin

Thermosetting and thermoplastic polymers are usually used for making natural fibre composites. These both types of polymers have different applications for their versatile properties. Both polymers have structural similarity as they contain long chains. But the major difference is that thermosetting polymers possess

Table 10.2 Mechanical properties of thermosetting plastics

Thermosetting plastics	Tensile strength (MPa) ASTM D638	Young's modulus (MPa)	Elongation at break (%)	Flexural strength (MPa) ASTM D790	Flexural modulus (GPa)
Epoxy resin	63	1,371	5.8	3,547	–
Phenol formaldehyde resin	8–12	180–220	0–0.5	5–10	1.8–2.0
Urea formaldehyde resin	30–40	3,500	0–0.8	60–80	6–8
Polyurethane	2.4–44	0.2–327	2.4–480	9–104	0.174–2.30
Polyester	22	47	<15	–	–

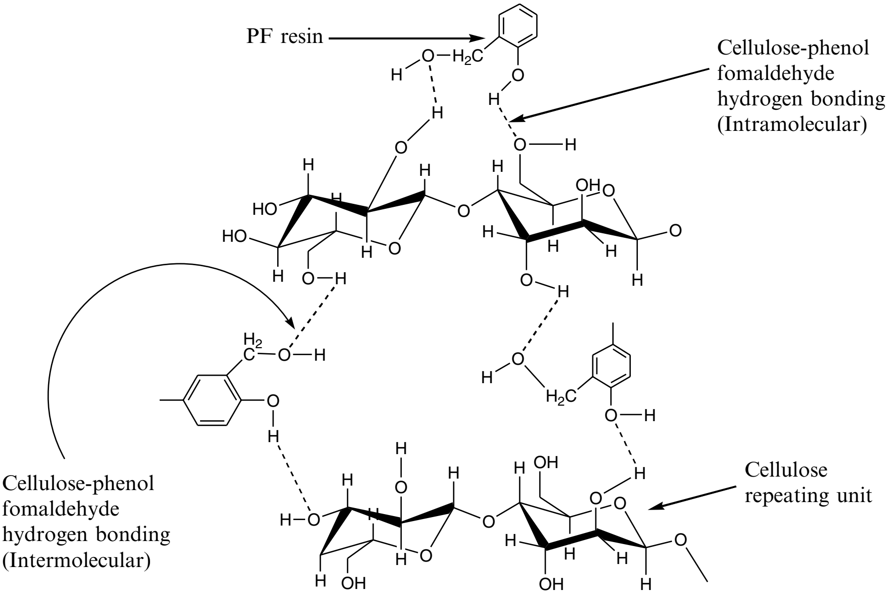

Fig. 10.3 Possible chemical bonding between cellulose and phenol formaldehyde resin

cross-linking chain which gives higher tensile strength and rigidity. That is why they are usually used in structural application and thermoplastics are considered for nonstructural products (Ganga Rao et al. 2007). The application of thermosetting polymers in natural fibre composites is shown in Table 10.2. Thermoset polymers, those that are used as matrices in composites, have sufficient viscosity to flow at some point during the cure process. They can be cast into plate forms to provide blanks. The finished specimens can be machined or moulded into even more complex geometries if necessary to create net-dimension specimens (Fig. 10.3).

The properties and structure of thermosetting resins mostly depends on polycondensation condition. A number of polycondensation resins such as polyester, polyurethane, melamine formaldehyde, urea formaldehyde (UF) and phenol

Table 10.3 Processing technique fibre-reinforced PF resin composites

Processing technique	Fibre	References
Hand lay-up method	Short banana fibre	El-Zawawy and Ibrahim (2003)
Hand lay-up method + compression moulding	Short banana fibre	Joseph et al. (2002)
Compression moulding	Sisal fibre	Lü et al. (2006)
Injection moulding	wood powder, flax, pulp, glass	Nystrom et al. (2007)
Resin transfer moulding	Glass fibre	Yan et al. (2002)
Pultrusion	Glass fibre	Ben and Shoji (2003)

formaldehyde (PF) are commercially available today (Pizzi et al. 1999). Among them, phenolic resins are well known for their tremendous mechanical properties, chemical resistance, thermal stability and strong adhesive capacity (Satapathy and Bijwe 2006; Park et al. 2006). This resin has been keeping its outstanding performance in synthetic polymer industry from the last 90 years (Shafizadeh et al. 1999). Resol is the commercial name of PF resin, which is produced by polycondensation reaction of formaldehyde and phenol under alkaline medium. A wide range of uses in wood industry, impregnation, thermal insulation and moulding is found for its highly cross-linked, versatile, cure capability and stable nature (Holopainen et al. 1997).

10.3.2 Fabrication Techniques

In many cases, polymer composite processing utilizes the same technique as polymer processing which includes injection moulding, compression moulding and extrusion moulding. There are some other techniques which are unique only to polymer composite processing. These include filament winding, pultrusion and hand lay-up. In spite of the fact that some techniques are used commonly with polymer processing, the operational conditions can be very different; thus, it is important not to directly transfer knowledge without careful consideration. In this section, a brief explanation of various processing methods is given in Table 10.3.

10.3.2.1 Compression Moulding

The compression is the most famous method for producing natural fibre-reinforced thermosets and thermoplastic composites (Khan et al. 2012; Sreekala et al. 2002; Lü et al. 2006). Natural fibre and resins are taken into mould after well mixing. The mould is then placed in between two plates. Those plates are joined with heating and cooling apparatus. Pressure can be fixed by using hydraulic press. A multiple type of finish products can be found with very simple operation.

10.3.2.2 Hand Lay-Up

The hand lay-up technique is extensively used for natural fibre-thermosetting polymer composites for simple processing procedures. In this process, short fibres, unidirectional and woven fabrics can be fabricated in resin. The resins are laid on the fabric by using a roller. Sreekala et al. (2002) have prepared the short random oil palm/glass hybrid fibre-PF resin composites by very simple hand lay-up along with compression moulding methods.

10.3.2.3 Vacuum-Assisted Resin Infusion Moulding

This method is used for making multilayer laminated composite. Unidirectional, nonwoven or woven mats are sized according to the shape of the mould chamber used in this process. The mould is set in between the resin container and pump. The resin and hardener are infused slowly for wetting mats by vacuum pump. Thereafter, curing is continued for a long time at ordinary temperature (Yuhazri et al. 2010).

10.3.2.4 Resin Transfer Moulding

Resin transfer moulding is a profitable technique for natural fibre composites. In this technique, resin and hardener are pumped separately to the mixing head before injection into the mould. The required amount of resins injected into the prearranged fabrics. Pressure can be applied from the opposite direction of injected mould. The wastage of resin is very less and good shape of product is found by this method. Indira et al. (2013) studied the effect of fibre length and fibre loading on the properties of banana fibre-reinforced phenol formaldehyde resin (PFR) composites. They found greater tensile and flexural properties in resin transfer moulded composites than in compression moulded composites. However, it needs big investment for large-scale production.

10.3.2.5 Bulk Moulding

A male–female combination of a closed mould is needed for bulk moulding. Short fibres are specially used in this process. Nowadays, thermoset bulk moulded product occupied the market of thermoplastic injection moulded compounds such as motor parts, electrical component and housing appliances. (Samivel and Babu 2013). The surface smoothness of finish product is good but contains some void portion which reduces composite strength.

10.3.2.6 Sheet Moulding

The sheet moulding process is completed in two steps. First, long sheet of composites is prepared with unique thickness, and then the sheets are passed through the different dimensional moulds to prepare various products. Short natural fibre is added with constant weight on carrier foil (conveyer). Resins and fillers are laid from a hopper on fibre. The mixture is then passed through the several ball mills. The prepared composite sheets are rolled with foil. The rolled composite sheets are further moulded for producing different products. Behzad and Sain (2005) established a novel processing method of natural fibre-thermoset acrylic resins with very short curing step (10 min). The final product has higher mechanical properties but needed huge establishment cost.

10.3.2.7 Pultrusion

The pultrusion technique is often investigated for natural fibre and thermoset resins (Akil et al. 2009). The yarn rolled roving is passed through the resin bath. A hot die helps them convert into profile (Van de Velde and Kiekens 2001). The profile then flows in profile drawer for completing cure process. The prepared composite has greater mechanical properties, but the production rate is not satisfactory. Among the above-mentioned processes, the compression moulding is a more viable method for fabrication of short OBF–PF resins in small-scale production. Short dried OBF with different weight fraction (9, 19, 29 and 38 wt%) is initially mixed thoroughly with PF resin. Composites are made using a stainless steel mould at 150 °C and 50 kN pressure. The curing is completed at room temperature for 24 h keeping the constant pressure 10 kN. The specimens for tensile and flexural tests are made by a cutting machine.

10.3.3 Mechanical Properties

10.3.3.1 Tensile Properties

Tensile properties of composite samples are tested using ASTM standard test method D638. The samples are conditioned at temperature of 21 ± 2 °C and relative humidity of 65 ± 5 % for more than 40 h prior to the test. The Universal Testing Machine (Hounsfield UTM 10KN) with a load cell of 1,000 N is used to measure the tensile properties at a crosshead speed of 8 mm/min. The length of composite specimen is 15 cm. Every test is done until tensile failure took place. All obtained results are the average of ten measurements. The maximum load (P, N) is read from the instrument. The tensile strength (σ, Pa) is calculated according to the following equation:

$$\sigma = \frac{P}{A};\ \text{where, } A = \text{cross} - \text{sectional area}\left(\text{m}^2\right)$$

The percent elongation is the increase in length of the specimen of composites at its breaking point and is calculated from the following equation:

$$\%\text{Elongation} = \frac{(\mathrm{L}-\mathrm{L}_0)}{\mathrm{L}_0} \times 100 \tag{10.1}$$

where L_0 and L are original measured length (m) and length of the specimen at its breaking point, respectively.

The Young's modulus is obtained from the slope of the stress–strain curve. In a tensile test, Young's modulus is calculated by the following equation:

$$E = \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon} \tag{10.2}$$

where $\mathrm{d}\sigma$ and $\mathrm{d}\varepsilon$ are stress at yield σ_y and strain at yield, respectively.

10.3.3.2 Flexural Properties

Three point flexural tests of composites are carried out using Universal Testing Machine (Hounsfield UTM 10KN) according to the ASTM standard (ASTM D790-98). The test speed is fixed at 5 mm/min. The flexural strength (*R*) is calculated according to the following equation:

$$\text{Flexural strength } R = \frac{3PL}{2bd^2} \tag{10.3}$$

where P is the maximum applied load, L is the length between points in the test setup, b is the width of the specimen and d is the average depth of the composite specimen. Flexural modulus is calculated according to the following equation:

$$\varepsilon = \frac{mL^3}{4bd^3} \tag{10.4}$$

where m is the slope taken from initial portion of flexural stress-strain curve.

10.3.3.3 Effect of Fibre Loading

Fibres play an important role of the properties of composite materials. A certain fraction of fibre can be able to minimize the stress onto composite materials. Whenever composite materials face any mechanical stress, polymer matrixes transfer it to filler. Since fibre possesses greater strength than matrix, it may compensate the stress and protect matrix from breakage. Therefore, good adhesion between fibre and matrix is compulsorily needed to transfer the external stress onto composite.

Table 10.4 shows the effect of fibre loading on the density of OBF–PFR composites. It is seen that the density of composites is decreased with the increase of fibre content. The tensile strength (TS), Young's modulus (YM), flexural strength (FS) and flexural modulus (FM) of untreated, alkali-treated, bleached and AN-grafted

Table 10.4 Physical and mechanical properties of OBF–PF resin composite

Composite types	Fibre loading (wt%)	Density (g/cm^3)	Void content (%)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (GPa)
Untreated OBF–PF resin composite	09	1.31	7.5	9	217	0.6	10.1	1.92
	19	1.28	8.4	13	339	1.2	12.7	2.03
	29	1.25	9.6	16	482	2.1	14.8	2.07
	38	1.21	10.8	15	492	3.4	13.2	2.09
Alkali-treated OBF–PF resin composite	09	1.27	4.1	10	323	1.0	15.6	2.01
	19	1.24	5.0	14	503	2.5	17.8	2.08
	29	1.22	5.7	19	633	3.4	20.1	2.11
	38	1.18	7.0	18	483	4.0	19.7	2.14
Bleached OBF–PF resin composite	09	1.28	3.8	11	343	0.9	13.4	2.00
	19	1.24	4.7	14	421	1.6	15.4	2.05
	29	1.22	5.4	18	720	2.7	19.7	2.09
	38	1.18	6.7	17	575	3.6	19.2	2.11
AN-grafted OBF–PF resin composite	09	1.29	3.1	13	426	1.4	15.3	2.05
	19	1.27	4.1	21	581	2.6	18.6	2.11
	29	1.25	5.2	24	803	3.8	23.8	2.16
	38	1.20	6.3	23	692	4.2	22.6	2.20

OBF–PFR composites with respect to different fibre loads are illustrated in Table 10.4. The optimum fibre load was fixed from which showing greater mechanical properties. It is revealed that the TS of composite increases continuously with the increase of fibre load up to 29 wt% and thereafter it decreases. A certain fraction of fibre is finely distributed in polymer resin; therefore, stronger interfacial bonding between the fibre and matrix is found. Similarly, YM increases with the increase of fibre load up to 29 wt%. The crystalline materials have shown higher modulus as compared to amorphous materials. Up to 29 wt% fibre fraction of composites are rearranged for crystalline structure.

Table 10.4 shows the FS of different fibre-loaded OBF–PFR composites. The FS increases with fibre loading up to 29 wt% and thereafter decreases with the increase of fibre load. The higher FS observed at 29 wt% fibre loading can be explained by better wetting of fibre in polymer resin which gives less fibre fractures during application of flexural stress. Therefore, the bond between fibre and matrix often dictates whether the fibre will improve the properties of composites by transferring an applied load. At above 29 wt% fibre-loaded composites, fibres may be agglomerated in composites; hence, FS was decreased.

10.3.3.4 Effect of Chemical Treatments

Table 10.4 also shows the comparison of the effect of chemical treatment on TS, YM, EB, FS and FM of OBF–PFR composites. Untreated fibre composite is taken as control for comparison. It shows that the AN-grafted OBF–PFR composite shows higher TS than those of untreated, alkali-treated and bleached OBF–PFR composites. It is also observed that alkali-treated and bleached OBF composites showed higher properties than untreated OBF composite. Bleached fibre composite shows higher strength and modus than alkali-treated fibre composites. The bleaching operation can able to increase surface energy of the fibre. Besides, fibre becomes cleaner due to removal of huge amount of impurities, i.e. pectin, waxes, part of hemicellulose and lignin. The fibre surface roughness becomes prominent; this is suitable for better adhesion with polymer resin. On the other hand, fibre surface layer covered by polyacrylonitrile (PAN) after modification with acrylonitrile monomer. At the same time, hydrophobic nature of AN-grafted OBF is developed which causes better adhesion with PFR matrix and forms stronger interfacial bond between them.

It is clearly observed that the highest value of YM is found for AN-grafted OBF–PFR composite. This may be due to the increase of surface free energy by chemical treatment of fibres. Consequently, the hydrophobic nature of AN-grafted fibre causes better adhesion with PFR and forms strong interfacial bond between them. Again, fibre surface area is increased by the removal of impurity from OBF surface and also by the removal of impurity from OBF surface by alkali treatment and bleaching operation. Both treatments have the same mechanism, which breaks the intermolecular and intramolecular hydrogen bonding of hydroxyl groups of cellulose molecule. Due to the presence of more reactive hydroxyl group after both chemical treatments, fibres easily form chemical bonds with PFR. That is why higher YM is found from alkali-treated and bleached OBF composites than untreated OBF composite.

By comparing the effect of chemical treatment of FS and FM composites, it is evident that treated OBF–PFR composites have higher FS and FM than that of untreated OBF composites. Because they contain more surface free energy, treated fibre composites are more stable against flexural load. Besides, due to the presence of better adhesion of treated fibre, PFR matrix forms strong interfacial bond between them given the higher FS and FM. Similar observations are also found in betel nut fibre-reinforced polypropylene composites (Khan et al. 2012).

10.3.4 Thermal Degradation

Thermogravimetry (TG) is a special measure of thermal degradation, where weight losses are calculated with the increases of temperature and time. Sometimes, TG is used to examine the kinetics of the physicochemical change involved in thermal reaction. Figures 10.4 and 10.5 and Table 10.5 show the TG & DTG for comparison among untreated OBF, 9 wt% OBF–PFR, 19 wt% OBF–PFR, 29 wt% OBF–PFR, 38 wt% OBF–PFR composites and 100 % PFR. It is seen that initial decomposition temperature (T_i) and final decomposition temperature (T_f) are found highest for PFR and lowest in case of OBF. Here, TG curve of composite samples shows two steps degradation: first is related to fibre degradation and the second is related to PFR degradation. Among the composite samples, 38 wt% OBF–PFR composite has the

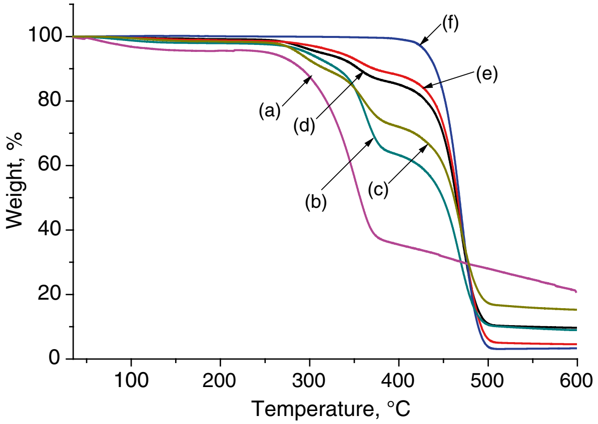

Fig. 10.4 TG curves of (a) OBF, (b) 9 wt% OBF–PFR composite, (c) 19 wt% OBF–PFR composite, (d) 29 wt% OBF–PFR composite, (e) 38 wt% OBF–PFR composite and (f) PFR

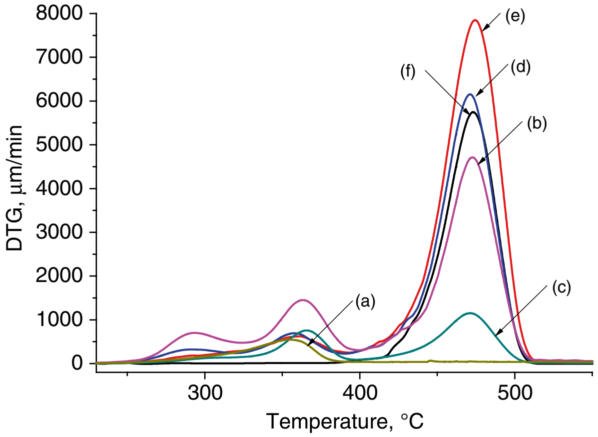

Fig. 10.5 DTG curves of (a) OBF, (b) 9 wt% OBF–PFR composite, (c) 19 wt% OBF–PFR composite, (d) 29 wt% OBF–PFR composite, (e) 38 wt% OBF–PFR composite and (f) PFR

lowest onset and decomposition temperature. It shows that 38 wt% OBF–PFR composites degrade in higher percentage than other composites, maybe due to moisture loss and more volatile content in fibre. The residual char or ash content at 600 °C temperature is higher in the case of OBF, and it decreases with the increases of PFR content in composites and the lowest value is found for pure PFR sample.

The first derivative of the sample weight with respect to time at constant temperature is termed as DTG. The DTG curves in Fig. 10.5 show rate of weight loss with temperature. The PFR gives single degradation peaks. On the other hand, fibre and composite samples show multiple degradation peaks due to weight loss in different stages of moisture and various constituents of fibre.

Table 10.5 TG and DTG of OBF, OBF–PF resin composite and PF resin

			DTG		
Types of composite	Temperature range (°C)	Weight loss (%)	Temperature (°C)	Rate of weight loss (mg/min)	Residual char (%)
Untreated OBF	0–168.7	5.4	79.4	0.063	22
	168.7–303.1	0.5	298.0	0.308	
	303.1–364.2	69.1	344.7	0.648	
100 % PF resin	1–325	0.1	–	–	3.3
	325–500	94.7	–	–	
	500–600	1.9	473.4	5.75	
9 wt% OBF–PF resin	1–275	1.5	294.7	0.7	4.6
	275–375	9.0	360.9	1.45	
	375–500	79.0	473.3	4.71	
19 wt% OBF–PF resin	1–275	1.5	–	–	9.7
	275–375	11.5	365.8	0.62	
	375–500	71.7	472.6	7.85	
29 wt% OBF–PF resin	1–275	2.3	293.6	0.32	18.2
	275–375	18.4	359.8	0.69	
	375–500	60.3	471.3	6.15	
38 wt% OBF–PF resin	1–275	2.4	285	0.2	15.3
	275–375	23.5	353.9	0.41	
	375–500	49.0	472.2	1.39	

Table 10.6 Biodegradation of OBF–PF resin composites

	Weight loss (wt%) after burial time					
Composites	20 (days)	40 (days)	60 (days)	80 (days)	100 (days)	120 (days)
100 % PF resin	2	5	6	7	8	10
9 wt% OBF–PF resin	3	7	9	11.9	14	16
19 wt% OBF–PF resin	5	9	11	14.1	18.1	22
29 wt% OBF–PF resin	6	10	13	18.3	22.4	28
38 wt% OBF–PF resin	10	14	17	22.8	27.5	33
Untreated OBF	18	42	72	–	–	–

10.3.5 Biodegradation

The soil degradation of OBF, PFR and their composites is measured in the function of weight loss with every 20 days of soil-burial time. The percentage weight loss with time is shown in Table 10.6. It can be noted that weight loss of PFR is very low, maybe due to antibacterial activities of formaldehyde. However, the degradation of OBF is faster than that of composites; hence, cellulose possesses the tendency to be degraded when buried in soil by the action of microorganism. Weight loss increased with the increase in burial time for all the specimens, and after 60 days, OBF is completely degraded in soil. It is also observed that up to 29 wt% OBF–PFR composites weight loss is not so prominent. This may be due to stronger interaction of fibre and PFR matrix beyond this percentage of fibre. Again, OBF is a natural biodegradable fibre which instantly absorbs water due to strong hydrophilic character. During soil degradation test, water penetrates from the cutting edges of the composites and degradation occurred in presence of microorganism. So, higher fibre faction composite shows higher tendency of biodegradation.

10.4 Conclusion

In this chapter, the properties of OBF–PFR composites including density, bulk content, mechanical properties, thermal and soil degradation properties are also discussed. The following conclusions can be drawn:

1. Enhancement of the content of OBF will improve the mechanical properties of OBF–PFR composites. Results suggested that the appropriate percentage of OBF in composite is 29 wt%, but a larger amount of OBF would decrease the tensile strength and flexural strength of OBF–PFR composites. However, 38 wt% OBF containing composite is given higher modulus than other composites.
2. The presence of hydroxyl groups of the OBF also increases water absorption and resultant poor compatibility between the OBF and the hydrophobic PFR. AN-grafting gives hydrophobic character of OBF and hence increases compatibility with PFR. On the other hand, the surface area is increased by alkali treatment and bleaching which is well distributed in PFR and hence gives higher mechanical properties.
3. It is also indicated that the initial degradation temperature and final degradation temperature of OBF is increased after composite fabrication. Higher fibre-containing composite has lesser thermal stability.
4. OBF is readily degraded when buried in soil. PFR restricted the biodegradation of OBF–PFR composites.

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Chapter 11
Okra Fibres as Potential Reinforcement in Biocomposites

C. Santulli, F. Sarasini, E. Fortunati, D. Puglia, and J.M. Kenny

Contents

Abstract The need to find environmentally friendly alternatives to traditional synthetic fibres such as glass fibres to be used as reinforcement in polymer matrix composites has attracted a growing interest in natural plant fibres in the last decade. In this regard, this chapter provides a comprehensive overview on a less common, but promising, natural fibre known botanically as *Abelmoschus esculentus*. It focuses on the origin, history and use of this plant with a particular emphasis on the fibres extracted from the stem of this plant, also known as okra fibres. A comprehensive mechanical, morphological and thermal characterization of the fibres is addressed in this work aiming at investigating their possible use as reinforcement in polymer matrix composites. The addition of okra fibres in thermoplastic and thermosetting

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_11, © Springer International Publishing Switzerland 2014

matrices is reviewed, while the last part of the chapter is devoted to the development of cellulose-based nanocomposites, which is unanimously perceived as one of the most promising research fields related to plant-based products. The extraction of cellulose nanocrystals from okra fibres and their incorporation in thermoplastic composites is described. The problems that appear as limiting factors for possible application of okra fibres as reinforcement for semi-structural components are highlighted and discussed.

Keywords Okra fibres • Thermoset composites • Thermoplastic composites • Nanocellulose extraction

11.1 Introduction

Okra (*Abelmoschus esculentus* (L.) Moench), also known as *Hibiscus esculentus* L., is a member of the mallow (Malvaceae) family, which includes also hibiscus and cotton among other species, and can be found as a tall-growing, warm-season annual (primarily in the United States) or perennial (in India and Africa) that is well suited to a wide range of soil types. It represents the only vegetable crop in the Malvaceae family, whose products have significant use in the food sector. In several parts of the world it is known also as Okra, Quingumbo, Lady's finger, Gombo, Gumbo, Bamia, Bhendi and Bhindi. The origin of Okra is disputable, but it seems to be native to the so-called Abyssinian centre of origin of cultivated plants, an area that includes Ethiopia, Eritrea and the eastern part of the Anglo-Egyptian Sudan. It is currently grown throughout tropical Asia, Africa, the Caribbean and southern United States.

Okra can grow up to 2 m tall and has leaves 10–20 cm long and broad, with lobes ranging from 5 to 7. The five white to yellow petals that constitute the flowers of diameters in the range 4–8 cm, are often characterized by a red or purple spot at the base of each petal. The seeds are contained in a capsule up to 18 cm long and that shows from 4 to 10 distinct ribs or ridges (Fig. 11.1). The immature young seed pods are the edible part of this plant. Most okra cultivars produce green pods, but a few varieties produce yellow or dark red pods. These pods are harvested when immature and high in mucilage, generally within 2–6 weeks after flowering. In some countries the most interesting part of okra plant is represented by the seeds, which yield edible oil with a pleasant taste and odour, and high in unsaturated fats such as oleic and linoleic acid. The ripe seeds can also be roasted and ground and used as a substitute for coffee. The last years have witnessed an increasing interest in fibres that can be extracted from the stem of okra plants, which are often considered as an agricultural waste product after the collection (Shamsul Alam and Arifuzzaman Khan 2007; Arifuzzaman Khan et al. 2009; De Rosa et al. 2010a, 2011). This is not surprising since roselle (*Hibiscus sabdariffa*, L.), a close relative of okra, is traditionally used as a source of fibres (Athijayamani et al. 2009, 2010; Methacanon et al. 2010).

The fibres can be obtained from the stems of okra plants by water retting for about 15–20 days (Arifuzzaman Khan et al. 2009; De Rosa et al. 2010a). From a

Fig. 11.1 Okra plant with mature and developing fruits. *Left image* from: http://www.neurophys.wisc.edu/ravi/okra/pictures/Aug200526_008b.JPG, and *right image* from http://images01.olx.com.pk/ui/7/91/81/1368960702_467699081_17-Vegetables-and-fruit-Suppliers-.jpg

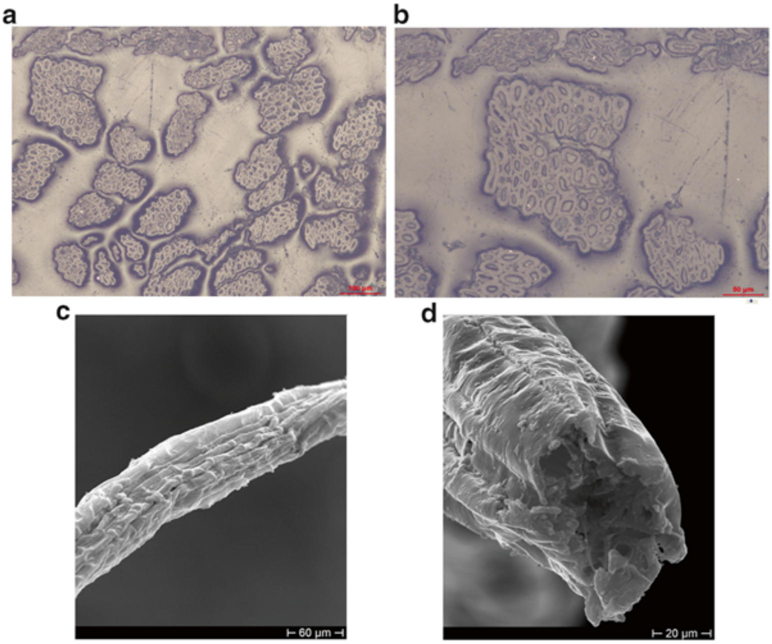

Fig. 11.2 (**a**, **b**) Optical micrographs showing cross section of several okra fibres; SEM micrographs of okra fibre longitudinal surface (**c**) and cross section (**d**)

morphological point of view, the microstructure of okra fibres is similar to that of other natural fibres, being a hierarchical structure, as confirmed by the investigation of both cross section and longitudinal surface by means of optical and electron microscopy (Fig. 11.2). As observed, okra technical fibre is made up of several elementary fibres (known as ultimate fibres) which appear to overlap each other along the whole length of the fibre while being firmly bonded together by pectin and other non-cellulosic compounds that provide strength to the bundle (De Rosa et al. 2010a; Fuqua et al. 2012). The highly irregular polygonal shape of okra fibre is apparent from Fig. 11.2a, b and its typical diameter is found to be in the range of about 40–180 μm. The shape variability affects the mechanical strength of fibres, being dependent on agricultural factors (stem age and plant variety, for instance) as well as the position of the fibres along the stem height (Ayre et al. 2009). The ultimate fibre appears to be roughly polygonal, with a central hole (lumen) of very variable dimensions. In particular, cell wall thickness and lumen diameter are reported being in the range 1–10 and 0.1–20 μm, respectively (De Rosa et al. 2010a).

The composition of okra fibres in terms of cellulosic and non-cellulosic constituents is reported in Table 11.1 along with the composition of other bast and leaf fibres commonly used as reinforcements in natural fibre composites. It is worth noting that the composition of okra fibres is very similar to that of other bast or leaf fibres. In this regard, comparable thermal behaviour and stability are expected. Okra fibres showed a traditional TG (thermogravimetric) curve characterized by three distinct weight loss steps, with a two-stage decomposition process (De Rosa et al. 2010a). The initial weight loss (≈8 %) occurring between 30 and 110 °C is due to water vaporization, while the onset of degradation occurs after 220 °C. The first stage (220–310 °C) is well described in terms of thermal depolymerization of hemicellulose, pectin and cleavage of glycosidic linkages of cellulose (weight loss of 16.1 %), while the second stage (310–390 °C) is characterized by the degradation of the α-cellulose that constitutes the fibre (Albano et al. 1999). The degradation of lignin is a phenomenon that takes place slowly in the whole temperature range owing to its rather complex structure. It can be concluded that okra fibres experienced a thermal stability comparable with that of other natural fibres, as can be inferred from Table 11.2.

As regards the mechanical behaviour, okra fibres are characterized by a brittle behaviour in single filament tensile test with a wide scattering of data (De Rosa et al. 2010a). This behaviour is common to the other vegetable fibres, being dictated by test parameters, plant characteristics and fibre diameter measurement (Symington et al. 2009; da Silva et al. 2012). The effect of okra fibre diameter can be reasonably described by a two-parameter Weibull distribution (De Rosa et al. 2010a) and the resulting mechanical properties are summarized together with the ones of other vegetable fibres in Table 11.3, from which the comparable mechanical behaviour with soft bast fibres, such as kenaf, and leaf fibres, such as date palm, henequen and sisal, is evident. From these results, the suitability of okra fibres as reinforcement in polymer matrix composites can be easily inferred.

11.2 Okra Fibre as the Reinforcement for Thermosetting Polymers

Using unconventional plant fibres, such as okra, as the filler for conventional thermosetting matrices can be considered a preliminary step towards the fabrication of fully biodegradable composites. The use of thermosets enables a reflection on a

Table 11.1 Fibre constituent content

Category	Fibre type	Species	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Source
Leaf	Sisal	*Agave sisalana*	56.5–78	5.6–16.5	8–14	Bledzki et al. (1996), Fuqua et al. (2012), Malkapuram et al. (2009)
	New Zealand Flax	*Phormium Tenax*	45.1–72.0	30.1	11.2	Carr et al. (2005), Fuqua et al. (2012), De Rosa et al. (2010b)
	Abaca	*Musa textilis*	56–63	20.8	7–12.4	Fuqua et al. (2012), Mohanty et al. (2005), Sun et al. (1998)
	Henequen	*Agave fourcroydes*	77.6	4–8	13.1	Fuqua et al. (2012), Malkapuram et al. (2009)
	Pineapple	*Ananas comosus*	70–82	15–19	5–12	Fuqua et al. (2012), Malkapuram et al. (2009), Saha et al. (1990)
	Banana	*Musa acuminata*	63–64	10–19	5	Fuqua et al. (2012), Mohanty et al. (2005)
Bast	Flax	*Linum usitatissimum*	71–81	18.6–20.6	2.2–3	Bledzki et al. (1996), Fuqua et al. (2012)
	Hemp	*Cannabis sativa*	70.2–74.4	17.9–22.4	3.7–5.7	Bledzki et al. (1996), Fuqua et al. (2012)
	Jute	*Corchorus capsularis*	61–73.2	13.6–20.4	12–16	Bledzki et al. (1996), Fuqua et al. (2012)
	Ramie	*Boehmeria nivea*	68.6–76.2	13.1–16.7	0.6–1	Bledzki et al. (1996), Fuqua et al. (2012)
	Okra	*Abelmoschus esculentus*	60–70	15–20	5–10	Arifuzzaman Khan et al. (2009), Shamsul Alam and Arifuzzaman Khan (2007)
	Kenaf	*Hibiscus cannabinus*	31–57	21.5	8–19	Mohanty et al. (2005)

Table 11.2 Decomposition temperatures for selected natural fibres (De Rosa et al. 2010a)

Natural fibre	T_0 (°C)[a]	T_p (°C)[b]
Okra	220	359
Hemp	250	390
Curaua	230	335
Kenaf	219	284
Jute	205	283

[a] Temperature of initial decomposition
[b] Maximum decomposition temperature

Table 11.3 Fibre mechanical properties

Category	Fibre type	Diameter (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Source
Leaf	Sisal	50–200	80–640	1.46–15.8	Fuqua et al. (2012), Jayaraman (2003), Mishra et al. (2004)
	Abaca	28	756	31.1	Shibata et al. (2002)
	Henequen	180	500	13.2	Herrera-Franco and Valadez-Gonzalez (2005)
	Pineapple	20–80	413–1,627	34.5–82.5	Mishra et al. (2004)
	Curaua	9–10	913	30	Gomes et al. (2007)
	Date palm	100–1,000	170–275	5–12	Al-Khanbashi et al. (2005)
	Sansevieria	80–90	630–670	5–7.5	Munawar et al. (2006), Sreenivasan et al. (2011)
Bast	Flax	30–110	450–1,500	27.6–38	Arias et al. (2013), Barkoula et al. (2009), Malkapuram et al. (2009)
	Hemp	53.7	690–873	9.93	Fuqua et al. (2012); Graupner et al. (2009)
	Jute	25–200	393–773	2.5–26.5	Fuqua et al. (2012); Malkapuram et al. (2009)
	Kenaf	43.3–140	223–624	11–14.5	Fuqua et al. (2012); Malkapuram et al. (2009)
	Ramie	34	400–938	24.5–128	Angelini et al. (2000); Goda et al. (2006)
	Okra	40–180	234–380	5–13	De Rosa et al. (2011); De Rosa et al. (2010a)

number of aspects. These include, for example, the possible maximum amount of fibres leading to an improvement of the composite properties, before effective impregnation gets hindered by an excessive amount of filler, and the evaluation of effectiveness of chemical treatment to provide a sounder fibre–matrix interface. It needs to be noted that plant fibre composites including kenaf fibres, which are botanically similar to okra, in thermosetting matrices are quite diffuse and a number of studies have been performed. In particular, it was demonstrated that alkali treatment with NaOH has some positive effect on fibre density and assists in improving the mechanical interlocking and chemical bonding between polyester resin and the fibre, resulting in superior flexural and impact properties (Aziz and Ansell 2004). Another significant observation is that kenaf is very suitable to manufacture fabrics, therefore producing composites with a sufficiently high amount of fibres, compatible, e.g. with the requirements of the automotive industry as regards the envisaged substitution of fibreglass (Na and Cho 2010). It is not surprising, therefore, that fibres such as okra are having some minor interest for application in thermoset matrix composites.

In particular, unsaturated polyester matrix was reinforced with a maximum of 36 vol% okra fibres: the fibres were defined as "woven" in that the whole usable length of the stem, equal to around 60 cm, is employed to reinforce the composites (Srinivasababu et al. 2009). The fibres were introduced either without treatment or subjected to two different procedures, both including an alkali pretreatment with sodium hydroxide, followed by a long-time (14 h) or short-time (5 min) treatment with a very diluted acid solution of potassium permanganate (Srinivasababu and Rao 2009; Srinivasababu et al. 2009). Both treatments brought to some improvement of tensile modulus and especially to a more consistent increase of it with the introduction of a higher amount of fibres, which may depend on their more uniform geometry after treatment. In contrast, tensile strength only shows some improvement for the highest volume of fibres introduced (36 %), being reduced at lower volumes of reinforcement with respect to untreated okra fibre composites (Srinivasababu et al. 2009). Another study was performed on the introduction of a limited amount, up to 20 wt%, of okra fibres bleached with sodium hypochlorite, in a Bakelite matrix. Here, the introduction of fibres did not result in an increase of tensile and flexural strength with respect to the pure matrix, even for the maximum amount of fibre introduced and the situation was not substantially improved by bleaching, although this treatment did lead to an increased strength of the fibres alone (Moniruzzaman et al. 2009).

To summarize these results, the problems linked to the reduced interface strength and to the anomalous section of the okra fibres, as extracted from the bast, appear still limiting factors for possible applications as reinforcement for semi-structural components.

11.3 Okra Fibre Based Thermoplastic Composites

Fibres from Malvaceae family, in particular the most studied Kenaf fibre (*Hibiscus cannabinus*) from the Hibiscus family, have been investigated in detail and many reports can be found on the enhancement of composite properties through the incorporation of this type of short natural fibre in non-biodegradable (Akil et al. 2011) and biodegradable matrices (Russo et al. 2013; Lee et al. 2012). The same approach was considered for the use of another similar fibre coming from the same family, okra (*Abelmoschus Esculentus*), and the recent study of thermal and mechanical behaviour of this reinforcement confirmed that okra fibres can be efficiently used for the production of biodegradable composites (De Rosa et al. 2010a; Monteiro et al. 2012).

Up to now, okra fibres in materials have been mainly used in mucilage-based moisture absorbers (Gogus and Maskan 1999) or in its gum form as a source of polysaccharides (BeMiller et al. 1993), which can be used after an appropriate chemical grafting (e.g. using poly-acrylonitrile) for the synthesis of biodegradable polymers or as a drug delivery system (Avachat et al. 2011) and viscosity modifiers for starches (Alamri et al. 2012). However, the possibility of using agro residuals in polymeric matrices implies, in the specific case of this herbaceous plant, a sound rethinking process, whose principal aim should be the possibility of using not only these fibres just as a waste material, but also ideally offering some reinforcement to a polymeric matrix. Our previous studies on okra fibres demonstrated that well-known chemical treatments usually applied for natural fibres, such as bleaching or alkalization, do not significantly improve the fibre properties (Moniruzzaman et al. 2009; De Rosa et al. 2011), so the use of okra reinforced composites in structural applications seems to be difficult to be considered. On a lower profile, which can be recommended for materials aimed at large volume applications, where the compostability is a fundamental requirement, the use of easily available biomass, such as herbaceous plants, hardly appropriate for the production of textiles, coupled with the biodegradable polymer can be successfully exploited. In this case, the use of short fibres is also recommendable, in particular because the large presence of defects and the uneven fibre diameter result in a rather ineffective stress transfer and as a consequence in lower mechanical performance of the composite for fibres exceeding 5–10 mm length (Kirwan et al. 2007; Juntuek et al. 2012).

The use of okra fibres as reinforcement in thermoplastic biodegradable matrix also belongs to the latter domain. An example of application of okra fibres in thermoplastic matrices comes from Fortunati et al. (2013c), in which poly(lactic) acid composites containing okra fibres were successfully produced and characterized. This study proved the potential of okra fibres in a context of applications for biodegradable packaging and also suggested that an alkali treatment on okra fibre can have some positive effect on their use for the fabrication of composites with biopolymer matrix. Specifically, PLA/okra composites were prepared with several amounts of okra fibres (10, 20 and 30 wt%) by using both pristine (UOF) and alkali-treated fibres (ODC, okra derivative cellulose), considering a treatment procedure able to remove the amorphous fraction of the raw fibres. Specifically, okra fibres were firstly treated with 0.7 wt/vol% of sodium chlorite, after that a treatment with sodium bisulphate solution (5 wt/vol%) was carried out. Following this pretreatment, holocellulose (α-cellulose + hemicellulose) was obtained by gradual removal of lignin (Chattopadhyay and Sarkar 1946). The obtained holocellulose was treated with 17.5 wt/vol% NaOH solution, then filtered and washed several times with distilled water. After that, the cellulose fibres were dried at 60 °C in a vacuum oven until constant weight. The introduction of these fibres in the polymer always resulted in a higher stiffness of the obtained composite system with an increase of about 30 % in Young's modulus value with respect to the matrix. Moreover, the addition of okra fibre to the PLA matrix led to a significant nucleation effect, which improved in turn the ability of the polymer to crystallize: this effect was more evident in the composites containing ODC. A disintegration test in composting condition has been

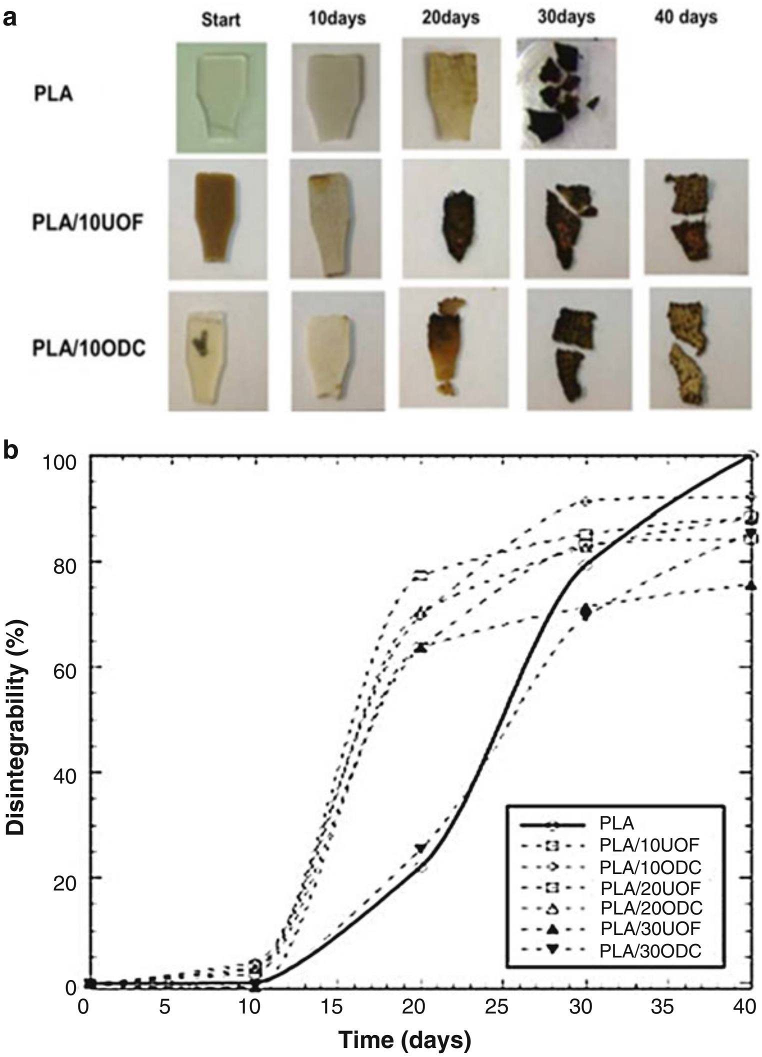

Fig. 11.3 (**a**) Photographs of neat PLA and PLA/okra composites containing 10 wt% of untreated (UOF) and okra derivative cellulose (ODC) at different incubation times and (**b**) disintegration curves of neat PLA and PLA/okra composites

also performed (Fig. 11.3), in order to have useful information about the post-use of the studied composite systems.

The introduction of 10 and 20 wt% of both untreated and treated fibres increased the disintegrability rate of PLA matrix; this behaviour can be explained considering that the hydroxyl groups of the cellulose structure act as catalysers for the hydrolysis of the ester groups of the polymer. This result suggests the possibility to induce an acceleration of PLA weight loss due to the natural fibre introduction useful for the environmental impact of these composites during their post-use.

11.4 Okra Fibres as a Possible Source of Nanocrystalline Cellulose

Cellulose, considered as one of the most abundant renewable polymeric material (Brinchi et al. 2013), is naturally organized as microfibrils linked together to form cellulose fibres, in which every single filament consists of several cells of cellulose-based crystalline microfibrils connected by lignin and hemicellulose (Siqueira et al. 2010). Cellulose consists of β-D-glucopyranose units linked together by β-1-4-linkages, containing hydroxyl groups able to form hydrogen bonds, playing therefore a major role in directing the crystalline packing and also governing the physical properties of cellulose (John and Thomas 2008).

Cellulose cannot be considered uniformly crystalline, but ordered regions distributed throughout the material, called crystallites, can be found in its structure. The linear association of these components is a microfibril, and can be considered the elementary unit of the plant cell wall. These microfibrils are found to be 10–30 nm wide, indefinitely long, and they can contain approximately 2–30,000 cellulose molecules in cross section. Individual cellulose nanocrystals (CNC) and cellulose microfibres (Fig. 11.4) can be isolated from crystalline cellulose core breaking down these crystalline regions (Oke 2010; Kalia et al. 2011).

There is a wide range of cellulose-based particle that can be considered different depending on cellulose source and extraction processes. Two main families of nano-sized cellulosic particles can be found: the first one consists of CNC or nanowhiskers (CNW) and the second one is the microfibrillated cellulose (MFC) (Belgacem and Gandini 2008; Lu et al. 2008; Brinchi et al. 2013). In this section, our attention

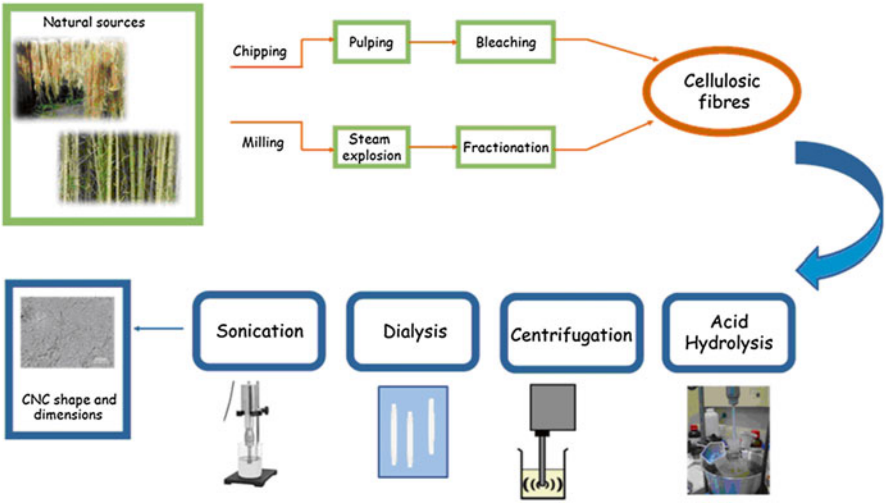

Fig. 11.4 Scheme of main steps needed to prepare CNC from natural sources

will be given to the extraction of CNC from natural sources, their specific properties and final application in polymeric matrices. CNC can be extracted from a variety of cellulosic sources, such as plants, bacteria and algae. The extended literature on this subject confirms that commonly studied source materials are represented by wood, plants, microcrystalline cellulose or bleached pulp because of their extensive availability and high content of cellulose. Essentially, CNC can be easily prepared from commercial microcrystalline cellulose or from filter paper, because of their purity and availability in laboratories (Klemm et al. 2011) and they can be isolated using a two-stage procedure, as shown in Fig. 11.4. The first one is a pretreatment of the source material, in which complete or partial removal of hemicelluloses and lignin, with consequent isolation of the cellulosic fibres, is obtained. The second treatment—generally a chemical hydrolysis—is able to remove the amorphous regions of the cellulose polymer, thus yielding a highly crystalline structure.

Azizi Samir et al. (2005) reported that even high-purity cellulose crystals starting from crystalline domains can be obtained, and together with these a non-crystalline state (amorphous) of the cellulose can be found. These cellulose amorphous regions are randomly oriented in a spaghetti-like arrangement having a lower density if compared to nanocrystalline regions (de Souza Lima and Borsali 2004; Saxena and Brown 2005). These amorphous regions are easily subjected to acid attack and they can be removed leaving intact crystalline regions (de Souza Lima and Borsali 2004). De Souza Lima and Borsali (2004) described how cellulose amorphous regions can be disrupted for the production of CNC. Going more into detail, hydronium ions can easily penetrate these amorphous domains, promoting the hydrolytic cleavage of the glycosidic bonds and isolating individual crystallites. Dong et al. (1998) firstly studied the effect of hydrolysis conditions on the properties of resulting CNC. They have shown that longer hydrolysis times lead to shorter monocrystals with increased surface charge. Indeed, Beck-Candanedo et al. (2005) studied the properties of CNC obtained by hydrolysis of softwood and hardwood pulps. They considered the influence of hydrolysis time and acid-to-pulp ratio in order to obtain CNC. From their analysis, they explained how reaction time is certainly one of the most important parameters to be considered for the acid hydrolysis of wood pulp, since too long reaction times can completely depolymerize the cellulose, up to yielding its component sugar molecules.

In contrast, lower reaction times will only yield large fibres and aggregates that cannot be easily dispersed. Araki et al. (1998) compared the effects of using both sulfuric acid and hydrochloric acid cellulosic nanocrystals (CNC), demonstrating that sulfuric acid is able to provide more stable aqueous suspensions compared to hydrochloric acid. Recently, CNC with an acicular structure ranged from 100 to 200 nm in length and 15 nm in width were extracted from *Phormium tenax* leaf fibres by acid hydrolysis (Fortunati et al. 2012d): in the cited paper, CNC extraction process was studied in terms of yield, thermal and chemical properties of the obtained nanocrystals and the results coming from the analysis of Phormium fibres were compared with those obtained extracting crystals from two reference materials, Flax of the Belinka variety and commercial microcrystalline cellulose (Fortunati et al. 2013a, b). Morphological, thermal and chemical characterization of the obtained CNC from different plant sources confirmed that natural fibres offered high levels of extraction efficiency if compared with commercial sources of nanocellulose. On the basis of these results, Fortunati et al. (2013c) extracted from the bast, for the first time in the case of okra (*Abelmoschus Esculentus*) natural fibre, cellulose micro- and nanofibres, with a view to obtaining cellulose structures with a high crystallinity and thermal stability. Previously obtained results on thermal and mechanical behaviour of okra fibre indicated it as a possible candidate for use in the production of biodegradable composites (De Rosa et al. 2010a); however, the use of okra bast fibres in textiles presents a number of drawbacks such as limited rub resistance, scarce colour fastness, sensitivity to wear and it is very much prone to creasing, possibly because of high degree of orientation of cellulose in the fibre. Furthermore, these studies demonstrated that commonly applied chemical treatments, such as bleaching and alkalization, do not substantially generate any improvement to okra fibre properties, indicating that high variability of their mechanical properties limits their use in composites (Moniruzzaman et al. 2009; De Rosa et al. 2011).

The possibility of using okra fibres as a source of CNC may be a viable alternative to employing them in the form of technical fibres. Fortunati et al. (2013d) demonstrated that hydrolysis parameters already applied for extraction of cellulosic fraction starting from microcrystalline material (Fortunati et al. 2012a, b, c) are adequately suitable for hydrolysis starting from a macrofibre, such as okra. In the specific case, the extraction of cellulose was carried out in a two-step procedure in which the holocellulose produced by the action of a first chemical treatment was then exposed to the action of sulphuric acid for further hydrolysis, allowing obtaining CNC in an aqueous suspension.

The use of cellulose nanostructures as a reinforcing phase in nanocomposites has numerous well-known advantages, e.g. low density, renewable nature, a wide variety of filler available through the world, low energy consumption, high specific properties, modest abrasion during processing, biodegradability, relatively reactive surface, useful for the grafting of specific groups (Siqueira et al. 2010). However, cellulose nanoparticles present some disadvantages, for instance, high moisture absorption, poor wettability and incompatibility with most polymeric matrices and limitation in the processing temperature. In fact, lignocellulosic materials start to degrade near 220 °C restricting the matrix types that can be used in association with natural fillers (Wambua et al. 2003). Several reviews have been written on these topics, demonstrating that CNC can be successfully used as filler in nanocomposites, improving mechanical and barrier properties of the matrix (Klemm et al. 2005, 2011; Hamad 2006; Dufresne 2008, 2010; Hubbe et al. 2008; Eichhorn et al. 2010; Habibi et al. 2010; Visakh and Thomas 2010; Siqueira et al. 2010; Duran et al. 2012).

New biopolymer nanocomposites using poly(vinyl alcohol) (PVA) as matrix and reinforced with CNC extracted from okra bast fibres were produced for the first time by Fortunati et al. (2013d). The partial aggregation of cellulose in PVA appears to demonstrate that a good level of compatibility between the hydrophilic crystalline nanocellulose and the polymer matrix was obtained. It has been demonstrated that CNC are able to increase the degree of crystallinity of PVA matrix, specifically the nanocomposites containing 5 wt% of cellulose appeared the most suitable formulation, with an increase of 40 % in crystallinity value and of 150 % in the elongation at break with respect to the PVA matrix. The result can be justified considering that this content may lead the available surface area of cellulose to its optimal dimension in the nanocomposite. Moreover, the obtained results showed how okra fibres, and in general bast herbaceous systems, can be applied in the CNC form in nanocomposite formulations to be used in some industrial areas, such as packaging.

11.5 Conclusions and Future Perspectives

Okra fibres, which are cropped in a number of countries across several continents, may represent a suitable example of by-product from an agricultural productive system involving mainly food-related applications. This offers a low cost availability of lignocellulosic fibres, which may be used for different possible purposes. In this regard, a number of issues were investigated, in particular their possible introduction as a filler, possibly with some reinforcement effect, both in conventional thermosetting and biodegradable thermoplastic matrices. This involved an evaluation of the effectiveness of different chemical treatments in modifying the resistance and morphology of the fibres, which, as microscopical investigation demonstrated, is rather variable with regard to diameters, lumen dimensions and overall shape. A possible alternative to application of okra fibres in the dimensions of technical fibres, therefore on the microscale, is their use as sources of CNC with the idea of providing a filler, usually applicable in small amounts, for biodegradable matrices, such as poly(vinyl alcohol) (PVA).

In general terms, the results obtained suggest that most suitable fields of applications for okra fibres in the material sector may refer to their use in the packaging industry, therefore mainly linked to the application of biodegradable matrices in short life products.

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Chapter 12
Biomass Resources in Environmental and Socio-Economic Analysis of Fuel-Wood Consumption

Tanvir Arfin, Faruq Mohammad, and NorAzah Yusof

Contents

Abstract Energy is said to be potentially at the core of modern civilization right from industrial revolution, where technology has modified and redefined the way in any individual or a group that uses the energy, but the technological advancement in all spheres continues to be dependent on its use. The prevailing trend has triggered the need for alternative, renewable and sustainable energy sources which are now being considered extensively and pursued globally to turn aside the possibility of

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_12, © Springer International Publishing Switzerland 2014

climate change at the range of attaining a state of irreversibility. A versatile raw material, biomass, can be used for the generation of energy by means of heat production, transport fuels and many essential bio-products which directly or indirectly contributes for the current growing demands of energy. When produced and used on a sustainable basis, the biomass-based energy production acts as a carbon-neutral carrier and thus contributes for the reduction of large amounts of greenhouse gas emissions, thereby finding its way for the prevention of global warming. In most developing countries, the quantitative information available on woody biomass resources, at scales related to the procurement area. Based on the growing demands of woody biomass for energy production in the current and near future, the present report is therefore aimed to provide an in-depth information about various agencies linked to biomass resources, leading economic factors of woody biomass, methods available for the estimation of costs associated with bioenergy, etc. Further, we also discussed about the methods to estimate biomass in forest ecosystems by means of destructive sample, microwave remote sensing-based assessment, woody vegetation indices and also provided the investigation methods during the estimation of error budgets.

Keywords BECCS • Allometry equation • Destructive sampling • Microwave remote sensing • Error budgets

12.1 Introduction

Biomass is mainly composed of organic matter derived from plant sources and the very exclusive process such as "photosynthesis" enables trees and plants to store the solar energy into the chemical bonds of their respective structural components. During the photosynthesis process, the carbon dioxide (CO_2) from the blanket of air present in the atmosphere vigorously reacts with the universal solvent, water from the earth to produce carbohydrates (mainly sugars in the form of glucose) and this constitutes the building block of biomass. The photosynthesis process in the presence of sunlight to form biomass has been expressed in the chemical equation given below.

$$6H_2O + 6CO_2 \xrightarrow{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$

The essential raw materials of photosynthesis, water and CO_2 on entering the cells of dorsal side of leaf produces simple sugar and oxygen. Since the earth's biomass exists in a thin layer called biosphere, where the life is supported and stores enormous energy constantly which is replenished by flowing energy from the sun as a result of photosynthesis.

Biomass has two main categories: "virgin biomass" which mainly comprises forestry and energy crops and "waste biomass" leading from the forest thinning, wood residues, recycling, sewage, municipal wastes, food and animal wastes as well as the domestic waste. Despite the advent of modern fossil energy technologies, the biomass still regarded as the vital source of energy for human beings and also for the advancement of raw materials used especially in the present era of the developing world. According to a recent estimation, it has been noted that the biomass production is about eight times higher than the total annual world consumption of energy from all other sources available on earth. According to literature reports in 2003, the world's population uses only a 7 % of the estimated annual production of biomass on the basis of new reading of the production rate (Koren and Bisesi 2003; Berndes et al. 2003).

It is to be noted that the principle of bioenergy production from biomass is the reversal of normal photosynthesis process by the plants, i.e. $CO_2 + 2H_2O \underrightarrow{\text{light, heat}} \rightarrow ([CH_2O] + H_2O) + O_2$. The direct combustion method is the simplest and most common method of capturing and generating the energy which is contained within the biomass. Combustion devices are commercially available and are also a well-proven technology for converting biomass into energy. However, improvements are continuously being made repeatedly in various processes such as fuel preparation, combustion and flue gas cleaning technology, as a result of demand to utilize new or uncommon fuels, improved efficiencies, minimized costs and reduced emissions in the current scenario (Hoogwijk et al. 2003).

The energy generated from biomass combustion is used as the basic heat source for all the processes and the heat energy is used to vaporize the working fluid in the medium available. The vapour is stretched downward in the turbine to produce mechanical energy which is further converted into electricity through hydroelectricity and geothermal energy as an alternative source of energy. During the process, an electric boiler is utilized for the preliminary investigation of the whole system and the energy liberated by the combustion of biomass lies in the range of 8 MJ/Kg for wet greenwood to 55 MJ/kg for oven dried plant material; while a 55 MJ/kg is generated from methane combustion and 23–30 MJ/kg for coal burning (Twidell 1998).

Basically, the biomass-based energy production is considered to be a carbon neutral process, i.e. the amount of carbon emissions released after combustion are wholly taken up by the plants during their catabolic activity of growth. This results in no net gaining of carbon dioxide by the atmosphere which proves the law of conservation of energy. If the forest and agricultural residues or wastes are allowed to decompose naturally on their own, the same amount of carbon emissions as biomass-based energy will be released into the atmosphere. The use of biomass as a source of fuel has much wider implications in terms of social, economic, biophysical, biological and environmental aspects. However, the excessive deforestation, i.e. cutting of the trees for fuel needs leads to a reduction in the biodiversity of plant species and also destructs habitat for wildlife, land degradation, soil erosion, etc. The loss of soil can be covered by the use of crop residues and overgrazing increases soil erosion and thus reduces the agricultural production and consumption. Also, the use of biomass fuels gives rise to high levels of indoor air pollution caused from various sources affects human health in a very indigenous way.

In recent years, due to the rapid development and existence of the "peak oil" theory into reality, the renewable carbon, i.e. the base of fuels for energy production has been playing a vital role in today's world economy. Further, in order to depend completely on the carbon-based economy and also to provide energy fully to the current growing population, the research and development efforts are continued to transform the existing fuel-wood technology into a high-tech liquid biofuel technology. Also, a continuous supply of funds have been provided for the research activities to meet the requirements of the international protocols and guidelines of various agencies such as Kyoto Protocol on the Climatic Changes, Reducing Emissions from Degradation and forest Degradation (REDD) and Cleaner Development Mechanisms at smaller village scales level (Gibbs et al. 2007; Woodhouse 2006a, b). The burning of biomass in the atmosphere, especially the fuel-wood, has served as a major source of energy production according to most of the recorded history. D.O. Hall indicates that biomass produces only a 14 % of all energy consumed on worldwide range (Hall 1991). In all the developing countries, fuel-wood produces up to 95 % of energy that is consumed yearly. The most dominant use of biomass energy is for cooking and heating and also for some other rural industrial activities including beer brewing, brick firing and pottery making. Other uses of biomass include medicine, food, building materials, household utensils and toys. While biomass fuel is essential for survival in many activities, its use is burdened with lots of problems. Its use is inefficient as it generates domestic indoor air pollution, resulting in various health problems leading to deadly diseases. It is normally women who are said to be affected the most, since they spend most of their time in cooking inside the dwelling. The gathering of fuel-wood is also labour demanding and excessive use of wood results in soil erosion as mentioned above. There are some major environmental problems arising in the world due to biomass consumption.

The scarcity in fuel-wood has nowadays resulted in the people of third world countries to rely on the enormous crop residues and animal dung as an alternative sources of fuel, where households are forced to purchase wood from vendors for domestic use. In such a situation, finding the necessary cash to purchase wood or an alternative energy sources, creates an additional burden on the people residing in rural areas. During the decline in woody biomass, a huge array of the use of this versatile resource is affected to its maximum. This means that as the woody biomass supply diminishes rapidly, the availability of all the artefacts that comes from trees are also affected due to the uprising circumstances. Since, the woody biomass serves as an important source of energy that is currently the most significant source of sustainable as well as renewable mode of energy production in today’s world. The woody biomass, due to its importance and continued dependence of limited, primarily fixed land occupancy are further burdening the available woodland resources in order to meet the energy needs of the ever growing population. Also in recent years, the occurrences of the continuous changes in woodland occupancy are significantly altering the overall biomass production and subsequent energy generation. Due to such unreliable statistics, the modelling of a structure to meet the domestic energy demands at a local level is becoming a challenge (Banks et al. 1996). In 2010, the extensive and global use of woody biomass for energy was about

3.8 Gm^3/year (30 EJ/year), which consisted mainly of 1.9 Gm^3/year (16 EJ/year) for household fuel-wood and 1.9 Gm^3/year (14 EJ/year) for large-scale industrial use in general. During the same period, the world's primary energy consumption was estimated at 541 EJ/year and world's renewable primary energy consumption was observed to be 71 EJ/year, according to International Energy Association (IEA) (2013, http://www.iea.org). Hence in 2010, the woody biomass formed roughly 9 % of the world primary energy consumption and 65 % of world renewable primary energy consumption. Despite the widespread uses of woody biomass for energy, the current consumptions are still substantially below the existing resource potentials available exclusively (Openshaw 2011).

The woody biomass energy potentials do not depend only on the available woody biomass resources but also on the competition between the factors such as alternative uses of those resources and alternative sources of energy in a very consistent manner (Radetzki 1997; Sedjo 1997). These effects can be depicted and separated by using the concept of supply and demand curves which has been defining its importance. The energy wood supply curve defines the amount of woody biomass which is made available for large-scale energy production at various hypothetical energy wood prices, i.e. it summarizes all the relevant information and data regarding its application from the biomass sector needed to model large-scale energy wood uses. On the other hand, the energy wood demand curve defines the desired amount of woody biomass required for large-scale energy production at various hypothetical energy wood costs.

The woody biomass is a prevailing attractive feedstock that can be sustainably obtained from nature through the process of photosynthesis for bio-ethanol production (Arato et al. 2005; Zhu et al. 2010). The hybrid poplars in well-managed plantations, native lodgepole pine represents a major wood species from forest thinning of the unmanageable forests that are available in large volumes. This requires value-added utilizations to diminish expensive thinning cost for sustainable healthy forest and ecosystem management exclusively in the environment. Thus the intensive utilization of lodge pole pine for bio-ethanol provides an important sector of the feedstock supply which in other words contributes to future economy based on biofuels. The woody biomass possess high fibre with strong physical characteristics in addition to significant amount of lignocellulose material than any other feedstock such as agricultural residues, grasses and agricultural waste which makes it more obstinate to enzymatic destruction leading to serious threat (Sassner et al. 2008; Shi et al. 2009). This gives an idea that the woody biomass research should emphasize majorly the upstream processing, i.e. the pretreatment and also the size reduction phenomenon to overcome the inherent recalcitrance which further enhances the subsequent enzymatic saccharification of polysaccharides. The chemical pretreatments are commonly capable of improving, generating the enzymatic digestibility of biomass by means of diminishing the non-cellulosic constituents (Chen et al. 2009; Rawat et al. 2013) increasing the size of pore (Grethlein 1985) and breaking down fibre crystallization in a very consistent order (Kamireddy et al. 2013).

12.2 Leading Economic Factor of Woody Biomass

World Induced Technical Change Hybrid (WITCH) is a regional integrated assessment model structure to provide normative and qualitative information on the optimal responses of world economies taking place due to climatic damages. It normally deals with the cost-benefit analysis or the optimal responses to climate alleviation policies such as the analysis of cost-effectiveness (Bosetti et al. 2007, 2009). WITCH has a very peculiar game-theoretical model which allows for the modelling of cooperative as well as non-cooperative interactions amongst all developing countries. According to RICE (Rice Integrated model of Climate and the Economy), the non-cooperative interaction is the result of an open-loop Nash game where the 13 regions of the world gets interacted on the environmental concerns in a non-cooperative manner, i.e. greenhouse gas (GHG) emissions, fossil fuels, energy research and development, and on learning-by-doing method in the available renewable sources (Nordhas and Yang 1996). With this, the investment decision in one particular region significantly affects many other regions' investment decisions at any point of time. Since the economy of a particular region is based on the lines of Ramsey-Cass-Koopmans optimal growth model and thus the model has been solved numerically by an assumption that the central planner is governing the economy (Barro and Sala-i-Martin 2003).

12.3 Bio-Energy in Combination with CCS Power Generation

Woody biomass is used only in integrated gasification combined cycle (IGCC) power plants with CCS (carbon capture and sequestration). As for all other power generation technologies, the electricity production based on bio-energy with carbon capture and sequestration (BECCS) is governed by a Leontief type production function as given below (Rose et al. 2012):

$$\mathrm{EL}_{\mathrm{beccs}} = \min\left\{\beta_{\mathrm{beccs}} F_{\mathrm{el,wbio}}; \sigma_{\mathrm{beccs}} \mathrm{CCS}_{\mathrm{wbio}}; \varsigma_{\mathrm{beccs}} \mathrm{OM}_{\mathrm{beccs}}; \eta_{\mathrm{beccs}} \kappa_{\mathrm{beccs}}\right\} \tag{12.1}$$

where $0\langle\beta_{\mathrm{beccs}}\langle 1$ is an efficiency parameter that determines the amount of biomass which is measured in units of energy as needed to generate 1 kWh of BECCS electricity. The demand of woody biomass is then formulated as:

$$F_{\mathrm{el,wbio}} = \frac{1}{\beta_{\mathrm{beccs}}} \mathrm{EL}_{\mathrm{beccs}} \tag{12.2}$$

$\mathrm{CCS}_{\mathrm{wbio}}$ is the storage capacity needed to sequester CO_2 from BECCS. The total amount of carbon dioxide removed and stored depends mainly on the carbon content of woody biomass, denoted by ω_{wbio}, and on the capture rate of power plant, which is denoted with $e : \mathrm{CCS} = e\omega_{\mathrm{wbio}} F_{\mathrm{wbio}}$. By using the Eq. 12.2 it can be possibly shown that $\sigma_{\text{beccs}} \equiv \beta_{\text{beccs}}/e\omega_{\text{beccs}}$. Henceforth, we generally omit the technology that subscript when no ambiguity arises in the process. K measures the BECCS generation capacity in units of power. η as an efficiency parameter which regulates the number of hours of operation of BECCS power plants. Power generation capacity grows in the following way as given below:

$$K(t+1,n) = (1-\delta)K(t,n) + I_{\text{el}}(t,n)/\varphi \tag{12.3}$$

where I_{el} are the investments in BECCS region n at time t, δ is the depreciation rate of power plants and φ is the investment cost of BECCS generation capacity. Finally, the operation and maintenance costs (OM) are needed to run power plants and their demand is regulated by ς reluctantly.

If any country is a net importer of biomass, the BECCS power plants pay the cost for transporting biomass (TC), which is proportional to distance D from major production regions. The transportation cost is generally paid on the share of imported biomass of total consumption, denoted by $\gamma : \gamma = 0$ if the region is a net exporter, $\gamma = 1$ if a region imports 100 % biomass. By denoting the interest rate of the economy with r, the cost of generating 1 unit of electricity with BECCS is thus equal to the equation given below:

$$C(\text{EL}) = \left[\frac{1}{\beta} p_{F_{\text{wbio}}} + \frac{1}{\beta} \gamma \text{TC}.D + \frac{1}{\sigma} C_{\text{CCS}}(\text{TCCS}) + \frac{1}{\zeta} + \frac{1}{\eta}(r+\delta)\varphi \right] EL \tag{12.4}$$

where BECCS power generation firms to maximize the profits $\pi_{\text{EL}} = p_{\text{EL}}\text{EL} - C(\text{EL})$. The optimality conditions require that $\partial C(\text{EL}^*)/\partial \text{EL}^* = p_{\text{EL}}$. Thus:

$$p_{\text{EL}} = \frac{1}{\beta} p_{F_{\text{wbio}}} + \frac{1}{\beta} \gamma \text{TC}.D + \frac{1}{\sigma} C_{\text{ccs}}(\text{TCCS}) + \frac{1}{\zeta} + \frac{1}{\eta}(r+\delta)\varphi \tag{12.5}$$

The optimality conditions in the final good sector resembles that the marginal product of electricity is equal to its price. In particular, the optimal power mix depends on the relative convenience of the power technologies, i.e. j. Thus, the following condition holds as: $\left(\partial \text{GY} / \partial \text{EL}_{\text{beccs}}\right) / \left(\partial \text{GY} / \partial \text{EL}_j\right) = p_{\text{EL}_{\text{beccs}}} \big/ p_{\text{EL}_j} \, \forall j$.

12.4 BECCS Under Climate Policy

The CO_2 emissions released during the combustion of woody biomass from short rotation of plantations were recently captured by some plants during their growth process. Therefore, it is the very standard convention to assume that burning biomass generates zero GHG emissions. However, emissions from fertilizers use (N_2O) and management activities represent a net contribution to the stock of GHG in the atmosphere on a wide range. While considering the emissions from long-distance transport, it is not possible to count all the emissions from fertilizers or from other local management activities, because of the lack of reliable data and also the exact information is not estimated yet. In this way, the biomass is exempted from any carbon-related taxes. This implies that a power plant that generates BECCS electricity receives a financial support which is equal to the value of the tax for capturing and storing CO_2 and pays tax only on emissions from the international transport of woody biomass. The price of BECCS electricity is obtained by modifying Eq. 12.5 as follows:

$$\begin{aligned} p_{\mathrm{EL}_{\mathrm{beccs}}} &= \frac{1}{\beta} p_{F_{\mathrm{wbio}}} + \frac{1}{\beta}\gamma \mathrm{TC}.D + \frac{1}{\sigma} C_{\mathrm{ccs}}\left(\mathrm{TCCS}\right) \\ &+ \frac{1}{\zeta} + \frac{1}{\eta}\left(r+\delta\right)\varphi - e\omega\frac{1}{\beta}T + \frac{1}{\beta}\gamma\xi D.T. \end{aligned} \tag{12.6}$$

BECCS power generation firms are eagerly willing to demand biomass subject to the optimality condition obligatory to Eq. 12.6. This states that, for a given price of electricity, the higher the tax is, the higher will be the price of biomass that they are willing to pay. The price of biomass increases with a proportional rate of carbon tax: $\partial p_{F_{\mathrm{wbio}}} / \partial T = e\omega + \gamma\xi D$. This suggests that the regional social planner may be willing to pay a price higher than the global marginal cost of biomass production, if the global demand of biomass is exceeding the global maximum endowment. Even if the carbon tax increases the marginal production, the cost of biomass remains the same when there are limitations for production. However, the value of biomass increases with the carbon tax and thus BECCS firms are willing to pay a higher price in the international market as well. A firm in the forestry sector captures all the rent as overall hinders are done to the BECCS firms. This is a peculiar outcome of the non-cooperative interaction in the environment. According to different settings, with strategic coalition formation, a group of importing countries would have the incentive to form and motivate a cartel to extract a part of rents from the forestry sectors of exporting regions (Rose et al. 2012).

12.5 Costs Associated with the Delivery of Woody Biomass to Power Plants

For the energy production, the amount of biomass used by a specific power plant is limited by the quantity at which the high grade biomass can be delivered at a feasible cost. The charges associated with the given amount of woody biomass were determined by the costs of stumpage, regression, harvesting, chipping and transportation. For any organization, the quantity of biomass available at a given cost is also influenced by the transportation distance to some extent (Goerndt et al. 2013). The following subsections describe the ways and conventions used for the estimation of the woody biomass available for the power plants during energy production process. It also mean to provide the cumulative information regarding the costs associated with the purchase of woody biomass and other associated charges including delivery in the successive larger procurement and consumption areas.

12.5.1 Costs Associated with Biomass Procurement

In view of the biomass-based procurement organizations, the extensive changes in the amounts of biomass available with respect to the county are observed and therefore, it may be more advantageous if one can estimate the biomass availability and costs associated with its supply to each selected power plant. Goerndt et al. (2013) estimated the biomass amounts and its delivered costs for a simulated concentric procurement radii (R) from 10 to 100 km by 10 km intervals around the selected powerplant locations in Northern America using the ArcGIS software (Environmental Systems Research 2013; http://www.esri.com). In the study while dealing with large procurement radii, they observed that the total procurement area around the major power plants is consisting of several counties of varying sizes. Hence based on this, Goerndt et al. (2013) anticipated that it is of extreme importance to estimate the total woody biomass (B) which can be available annually from each procurement area at a county level of any size. The following Eq. 12.7 can be used to estimate the total amount of annually available woody biomass per county and is based on an assumption that the biomass resources are distributed uniformly across the county.

$$B = \sum_{i=1}^{m} a_i b_i \tag{12.7}$$

where a_i is the percentage of the area of a county i and b_i is the total annually available woody biomass for the same county i that falls within the procurement area under study.

12.5.2 Costs Associated with Biomass Delivery

In order to obtain the total costs associated with the delivery of woody biomass in dried form to the selected power plants from the selected procurement areas in North America, Goerndt et al. (2013) considered both of the marginal operational costs (i.e. costs of stumpage, harvesting, chipping) and the transportation costs. It was observed that a portion of the transportation costs of woody biomass to the power plants located in respective area is fully influenced by the maximum transport distance. Therefore, the maximum transport distance (d) to carry a mega-gram biomass is calculated by using the formula shown in Eq. 12.8, and is based on the similar assumption of Eq. 12.7 that the biomass being collected is evenly distributed within the given radius of a plant (Huang et al. 2009; Overend 1982):

$$d = R\tau \tag{12.8}$$

Where R corresponds to the biomass procurement radius in kilometres and τ represents the tortuosity factor, i.e. the ratio of road transport distance to line-of-sight distance which generally varies in the range of 1.2–1.5 as per the geographic location (Huang et al. 2009; Perez-Verdin et al. 2009).

According to Goerndt et al. (2013) therefore, the total delivery cost (C) for the woody biomass in each procurement area and procurement regime can be calculated by using the following Eq. 12.9:

$$C = \left(T_{\mathrm{v}} d\right) + T_{\mathrm{f}} \tag{12.9}$$

Where d represents the maximum transport distance of biomass, T_{v} corresponds to the costs related to incremental transportation and T_{f} is the operational costs which includes loading/unloading of biomass in trucks.

12.6 Methods for the Estimation of Woody Biomass

12.6.1 Destructive Sampling-Based Biomass Estimation

Estimating the total biomass in forest ecosystems is challenging due to the difficulties associated with the assessment of carbon stocks below-ground. The above-ground biomass can be easily estimated with highest accuracy in most cases; however, the below-ground biomass estimation is still labour intensive and time consuming. To overcome these limitations, the destructive sampling approach was introduced. The first step in this method involves the chopping of selected trees within some definite plots or transects, and digging out their root systems in order to establish the biomass above- and below-ground with the highest possible accuracy. Further, the field inventory measurements are collected by making use of the tools such as diameter tapes, spring scales, clinometers, pruning saws and shears, shovels, measuring tapes, field data recording accessories and paper bags (Avitabile et al. 2008; Chidumayo 1997; Japanese International Cooperation Agency JICA 2005). In the following step, the segments of stems and branches are weighed first in wet form in the field itself and then in an oven dried form in the laboratory for different significant purposes (De Gier 2003; Nogueira et al. 2008). Up to this level of data analysis provides cumulative information about the biomass levels per tree (both above- and below-ground). To obtain the complete information in a broad way to the whole area of interest by destructive sampling approach, the Allometry equation is employed.

12.6.1.1 Allometry Equation Development

Allometry equations are used to extrapolate the remotely sampled data to any larger area using the mathematical formulas. By using Allometry equations, the difficult variables associated with the measurement of wood and leaf biomass from easy-to-measure tree parameters, such as the stem diameter (at tree base or breast height), tree height or canopy and tree's crown width, can be easily calculated (Chidumayo 1997; Netshiluvhi and Scholes 2001; Santos et al. 2002). The Allometric equations are commonly derived by making use of the regression analysis of the relationship between the weight in dry form obtained from the destructive sampling (as described above) and the measured dimensional parameters of the fallen trees (De Gier 2003).

The equations are expressed in power law form or logarithmic form as shown in Eqs. 12.10 or 12.11 (Japanese International Cooperation Agency JICA 2005):

$$y = b * x^{\mathrm{a}} \tag{12.10}$$

or

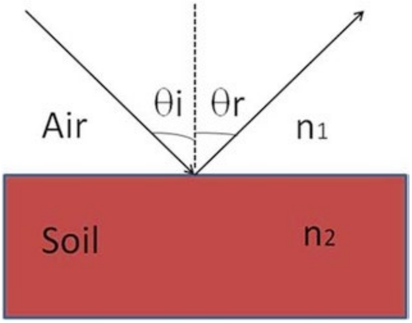
$$\ln y = \ln b + a \ln x \tag{12.11}$$

Where y is the weight of tree in kilograms, b is the allometric coefficient, a is the allometric exponent and x is the measured tree parameter which is significantly related to tree biomass such as basal diameter in the units of centimetres (cm).

12.6.2 Microwave Remote Sensing or Radar-Based Remote Sensing

The microwave remote sensing technology can be used to acquire the qualitative and quantitative information related to earth's surface from space or airborne platforms and is not influenced by the presence of clouds, light conditions and heat reaching towards it. The microwave systems are principally well suited for the assessment of woody biomass and other applications related to agriculture due to the fact that the signals of different wavelengths interact with particular part of the vegetation structure at different range of wavelengths. Thus interacting microwave radiation enables the rescue of vegetation structure parameters and related components of the standing woody biomass, rather than just the greenness of the top layer of a canopy which is depicted by the visible and infrared remote sensing technology (Koch et al. 2008; Woodhouse 2006a, b). The microwave radiation used for interaction with woody vegetation is categorized according to the applied parameters such as frequency, wavelength, reflection, refraction, diffraction, interference, polarization and scattering. When compared to each other, these characteristics leads to the distortion of incident waves following the interaction in different forms of scattering such as reflection, diffraction and reflection by the elements present in biomass and this distortion is similar in size or less than for what can be observed during the change of wavelengths. However, the occurrence of reflection is due to the scattering of waves from vegetation surfaces with specific features that are much smaller than the wavelength scale and similarly, the generation of diffraction signal are due to the scattering of incident waves at distinct boundaries. The radar remote sensing technology utilizes the backscattering signal, i.e. the intensity of signal which is reflected by the target and is received by the antenna. For point that is coherent targets, the radar equation provides the estimation for magnitude of received power and is shown in Eq. 12.12 (Woodhouse 2006a).

Fig. 12.1 Schematic representation of Fresnel reflection onto a natural surface



$$P_{\mathrm{r}} = \frac{P_{\mathrm{t}} G A_{\mathrm{e}}}{\left(4\pi R^2\right)^2} \cdot \sigma \tag{12.12}$$

where P_{r} and P_{t} corresponds to the received power and transmitted power, respectively; R is the distance between radar site and the location of target; G is the signal gain by the antenna; A_{e} is the effective area of the antenna; and σ is the radar cross section of the object. The radar cross section (σ) is the measure of radar reflectivity which indicates the strength of radar signal reflected from unit area of the target (Boyd and Danson 2005). When dealing with distributed targets especially the incoherent targets, σ is replaced by sigma nought ($\sigma°$)[10] which is defined as the radar cross section per unit area (Woodhouse 2006a; Raney 1998).

12.6.2.1 Interaction of Microwaves with Woody Vegetation

The microwave interacting vegetation surfaces are composed of layered media and is made up of the layers of consecutive leaves, branches, roots and stems of varying dielectric constants situated at a certain level above the surface of earth (Woodhouse 2006a, b; Santoro et al. 2005; Moghaddam 2009). The microwave interacting woody vegetation with variable dielectric constants (due to compositional change) may lead to a change in the direction of reflected microwaves at least to some extent. The microwaves following the interference with woody vegetation, the reflected signal properties such as the wavelength, incidence angle, polarization and terrain surfaces are greatly influenced by the surface roughness, local incidence angle, dielectric constant and surface morphology, respectively (Raney 1998; Leckie 1998). In order to address the reflection properties of a relatively smooth surface from any part of the vegetation, the Fresnel reflectivity can be employed. For understanding, the schematic representation of the Fresnel reflection in two different media of varying dielectric constants for air and homogeneous soil which corresponds to the refractive indices, n_1 and n_2 (respectively) is shown in Fig. 12.1 (Hajnsek and Papathanassiou 2005). Based on this, the following Eqs. 12.13 and 12.14

can be used to calculate the Fresnel reflection constants for horizontal and vertical polarization, respectively.

$$\Gamma_{\mathrm{h}}(\theta)=\frac{\mu\cos\theta-\sqrt{\mu\varepsilon-\sin^{2}\theta}}{\mu\cos\theta+\sqrt{\mu\varepsilon-\sin^{2}\theta}} \tag{12.13}$$

$$\Gamma_{\mathrm{v}}(\theta)=\frac{\varepsilon\cos\theta-\sqrt{\mu\varepsilon-\sin^{2}\theta}}{\varepsilon\cos\theta+\sqrt{\mu\varepsilon-\sin^{2}\theta}} \tag{12.14}$$

Where ε corresponds to the dielectric constant and μ is the unit applied to a natural material of non-ferromagnetic behaviour (natural soil).

12.6.3 Vegetation Indices-Based Biomass Estimation

Normalized Difference Vegetation Index (NDVI) is a simple graphical indicator used for the analysis of remote sensing measurements most probably recorded from a satellite. By making use of this, one can estimate the biomass by generating target images in colourful format and then comparing it against the greenery vegetation. The multispectral systems which function on Landsat and SPOT (Satellite Probatoired' Observation de la Terre) programs are used by NDVI for accessing the greenery biomass. The NDVI serves as a valuable quantitative vegetation monitoring tool on a worldwide basis, in addition to several other applications including the continuous monitoring and estimation of agricultural production, extrapolation of hazardous fire zones related to forest fires and infringements of desert maps (Lillesand et al. 2004).

According to Rouse et al. (1974), the following Eq. 12.15 can be used to calculate the NDVI

$$\mathrm{NDVI}=\frac{\mathrm{IR}-R}{\mathrm{IR}+R} \tag{12.15}$$

Where IR and R corresponds to the spectral reflectance measurements in the near-infrared band and visible red band, respectively.

12.7 Error Budget Investigation During Biomass Estimation

The estimation of available woody biomass resources in general are associated with several forms of errors such as the inherent errors as per the field assessment data and the errors due to misalignment of various factors, for example, lack of coherence between satellite geometry and training plot positions. To overcome the errors which originate during ground biomass estimation, the standard errors were derived by making use of the principles of error propagation for products or quotients (Barry 1987). The following Eq. 12.16 can be used to determine the uncertainty while estimating the ground biomass density in the biomass density class covering an area, A_{class}, with a standard error of σ_{A}, i.e.

$$\sigma_i = \left(A_{\text{class}} * \text{AGM}_{\rho}\right)\sqrt{\left(\frac{\sigma_{\text{A}}}{A_{\text{class}}}\right)^2 + \left(\frac{\sigma_{\text{AGB}_\rho}}{\text{AGB}_\rho}\right)^2} \tag{12.16}$$

where σ_i and σ_{AGB_ρ} correspond to standard error and mean square error (respectively) of the estimating ground biomass density in a particular biomass density class, AGBρ represents the mean value of the predicting ground biomass density in the biomass density class.

Similarly, the overall uncertainty in the estimation of total ground biomass is determined by using Eq. 12.17, i.e. the sum-up of all the ground biomass estimates in the verified biomass density classes in the specified area of interest finally gives the total ground biomass.

$$\sigma_{\text{AGB}} = \sum_{i=1}^{N}\sqrt{\sigma_i^2} \tag{12.17}$$

where N is the number of biomass density classes in a specific area of interest.

12.8 Conclusion

In conclusion, we reviewed the methods available for the estimation, analysis, production and consumption of biomass and related products for the fulfilment of various forms of energy needs in the current world. The work presented here broadens the understanding of economic analysis of the operational and transportation costs in addition to technological innovations required for the production and consumption of biomass. Further work in this field is to explore and enhance the individual web-based options for serving the information to various practitioners working in various fields like woodland dynamics, socio-economic and energy security domains. A thorough understanding of these factors not only entrench poverty, unemployment but also have terrible implications for a nation's economy from rural backgrounds. Also, the continued dependence of rural lifestyle on biomass resources to meet the sustenance and livelihood in poor economic conditions are exerting unsustainable pressure on the limited resources that are available. For example, the diminishing of fuel-wood supplies is making the rural people to spend more time to collect wood from the forests and in this way, they spend less time on food preparation and other activities such as farming, childcare, housekeeping, sanitation, socializing and education. The other issue of concern includes the high cost of wood purchasing from vendors and the personal security in and around the places where wood is collected.

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Chapter 13
Production of Algal Biomass

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_13,

Abstract Among renewable resources, algae have proven to be an attractive feedstock for rapid generation of carbohydrates and lipids by utilizing its photosynthetic ability to present itself as an alternative energy source. Different species of algae, being environmental friendly, are strong candidates for generation of biomass, and are used in production of biogas and biofuel. Continuous efforts are being made to increase its large-scale production by application of specific methods chosen on the basis of desired downstream processing and final application of algal biomass. Biomass production is dependent upon cultivation methods for harvesting, followed by quantification of biochemical composition of biomass. Harvesting of algal mass is a major concern playing crucial role in determination of process economy required for further applications including biofuel production. Although algal biomass appears to be an efficient substrate for biofuel production, the progress is hindered by ammonia inhibition and ion toxicity. Further research is needed to replace the continuously depleting energy sources with renewable, eco-friendly sources.

Keywords Algal biomass • Biofuels • Feedstock • Bioreactors • Algae

13.1 Introduction

With an immense increase in world population over the past few decades, man has been forced to endeavor the alternative energy sources to meet the ever-increasing energy demands. Renewable sources are the areas of interest for researchers of which biomass and biodegradable organic wastes have shown high potential to be used in the production of biofuels (Chynoweth et al. 2001). Most bioenergy is generated from organic matter through the process of anaerobic fermentation. Anaerobic fermentation of biomass results in the production of biogas that is useful and eco-friendly fuel and releases quite a fewer amount of greenhouse gases and other toxic particulate matter than any other conventional fuel. There are a number of materials utilized in producing biofuel through anaerobic fermentation such as edible oil, maize seeds, and sugarcane (Mussgnug et al. 2010). Among these materials, algae have appeared to be the most attractive feedstock. This is due to the fact that algae are prokaryotic or eukaryotic photosynthetic microorganisms with high rate of productivity, rich in lipid content and depicts no competition with food crops since it does not require arable land and can grow in any harsh conditions owing to their simple organization (Vandamme et al. 2011). Algae contain high content of biodegradable components, which can be renewed to methane-rich biofuels (Sialve et al. 2009). Microalgae are well adapted to all ecosystems of the earth including aquatic as well as terrestrial environments. There are approximately 50,000 species of microalgae on earth indicating the immense variety of strains adaptable to variety of environmental conditions (Richmond 2004). Microalgae have been divided into three broad categories based on their pigment; one is red seaweed also known as Rhodophyceae, second is green seaweed or Chlorophyceae, and third is brown seaweed or Phaeophyceae. First time in 1952, a paper on “Algal culture from laboratory to pilot plant” was published by the Carnegie Institution of Washington demonstrating the work done on algal culture during World War II era. This paper illustrated the promising potential of algae as a source of agricultural and chemical commodities (Burlew 1953). The first use of algal biomass was as feed supplement for animal proteins to be consumed by humans directly. An aspect of using microalgae biomass is that there is a minimal nutrient requirement so it can be grown on a range of sewage and waste water from where it derives its nitrogen and phosphorus requirement (Malik and Prajapati 2012). For the production of algal biomass, water, CO_2, and essential nutrients are provided according to the strains used while oxygen is removed. Nutrients can also be provided from runoff water from nearby lands. Microalgae can also grow on large ponds and pools adding to its benefits as economically feasible and the most successful candidates for biogas production. Cultivation of microalgae is done using sunlight in covered or open ponds or pools or closed photobioreactors depending upon the designs. However, closed systems are more expensive than open ponds and present more technical problems. Individual closed system unit cannot be extended beyond 100 m^2 due to gas exchange limitations and other problems (Demirbas 2010). Another important aspect in the economics of algal biomass production is the harvesting and CO_2 supplementation as elevated levels of CO_2 help in increased growth of algal biomass and subsequently increased bioenergy production (Yoo et al. 2010; Prajapati et al. 2013; Chinnasamy et al. 2009; Jiang et al. 2011). The method of harvesting algal biomass depends upon its application. Since the harvesting of algal biomass is energy requiring process, it should be carefully designed. A major challenge is the small size of algal cells and their subsequent low concentration in the culture medium ranging between 0.5 and 2.0 g/L approximately (Prajapati et al. 2013; Christenson and Sims 2011; Vandamme et al. 2011). Algae cultures may contain either a single or multiple specific strains in order to optimize the production of desired product. There have been a number of microalgae species used for the production of biogas. It includes the *Chlorella* spp., *Oscillatoria* spp., *Euglena* spp., *Scenedesmus* spp., and *Synechocystis* spp. along with a number of others. However, there are certain limitations that have been encountered using algal biomass during anaerobic digestion (Sialve et al. 2009). These include low digestibility of algal cell wall, ammonia inhibition, and the sodium toxicity to methanogens (Mussgnug et al. 2010). In the first phase of anaerobic digestion of algal biomass, hydrogen gas is released which may lead to feedback inhibition to acetate forming bacteria (Gerardi 2003). To counter the low digestibility of algal biomass and to obtain maximum amount of biogas, high hydraulic retention time (HRT) is required under mesophilic conditions (Zamalloa et al. 2012). Therefore a number of pretreatment methods have been established to remove or rupture the algal cell walls to reduce HRT (Alzate et al. 2012).

There is a great need to replace petroleum-derived transport fuels with renewable biofuels, which are more long-lasting and least contributing towards global warming. The most attractive of these renewable resources for transport fuel is biodiesel and bioethanol. Agricultural crops have been used for the production of bioethanol and biodiesel, however, the present techniques failed to substantially replace fossil fuel-based transport fuels; therefore a more attractive alternative is the use of microalgae (Chisti 2008). Even the most widely used oil crops including oil palm and sugarcane can not match the amount of bioenergy produced through microalgae. Production of biodiesel involves the process of transesterification in which ester compound's alkoxy group is exchanged by specific alcohol. Transesterification involves fat or oil reaction with the alcohols to produce esters and glycerol. When algal oil product is combined with alcohol and H^+ or OH^- group, fatty acid methylesters are produced to form biodiesel. The important requirement in this regard is to select those algal strains, which are rich in oil, since most of the microalgae are rich in oils and some even exceeds 80 % of dry mass of algae biomass, thus there is a great potential in the use of algal biomass in biodiesel production (Demirbas 2010).

13.2 Cultivation of Algae

13.2.1 Internal and External Factors Required for Growth of Algal Biomass

13.2.1.1 Water

Being photosynthetic organisms, algae have comparatively simple requirements for growth. Water, containing the accurate amounts of salts and minerals, is a particularly essential component needed for algal cultivation. Based on the need for water, algae are basically categorized into aquatic or semiaquatic species. The standard quantity of water required for effective farming of aquatic algae is approximately 1.5 L/ha. This figure is valid considering the fact that growth occurs in an open pond and roughly 7–11 million liters of water is evaporated from that region annually. Algal production can be linked to the remediation of wastewater from both domestic and industrial sources. The wastewater, containing the essential elements, can be directly supplied to the algal culture. This allows nourishment of algae while simultaneously treating wastewater.

13.2.1.2 Carbon

Algae require very high amount of carbon for efficient growth. Procuring carbon for algal growth costs up to 60 % of the total nutrients budget. Carbon can be obtained from multiple sources, which include (1) CO_2 from the atmosphere (2) CO_2 contained within industrial smoke (3) CO_2 from soluble carbonates. For each kilogram of algae that is grown, approximately 1.65 kg of CO_2 is used.

13.2.1.3 Light

The key ingredient to initiate photosynthesis is light as it is involved in the conversion of carbon dioxide to carbohydrates. As compared to higher plants, algae require relatively low intensity of light for proper development. Solar waves are the primary source of light. Only 43–45 % of the total solar radiations are involved in commencement of photosynthesis. These radiations are termed as PAR or Photosynthetically Active Radiation. About 27 % of PAR is converted to carbohydrates. The rate of biomass growth can be established by considering the following relation:

$$P = \alpha E.I$$

where P is the rate of production of dry algae and is measured in g/m^2/day, E is the efficiency of photosynthesis, I denotes light energy in kcal/m^2/day, and the symbol α represents the conversion coefficient (g/kcal).

The light source in the cultivation system can be either natural, artificial, or combination of different light sources. The cheapest source is the solar energy, which is utilized in open pond systems, which require a large area for construction and have a higher contamination risk. In closed systems, fiber optics and solar concentrators can be used to maximize the effect of sunlight. As compared to fluorescent lamps, LED lights are shown to be more economically stable.

13.2.1.4 Nitrogen

Being the main constructing element of proteins and nucleic acids, nitrogen plays a significant role in algal metabolism.

13.2.1.5 Phosphorous

This element is used in the form of phosphates because if it is present in any other state, it may become unavailable to the algae due to its ability to combine with other metallic ions, which results in precipitation.

13.2.1.6 Additional Nutrients

Apart from the above-mentioned nutrients, trace amount of vitamins and metals like sodium, calcium, magnesium, manganese, zinc, copper, iron, and molybdenum are also required for efficient growth of algal culture.

13.2.1.7 Space

Unlike other organisms, algae are very versatile and do not require arable land for productive growth. They can be cultivated in ponds, water bodies, and even reactors. Issue of appropriate space is not a concern and does not put a strain on the budget or available resources.

13.2.2 Methods for Cultivation of Algal Biomass

Some of the techniques used for biomass cultivation are:

13.2.2.1 Photoautotrophic Production

This form of cultivation takes place when algae utilize an energy source (light) and a carbon source (inorganic carbon) to form carbohydrates through a process termed as photosynthesis. This is the most general method used for cultivating algae and results in the formation of algal cells with lipid content ranging from 5 to 68 % depending on the algal specie being cultivated. If algae are cultivated for oil production, then the prime advantage of using this cultivation technique is to utilize carbon dioxide to meet the carbon requirement.

13.2.2.2 Heterotrophic Production

In this method, the algal specie is grown on a carbon substrate like glucose thus eliminating the need of light energy. This process can be performed in a reactor with a small surface to volume ratio. A much higher degree of growth control is achieved and harvesting budget is lowered due to production of high-density cells. The set-up cost is negligible but more energy is used as compared to the process utilizing light energy because photosynthetic processes are utilized to form the carbon source on which the algae are grown. Studies have shown that heterotrophic method of biomass production has a higher yield and cells have higher lipid content (55 % as compared to 15 % in autotrophic cells).

13.2.2.3 Mixotrophic Production

Some algae have the capability to obtain nutrition by both autotrophic and heterotrophic methods. This means light energy is not a primary need for mixotrophs as cell growth can occur by digesting organic material. These cultures are shown to lessen photo inhibition with enhanced growth rates as compared to autotrophic and heterotrophic cultures. This is because cultivation of mixotrophs utilizes both photosynthetic and heterotrophic elements, which decreases loss of biomass and reduces the quantity of organic substrate consumed.

13.2.2.4 Photoheterotrophic Cultivation

This mode of cultivation refers to the process in which alga requires light energy and obtains carbon from an organic source. Unlike mixotrophs, photoorganotrophs cannot grow without light energy. Although this process can enhance the production of certain useful light-regulated metabolites, this mode of cultivation is not preferred in case of procedures like biodiesel production.

13.2.3 Comparison of Different Cultivation Techniques

In case of heterotrophic cultivation, the culture has a high chance of getting contaminated especially in open pond cultivations. Apart from this, carbon source is also purchased at a high cost. Photoautotrophic system of algae cultivation is the most frequently used method for biomass growth. It is easy to scale up and can easily take carbon dioxide from the surface air.

13.3 Cultivation Systems

There are two main cultivation systems used for the production of algal biomass:

13.3.1 Open Ponds

The average volumetric yield for this system lies between 0.06 and 0.42 g/L per day. The efficiency of the system depends upon the configuration of the pond and the algal specie that is being cultivated. Open tanks or naturally existing water bodies (ponds, lakes, lagoons, etc.) are collectively termed as open ponds and are unproblematic to construct and maneuver. These ponds are kept shallow for the easy penetration of solar radiations. Water and nutrients are continuously circulated in the culture. Output of the pond is measured by calculating the biomass produced each day per unit area. Circular ponds and raceways have an area of about 1 ha whereas extensive ponds can be about 200 ha. Artificial open ponds are further categorized as:

13.3.1.1 Unmixed Open Ponds

This system is without the ability to keep a control on the factors involved in the cultivation process. For example, algal cells have a propensity to settle in the form of residue under the influence of gravity and therefore, availability of CO_2 and light is sufficiently reduced. In addition to this, this system also lacks the capacity to supply an efficient amount of CO_2 to algal biomass, thus decreasing the yield.

13.3.1.2 Circular Ponds

This system has the credit for being the first design to be commercially used for algae fostering. The major drawback of this system is that its scale is limited to an upper range of approximately 1,000 m^2. At this range, the stress makes the core pivot mixer unmanageable.

13.3.1.3 Open Raceway Ponds

In early 1950s, Oswald and his colleagues introduced this system, which is also known as high rate algae ponds (HRAP). This system is basically used for the treatment of wastewater by supporting the symbiotic relationship between aerobically active bacteria and algae. Circulation of broth and nutrients using a paddle wheel is performed in looped channels. The ponds are made up of concrete, PVC, or clay and are about 0.2–0.5 m deep, allowing deep penetration of sunlight. Carbon dioxide is directly taken from the surface air but aerators can easily be installed inside the pond to increase the level of CO_2. Although this system is well developed, yet it still presents the problem of infection with unwanted algal species.

13.3.2 Closed Photobioreactors

Reportedly, the yield of photobioreactors (PBR) system ranges from 0.02 to 3.22 g/L per day and are used to cultivate algae in closed environment under manageable conditions. Efficiency of this system can be appreciated by considering the fact that it does not permit the algae to be exposed to the external environment. There are various configurations of the PBR systems like:

1. Vertical tank
2. Polybag
3. Helical tube
4. Horizontal tube
5. Inclined tube
6. Flat-plate
7. Vertical-column photobioreactor

13.3.2.1 Tubular PBR

A tubular PBR is constructed by arranging linear tubes made up of plastic or glass. This configuration can be easily manipulated to form arrangements like helical tubes and fence-like PBR. The ability of this configuration to expose the culture to maximum sunlight makes it suitable to use during outdoor cultivation. A slight glitch in tubular PBR is the settling of algae at the bottom of the tubes. Sedimentation can, however, be avoided by utilizing an airlift propeller to maintain an exceedingly turbulent flow. Tubular PBR are the largest in terms of size with areas reaching up to 750 m^3.

13.3.2.2 Flat-Plate PBR

Another widely used configuration is the flat-plate PBR, which is constructed by employing slender rectangular containers composed of transparent material. These cylinders are tilted at certain angle, which allows maximum coverage of sunlight. Photoautotrophic cells cultivated in this PBR have high densities (>80 g/L). These are more appropriate for cultivation since they allow low accumulation of dissolved oxygen and allow photosynthesis to occur proficiently. Still, problems like temperature control and adherence of algae to reactor walls exist.

13.3.2.3 Column Photobioreactors

This configuration of a photobioreactor offers the finest mixing, most manageable cultivation conditions and greatest volumetric mass relocation rates. They are economic and the setup is comparatively easy. Column PBR are aerated from the base and their translucent walls allow maximum exposure to light. They can also be illuminated internally.

13.3.2.4 Continuously Stirred Tank Reactors

The tank is in the shape of a broad, hollow, and capped cylindrical duct that has the potential to operate both outdoor and indoor. Risk of culture infection is extremely low. Stirring and illuminating apparatuses are inserted from above. Drainage systems and gas injectors are placed at the bottom and in the mid-section. The consistent turbulent flow induces algal growth and averts fouling of the culture.

When judged against the open pond systems, in a PBR the algal culture is efficiently protected from any sort of pollutant and loss due to low evaporation. The cultivation parameters (level of nutrients, temperature, pH level, etc.) can also be effectively managed.

13.3.3 Hybrid Production System

The hybrid system is a cultivation method comprising of two stages and utilizes both open ponds and PBR for different growth phases. The first stage of cultivation is completed in a photobioreactor where uninterrupted cell growth occurs in a pollution-free environment under controlled conditions. The second stage of cultivation occurs in open ponds and is intended to expose the culture to ecological and nutrient stresses. This enhances the production of desired lipid product.

The methods, which are presently being profitably used for algae cultivation, are raceway ponds and tubular PBR. Open ponds are a much cheaper method for algal cultivation. Setup and maintenance are also easier. Open ponds require less energy as compared to PBR. Open ponds are, however, less efficient as compared to PBR. Contamination, losses due to evaporation, temperature vacillation, inept mixing, and light limitations are some of the malfunctions associated with open pond systems.

13.4 Problems Associated with Production of Algal Biomass

13.4.1 Production Cost

Photosynthetic development of algae requires not only sufficient supply of light, carbon dioxide, water, and salts but the temperature must also linger within 293–303 K. Maintenance of these conditions is not possible without putting a stress on the budget. Cultivation in a photobioreactor is advantageous when we consider the fact that it requires less light energy and the conditions are also controllable but PBR setup is quite expensive.

13.4.2 Large-Scale Production

Growing our selected algal specie in ample volume of hundreds of cubic meters is one of the chief problems in the large-scale algal cultivation. When efforts are made to induce an increase in the volume of the algal strain, a premature collapse may take place due to the semi-sterile conditions of the environment.

13.4.3 Temperature

After light, temperature plays the most significant role in determining the effectiveness of algal growth. Some species of microalgae have the ability to endure temperature that is approximately 15 °C lower than their optimum temperature but a rise in temperature of only 2–4° may result in absolute loss of culture. When it comes to maintaining temperature in closed cultivating systems, favorable results have been shown by employment of evaporative water coolers.

13.4.4 Salinity

Dealing with salinity is a main problem while cultivating algae. Salinity plays a role in determining the growth and composition of algal cell. In high temperature, the salinity of algal biomass can increase due to evaporative losses. Deviation in the optimum salinity conditions can affect the algal strain by producing an osmotic and ionic stress. In addition to that, there occurs a change in the ionic ratios of the algal cell. These problems can be managed by addition of water or salt according to the need.

13.4.5 Mixing

Blending is another important factor when it comes to cultivating algae. It is important for regulating the distribution of cells and heat. It also dispenses the metabolites and aids in the transportation of gases. While cultivating algae in a reactor, a system is required that transfers the algae from the light to dark region, which is accomplished by generating a certain magnitude of turbulence. An unchecked increase in the velocity of mixer leads to cell damage owing to shear stress.

13.4.6 Contamination

Biological elements that pollute the algal culture include undesirable strains of algae, yeast, mould, bacteria, and other strains of yeast. Degree of contamination is high in raceway ponds because the culture is more susceptible to contaminants like protozoa and foreign algal species. Studies have shown that contaminants can be eliminated by temporarily exposing the culture to an environment with extreme conditions of growth factors like temperature, light, pH, etc.

13.5 Harvesting of Algal Biomass

The main step after the bulk cultivation of algae is its harvesting, which performs a very vital part in shaping the process budget of algal biofuels. Despite the excessive presence of algal biomass, the harvesting of macro-algal biomass is considered as simpler and less costly as compared to the harvesting of algal biomass. Due to the diluted nature of algal culture cells and small size, the operating expenses of dewatering and harvesting of algal biomass is high. The typical size of single-celled eukaryotic algae is measured around 3–30 μm (Grima et al. 2003), and the range of cyanobacteria is 0.2–3 μm (Chorus and Bartram 1999). The improvement and wide-scale application of different technologies for energy generation is currently a great challenge and of a significance to the scientists and the machinists of active systems. It is generally believed that numerous roots, properties, and active transformation of biomass are the main bases of renewable energy (McKendry 2002; Goyal et al. 2008). A number of procedures including chemical as well as mechanical can be performed, which includes centrifugation, flotation, flocculation, filtration, screening and gravity sedimentation, and electrophoresis for harvesting of algal biomass (Uduman et al. 2010). There are critical parameters to consider for the selection process of algae for harvesting. Such parameters include density, size, and value of the desired products. Two-step processes are usually used for the harvesting of algae:

1. Bulk harvesting: This step is performed for the separation of algal biomass from the bulk suspension. The techniques that can be used to complete this process are flocculation, flotation, or gravity sedimentation.
2. Thickening: the second step required for harvesting of algae is thickening which is performed to thicken the slurry by filtration or centrifugation (Brennan and Owende 2010).

The most important and the most operative method used for the separation of algal biomass is by centrifugation technique in algae harvesting, but it is only done on high-valued products due to high operational and functional cost (Grima et al. 2003).

13.5.1 Flocculation

This is the process in which circulated algae cells are combined together to form bulky biomass collection for settling. The precipitate of carbonates with algal cells at high pH, due to CO_2 ingestion by the algae, results in auto-flocculation (Sukenik and Shelef 1984).

13.5.2 Chemical Coagulation

Chemical coagulation is performed by making the mixture of chemicals for initiation of flocculation in the fusion of algae. The mixture of chemicals includes inorganic flocculants and organic flocculants or poly-electrolyte flocculants. The activity of two predictable chemical coagulants ($FeCl_3$ and $Fe_2(SO_4)_3$) and five commercial polymeric flocculants (Drewfloc 447, Flocudex CS/5000, Flocusol CM/78, Chemifloc CV/300, and Chitosan) was matched by de Godos et al. (2011) to check their capability to eliminate bacterial biomass in algae from the discharge of a photosynthetically oxygenated piggery wastewater biodegradation process. Ferric salts achieved the uppermost biomass elimination (66–98 %) at the absorption of 150–250 mg/L. Polymer flocculants were considered sufficient for the similar elimination efficacies and eliminated the bacterial biomass at lower concentration (25–50 mg/L), though the efficiency reduced at upper polymer flocculants amount.

13.5.3 Combined Flocculation

Combined flocculation is a multi-step process, which consists of the use of more than one type of flocculants and electro-flocculation or electrocoagulation (Chen et al. 2011). For harvesting of marine and fresh water algae, Vandamme et al. (2011) has inspected the method of electrocoagulation–flocculation. Continuous-flow electrocoagulation has also been examined by Azarian et al. (2007) for the separation of algae from industrial wastewater. Throughout electrocoagulation, no sulphate chlorine anions are produced. It is also noted that unlike centrifugation process, power consumption is less in electrocoagulation–flocculation (Vandamme et al. 2011). These are the advantageous reasons, due to which electrocoagulation–flocculation is considered as a convenient procedure, which can be used for harvesting of algae. There are certain shortcomings such as inconsistency in speciation of metal hydroxides as well as disturbances by pH, chemical configuration and conductivity of water required to be considered and addressed.

13.5.4 Gravity Sedimentation

Gravity sedimentation is a simple process used for the separation of algae in water and wastewater treatment, which is often supported by flocculation to upsurge the effectiveness of gravity sedimentation (Chen et al. 2011). Another model of gravity sedimentation procedure is flotation, which is considered more effectual and advantageous as compared to sedimentation and can capture the bits with thickness of less than 500 μm (Yoon and Luttrell 1989). The operative and efficient methods for harvesting of algal biomass include centrifugation and chemical precipitation (Chen et al. 2011). These procedures are not economically practicable for harvesting of algae due to high procedure charge of centrifugation or chemical flocculants for the production of biogas. Filtration also appears to have great prospective for condensing algal biomass from bulk culture, integration of different techniques such as flocculation, gravity sedimentation, or flotation can also be done. For biogas production, concentrated slurry is considered as a good substrate for anaerobic digestion (Prajapati et al. 2012, 2013). The consumption of wet algal biomass reduces the water necessity, which is required in excessive amount for the digestion of conventional biomass, for biogas production.

13.6 Reservoirs of Algal Biomass

Optimized culture technologies are the key elements to regulate the effective cost of production of algal biomass for biogas production. There are various approaches for cultivation of algae, starting from solutions that are technically advanced in which the procedure is methodically checked and measured, to the low expected methods consisted of open tanks. Algal biomass is usually taken from the natural, degraded and eutrophic water bodies for the production of biogas (Zhong et al. 2012).

There are two processes by which algae is grown, (1) open culture system and (2) closed systems (also named as photobioreactors). In the course of the Second World War, Germans were the first, who comprehended the idea of growing algae in open ponds. Before that, algae were cultivated and used as food supplements. For CO_2 reduction, mass harvesting of algae was initiated by a bunch of staff at Carnegie Institute in Washington when industrial development originated (Burlew 1953). Algae were commercially produced during early 1970s and late 1970s in Israel, Eastern Europe, and Japan. It was cultivated as nutritious diet in open ponds during 1970s period. Lake Chadand and Lake Texcoco in Africa were the main sources of production of *Spirulina* specifically for the families living in these zones. Cultivation of algae was also influenced by food and nutritious requirement of people living in these area. For water management in the United States, algal open pool system was established and the recovered enriched algal biomass was then transformed into methane, which was considered as the chief energy source (Burlew 1953). With the passage of time, in the aquaculture field, algal biomass production was considered as the most important (Muller-Feuga 2000). Algae have gained a lot of attention in recent years because of its capacities in chemical production (Borowitzka 1999; Lorenz and Cysewski 2000) and also due to its use as the food supplement by both animals and humans (Dallaire et al. 2007). Some other applications of algae include the biosorption of heavy metals (Wilde and Benemann 1993; Lodeiro et al. 2005; Karthikeyan et al. 2007) and fixation of CO_2 (Benemann 1997; Sung et al. 1999; Chae et al. 2006). There are certain advantages of closed system as compared to open pond system. The recommendations for photobioreactors have been made from laboratory to industrial scale. Because of the improved customized and controlled cultivation settings, closed photobioreactors have gained a lot of attention than open pond system. Adulteration can be avoided and greater algal biomass production can be attained in closed photobioreactor. A large number of photobioreactors have been examined for biomass production and cultivation of algae but only a limited number of them are able to use solar energy. The main hindrance in the algal biomass production is the deficiency of effective photobioreactors. Transferal of photobioreactor and detailed study of certain parts of hydrodynamics is essential for the improvement of algal biomass production. Characteristics of maximum number of open-air photobioreactors include uncovered illuminating areas. Flat and cylindrical photobioreactors are considered favorable apart from facing the difficulty in surmounting the photobioreactor up. There are bioreactors that have better scaling ability but their usage in open-air cultures is restricted due to having less illuminating exterior. Such bioreactors include airlift, stirred tank, and bubble-column (Prajapati et al. 2013).

13.7 Main Hurdles and Possible Solutions

Though algal biomass appears to be a good substrate for the production of biogas, there are certain restrictions due to anaerobic digestion of algal biomass. It has been reported by Sialve et al. (2009) that there are two major problems of microbial flora of anaerobic absorption: sodium ion toxicity and ammonia inhibition.

Toxicity of ammonia mainly arises because of excessive C/N ratio of the algal biomass. Free ammonia present during the harvesting procedure barely disturbs the acidogens and mostly hinders acetoclastic methanogens. The range of obstructive concentration of ammonia varies widely (1.7–14 g/L) because there are several other factors contributing to inhibition of ammonia. These factors are nature of the feed, inoculum, operating and functioning conditions, i.e., pH and the presence of antagonistic ions like sodium ion, calcium ion, and magnesium ion (Angelidaki and Ahring 1993; Chen et al. 2008; Koster and Lettinga 1988; Sialve et al. 2009). Furthermore ammonia when released in the course of hydrolysis of amino acids causes an upsurge in both alkalinity and pH of digester liquid. At elevated concentration of ammonia and alkaline pH, acetate ion, which is the basic substrate for the methanogens, gets transformed into ammonium acetate or ammonium bicarbonate leading to the reduction of accessible acetate to methanogens (Shanmugam and Horan 2008, 2009). This reduction of acetate ion and subsequent less development of methanogens due to high ammonia released during algal biomass ingestion can be the main reason of low methane in the headspace biogas (Shanmugam and Horan 2009).

13.8 Conclusions

Algal biomass can prove to be the most promising source of bioenergy to cope with high energy demands. Algal biomass can generate improved quantities of biogas and biodiesel as compared to traditional substitutes. With the latest and more advance technologies, it can successfully replace the conventional feedstock. If the internal and external factors are carefully controlled such as increased water, CO_2, light, and sufficient space, the algal feedstock can generate maximum biomass and in turn maximum bioenergy output. The biofuels generated through algal biomass is more environment-friendly with minimum contribution towards global warming. Among different methods of algae cultivation, the most successful is the mixotrophic production, which possesses both photoheterotrophic and photoautotrophic capabilities. Open and close pond systems are used equally with certain benefits and limitations, however, if the problems associated with production of algal biomass such as cost, temperature maintenance, salinity control, and contamination are eliminated, algal biomass can be grown to its maximum. Harvesting of algal biomass after mass cultivation plays a vital part in shaping the process budget of algal biofuels. The harvesting of macroalgae biomass is a simple process as compared to the microalgae harvesting. Due to the diluted nature of algal culture cells and small size, the operating expense of dewatering and harvesting of algal biomass is elevated. To resolve this challenge, a number of procedures including chemical as well as mechanical, can be performed which includes centrifugation, flotation, flocculation, filtration, screening and gravity sedimentation, and electrophoresis with beneficial output. Optimized culture technologies are the key elements to regulate the effective cost of the production of algal biomass for the purpose of biogas production. With the selection of those algal strains that are rich in oil, there is a great potential of algal biomass in biodiesel and biogas production.

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Chapter 14
Natural Fibers Reinforced Polymeric Matrix: Thermal, Mechanical and Interfacial Properties

Abou El Kacem Qaiss, Rachid Bouhfid, and Hamid Essabir

Contents

Abstract Natural fibers have recently become attractive to researchers, engineers, and scientists as an alternative reinforcement for fibers–polymer matrix composites. This interest comes from the combination of several advantages of natural fibers such as low cost, low density, non-toxicity, high specific properties, no abrasion during processing, and the possibility of recycling. The lack of compatibility between hydrophilic fibers and hydrophobic polymers (thermoplastics and thermosets), results a poor interfacial adhesion, which may negatively affect the final properties of the resulting composites. The tensile properties of composites based on natural fibers are mainly influenced by the interfacial adhesion, dispersion/distribution of fibers, and fibers loading. Several chemical modifications are used to enhance the interfacial adhesion resulting in an improvement of thermal and mechanical properties of the composites. This chapter presents a description of the natural fiber

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_14, © Springer International Publishing Switzerland 2014

reinforcement composites/polymer matrix, and the context for the development and use of these products. The fibers used as reinforcement of thermoplastics matrix are Alfa, Doum, Pine cone, Hemp, Coir, and Bagasse. The knowledge of the structure and chemical composition of each component is required to understand the study of interactions between the reinforcing fibers and matrix.

Keywords Natural fibers • Matrix • Thermal properties • Mechanical properties • Interfacial properties

14.1 Introduction

In recent years, the polymer materials are widely used in various applications, such as automotive, construction, aerospace, and sports, the most important polymer benefits are ease in processing, the productivity and reduce costs. Fibers reinforced polymers matrix, such as aramid, basalt, carbon, and glass fibers are most commonly used in industry applications due to their low cost, ease of production, and their important specific mechanical properties (Ku et al. 2011; Wambua et al. 2003; Pickering et al. 2007). However, the problem encountered in the use of these materials is their negative impacts to humans and the environment. Although, addition of renewable resources as reinforcement in materials composite is becoming more frequent (Beckermann and Pickering 2008; Torres and Cubillas 2005). Markets are becoming more oriented to demand more environmentally friendly products. Natural fibers are now promising as replacements for usual synthetic fibers for various applications such as aerospace, automotive parts and applications of high performance, etc. (Ofomaja and Naidoo 2011; Yanjun et al. 2010). The industry of natural fiber composite has widely invaded the world; the automotive industry is the prime driver of “green composites” because the industry is faced with issues for which green materials offer a solution. These new materials are called eco-materials, bio-composites, or eco-designed materials. The natural reinforced composites have therefore attracted attention more high due to their availability as renewable, and ecological material (Cao et al. 2006). They exhibit advantages such as low cost, low density, biodegradability, availability, good thermal and mechanical properties (Malha et al. 2013), ease of implementation (Arrakhiz et al. 2012a), their ability to be recycled (Essabir et al. 2013a) and to their environmental friendliness (Arrakhiz et al. 2012b; Essabir et al. 2013c). Polymers reinforced with natural fibers have been shown to exhibit enhancements in thermal (Essabir et al. 2013b), mechanical (Arrakhiz et al. 2012c), and rheological properties (Arrakhiz et al. 2013a; Essabir et al. 2013c). Fibers are often added to a plastic matrix to reduce the cost of a component and to improve some mechanical properties such as stiffness. In terms of markets and applications, it is particularly the automotive industry, the building and construction industry which have expressed interest in using such materials.

A better understanding of the morphological, structural and chemical composition of natural fibers is essential to developing materials composites. Lack on compatibility between fibers and matrix is the biggest challenge in developing these composite materials (Freire et al. 2008; Sawpan et al. 2011). Natural fibers are hydrophilic, they are essentially composed of lignocelluloses, which contain hydroxyl groups (Freire et al. 2008). These hydrophilic fibers are therefore incompatible with hydrophobic thermoplastic matrix, such as polyolefin and have low resistance to humidity (Arrakhiz et al. 2012a). Another important factor to obtain high mechanical properties is the fiber dispersion/distribution in matrix. These problems are the main limitations in polymers composites based on natural resources (Essabir et al. 2013b) Several reports show that the properties of composites were improved when the surface of the natural fibers or the polymer was modified (Arrakhiz et al. 2013a, c).

14.2 Natural Fiber Characterizations

The microstructure composition of natural fibers is complex due to the hierarchical organization of the different compounds present at various amounts. Natural fibers are composed of a plurality of walls. These walls are formed of crystalline microfibrils based on cellulose connected by lignin and hemicelluloses. These walls vary in their composition (ratio cellulose, lignin, pectin, and hemicelluloses ratios) and the orientation of microcellulose fibril.

Chemical composition varies with the type of fibers. These constituents contribute to the overall properties of the fibers. The concept of variability of fiber is important and must be considered in the case of the natural fibers. The origin and method of extraction of fibers lead to variation in dimensional and structural properties of fibers (density, diameter, length, cellulose percentage, microfibrillar angle). These different structural and dimensional characteristics will influence mechanical and thermal properties of fibers. The technique used to determine the structural properties of natural fibers is the Fourier transform infrared spectroscopy (FTIR) (Fig. 14.1).

Figure 14.1 shows the FTIR curves of some raw natural fibers performed in the range of 4,000–600 cm^{-1}. It was observed the main peaks of fiber constituent as lignocellulosic compounds: cellulose, hemicelluloses, and lignin (Yang et al. 2007) (1,730, 1,630, and 1,030 cm^{-1}).

Generally, in a composite material the content and orientation of reinforcement fibers determine the elastic properties. Similarly, natural fibers, the characteristic properties of fibers are mainly determined by chemical and physical composition such as structure, cellulose percentage, microfibrillar angle, and polymerization degree (Rowell et al. 2000; Bledzki and Gassan 1999; Arrakhiz et al. 2013b). Similarly, the microfibrillar angle is inversely proportional to the resistance and hardness of fiber (Yang et al. 2007).

The scanning electron microscopy is used for determination of morphologic properties of the fibers. The samples were coated with gold prior measurement. The Fig. 14.2 shows the Alfa, Doum, Pine cone, Hemp, Coir, and Bagasse fibers of

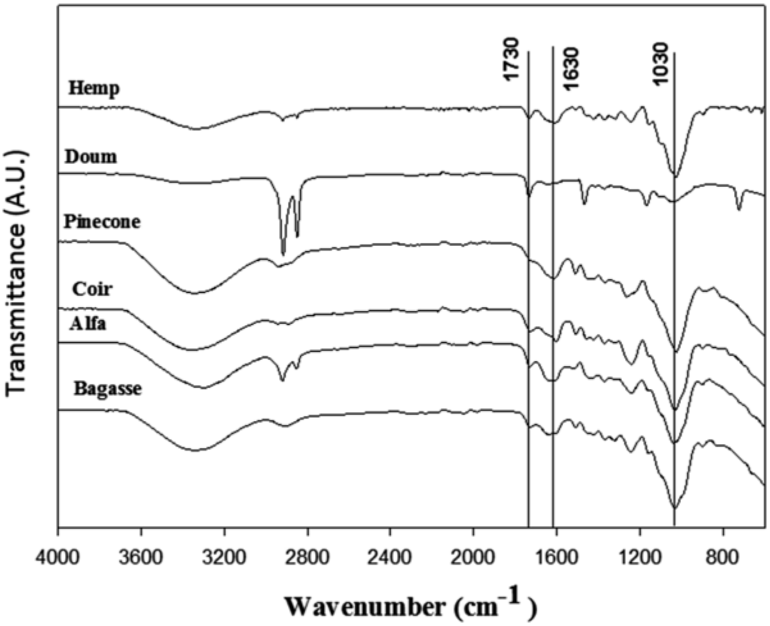

Fig. 14.1 FTIR spectra of raw Alfa, Doum, Coir, Pinecone, Bagasse and Hemp fibers

cross-section and along the fiber. It's clearly observed that the microfibrillar shape is tubular and the fiber section is circular; at high magnification a single fiber is composed of several microfibers. It was also shown that the fibers are twisted.

The natural fibers area subjected to degradation during composite processing. The thermal degradation of fibers (a critical feature for their application as filler or reinforcement) is reduced to a low level of hemicelluloses. The temperature degradation of fibers limits the choice of the matrix. The thermal decomposition of natural fibers was investigated by thermogravimetric analysis (TGA). Natural fibers were heated under air to 600 °C at a rate of 10 °C/min to provide the mass loss, decomposition temperature, and maximum decomposition peak.

The TGA curves of fibers (Hemp and Coir) generally show two major degradation temperature peaks, which are known as the two main-stage degradation of natural fibers, the first at range of 220–260 °C and the second at range of 430–460 °C (Fig. 14.3). The first shoulder peak is corresponding to the hemicelluloses degradation and the second shoulder peak is due to the cellulose and lignin degradation.

14.3 Processing Techniques for Polymer Composites

The process of implementation of composite materials is an important step that affects the final properties of the material. The process of implementation of material composites (thermoplastic matrix reinforced with natural fibers) is carried out

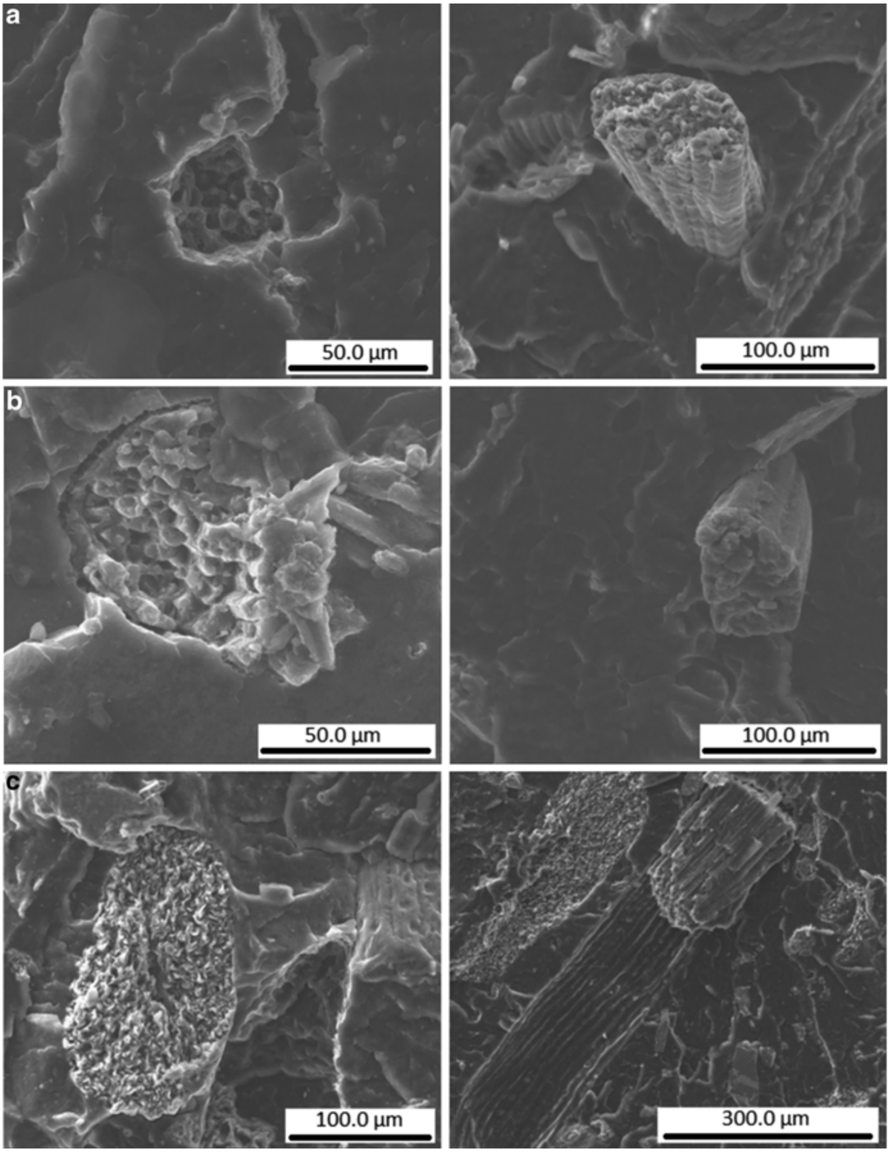

Fig. 14.2 (**a**) SEM micrographs of Alfa fibers. (**b**) SEM micrographs of Doum fibers. (**c**) SEM micrographs of Coir fibers. (**d**) SEM micrographs of Bagasse fibers. (**e**) SEM micrographs of Hemp fibers. (**f**) SEM micrographs of Pine cone fibers

using the extrusion process, which allows the mixture of the two components at molten state. Melt blending processing is considered the method most used to compound material composites (Arrakhiz et al. 2013a), it's more economical, flexible for formulation (Abu-Zahra et al. 2010), and compatible with industrial practice (Kannan et al. 2010). The conditions of implementation are selected so as to

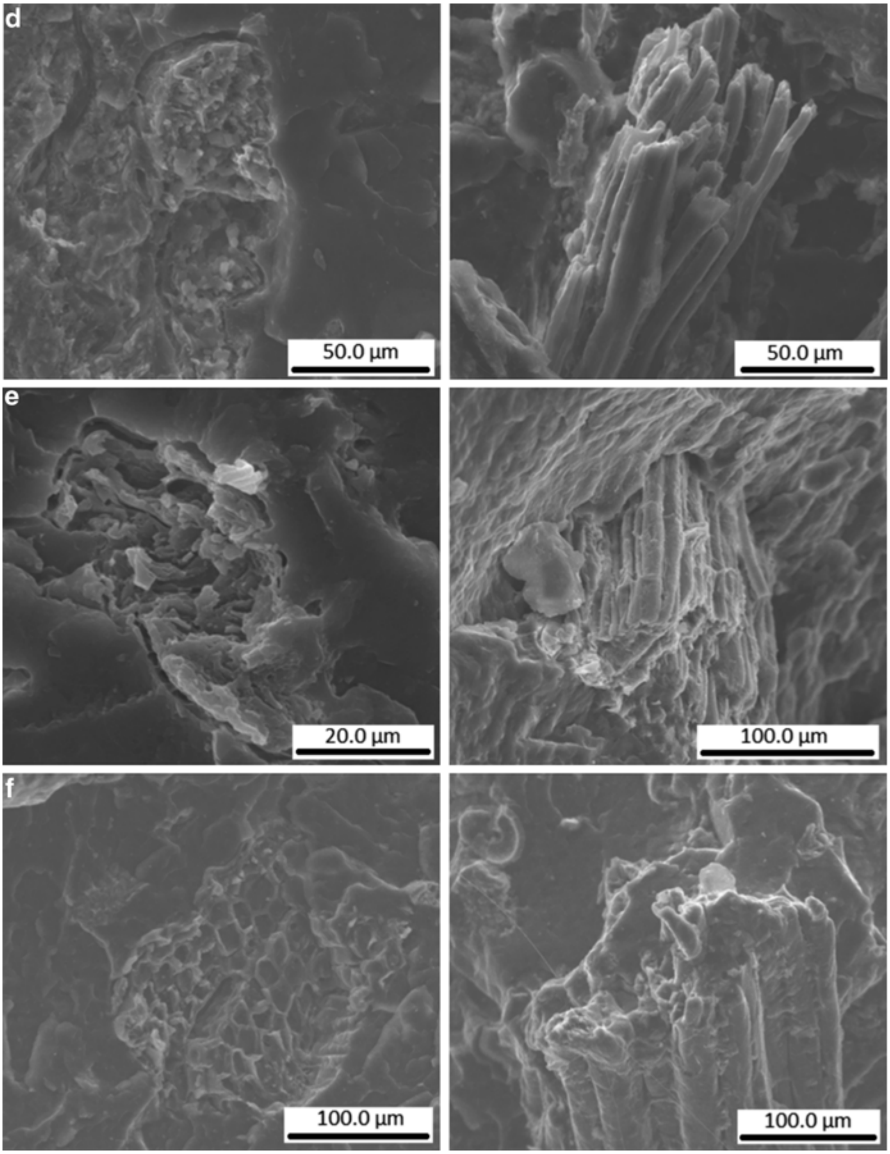

Fig. 14.2 (continued)

homogenize the fiber/matrix mixture and ensure a good dispersion/distribution of fibers in the matrix, without degradation or fiber polymer matrix.

Extrusion is a process of forming material, but also for the continuous production of final or semifinal products (compound as granules, films, plates, tubes, insulation of cables....) within a system screw/barrel called extruder (Qaiss and Bousmina 2011). The term "extrusion" characterizes the processes constituting to force a material to

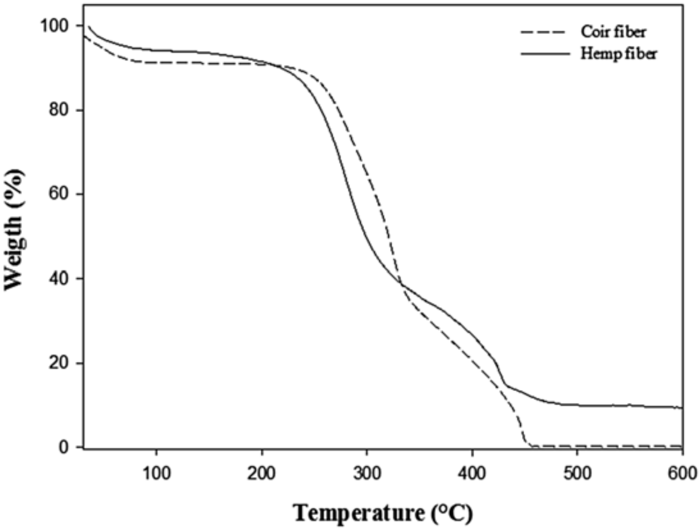

Fig. 14.3 TGA curves of coir and Hemp fibers

flow through an orifice (the dye). The matrix is then carried under the action of pressure obtained by screws. Polymers in the form of powders and pellets are drawn from a hopper of the gap between a rotating screw and heated barrel. They are carried forward, compacted, and the melt is convoyed through the dye before solidification by external cooling. Extrusion process offers also, the possibility to add support for the new polymer composites.

A various concentration of natural fibers (0, 5, 10, 15, 20, 25, 30 wt.%) were blended simultaneously with thermoplastic polymer using a single or twin screw extruder operating at 125 rpm screw for the polymer and 40 rpm for natural fibers . The extruder barrel (seven zones), was heated from hopper to dye in the case of natural fibers at optimized temperatures (respectively to 200, 200, 200, 180,180,180, and 180 °C) (Qaiss et al. 2012, 2013). The fibers are fed from the third heating zone to minimize the residence time of fibers and avoid fibers degradation. The composites (cordon out of the extruder) were cooled in a water bath and then pelletized into granules of 2 mm length. The final shapes of the specimens for various characterization analyses were molded in an injection molding machine. The optimized temperature of injection press barrel was fixed at 200 and 180 °C for nozzle, the mold temperature was fixed at 45 °C (Arrakhiz et al. 2013a).

14.4 Problematic

The components of lignocellulosic fibers include water soluble substances, hemicelluloses, cellulose, pectin, lignin, and waxes. Cellulose is a semicrystalline polysaccharide, the large amount of hydroxyl group in cellulose gives natural fibers

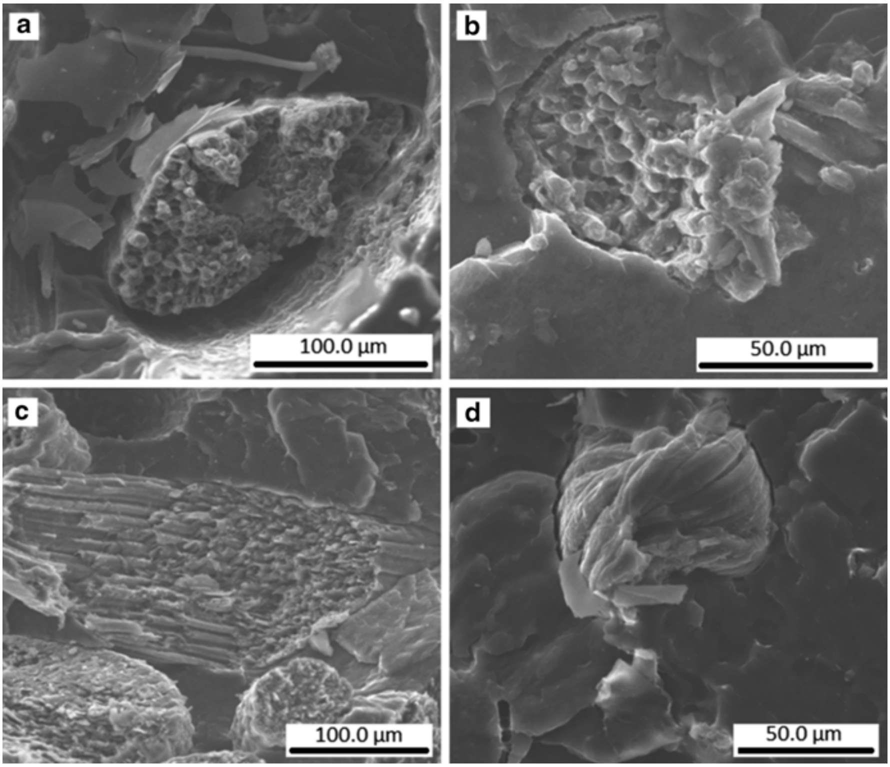

Fig. 14.4 SEM micrographs of composites: (**a**) PP/Alfa, (**b**) PP/Doum, (**c**) PP/Coir, (**d**) PP/Bagasse

the hydrophilic character; when used to the hydrophobic matrix, the result is an incompatibility (poor adhesion) between matrix and fibers and poor resistance to moisture absorption (Yang et al. 2007). The strength of the interface adhesion (fiber/matrix) depends on the degree of mechanical, chemical and electrostatic bonding, and level of interdiffusion between the matrix and fibers. The compatibility between the two components can be achieved by physical and chemical modification of the fibers and polymer surface, or by use of coupling agents and compatibilizers. Figure 14.4 shows SEM image of fractured surfaces of composite without coupling agent. It can be seen clearly a decohesion zones fiber/matrix. This is a clear indication of the poor adhesion between fibers and the matrix.

Alkali treatment was the standard chemical modification of fibers surface. The fibers are alkali washed using sodium hydroxide to remove amorphous materials from the fibers surface such as waxes, pectin, and other non-cellulosic components. Figure 14.5 shows the FTIR spectrum of hemp fibers, as example, before and after alkali treatment. It was observed in the Fig. 14.5 that a disappearance of the peaks around 1,730 and 1,230 cm^{-1}, which correspond respectively to the carboxylic

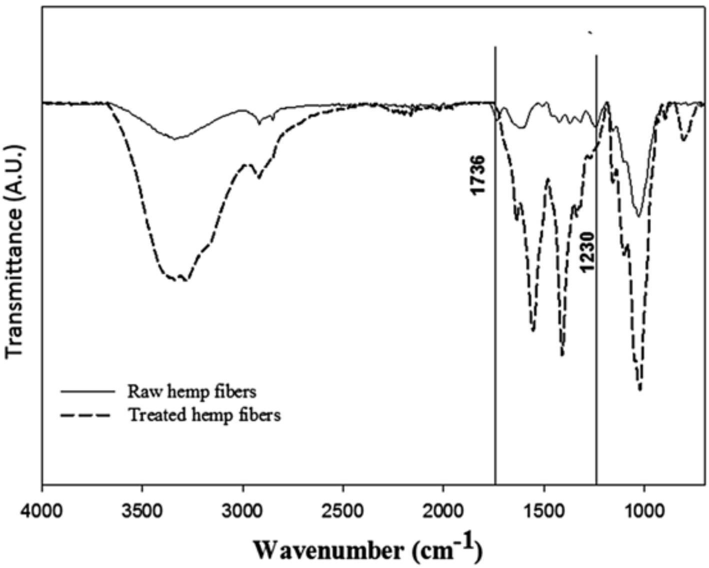

Fig. 14.5 FTIR spectra of Hemp fiber before and after an alkali treatment

ester in pectin and to the C–O stretching in lignin, respectively. The chemical treatment used has eliminated pectin and waxes in the fibers and also it has reduced lignin rates in the fibers surface.

14.5 Mechanical Properties

The mechanical properties of material composites based on natural fibers as reinforcement depends strongly on the fibers morphology, fibers concentration, dispersion/distribution of fiber into matrix, and interfacial adhesion between fiber and matrix. A good dispersion and distribution of the fibers into the matrix can be achieved by effective compounding of the various components and by a suitable compounding process. Scanning electron microscopy (SEM) was used to evaluate fibers' dispersion/distribution in the matrix and to show the fibrillose morphology of the fiber's into matrix. Figure 14.6 shows SEM images of composites after cryo-fracture, at 30 wt.% of fibers content (Alfa, Doum, Pine cone, Hemp, Coir and Bagasse fibers). It can be observed that the surface morphology of the different composite systems show the good distribution (low magnification) and dispersion (high magnification) of fibers on the matrix, which indicates despite the adhesion problem at the interface, the fibers are well distributed and dispersed in the polymeric matrix. It was also observed the absence of agglomeration. This is a result of the compounding process which ensures the good dispersion/distribution of fibers in polymer matrix.

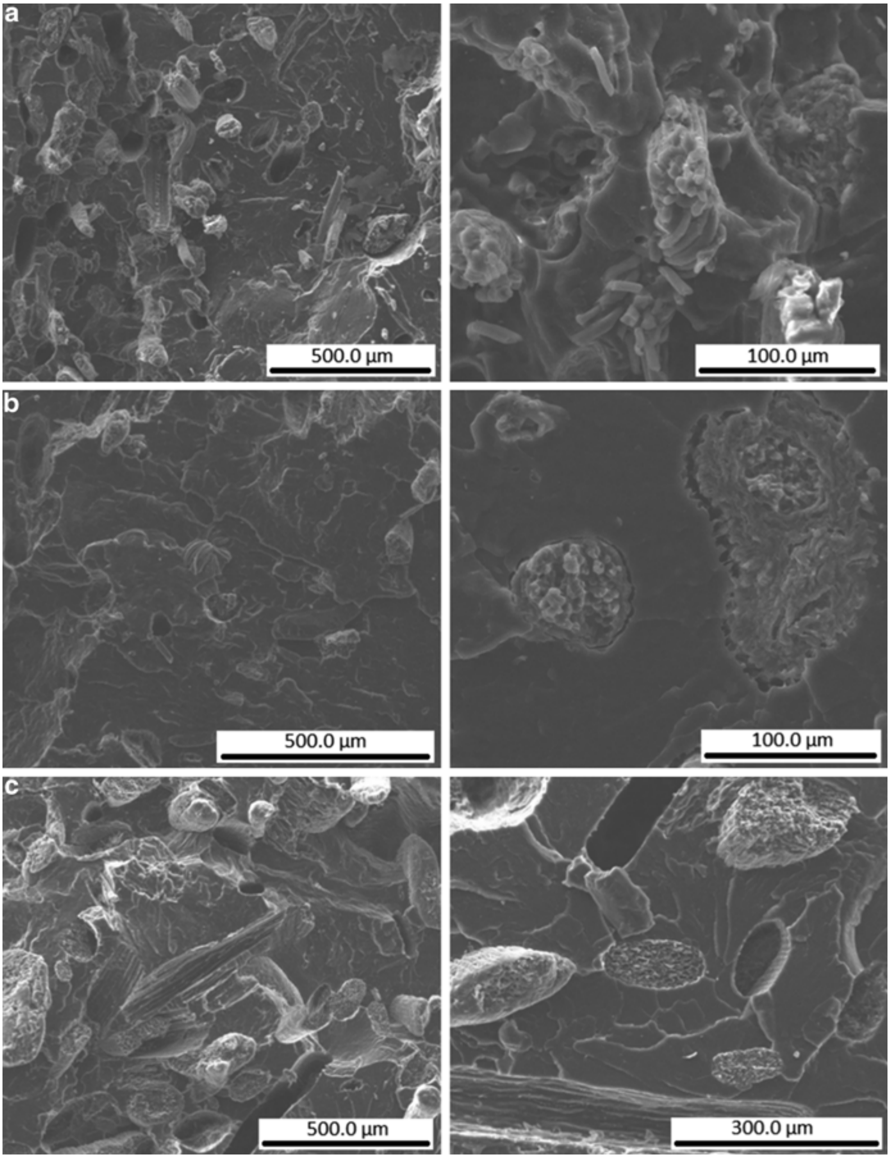

Fig. 14.6 (**a**) SEM images of the fracture surface of PP/Alfa composites at different magnification. (**b**) SEM images of the fracture surface of PP/Doum composites at different magnification. (**c**) SEM images of the fracture surface of PP/Coir composites at different magnification. (**d**) SEM images of the fracture surface of PP/Bagasse composites at different magnification. (**e**) SEM images of the fracture surface of PP/Pine cone composites at different magnification

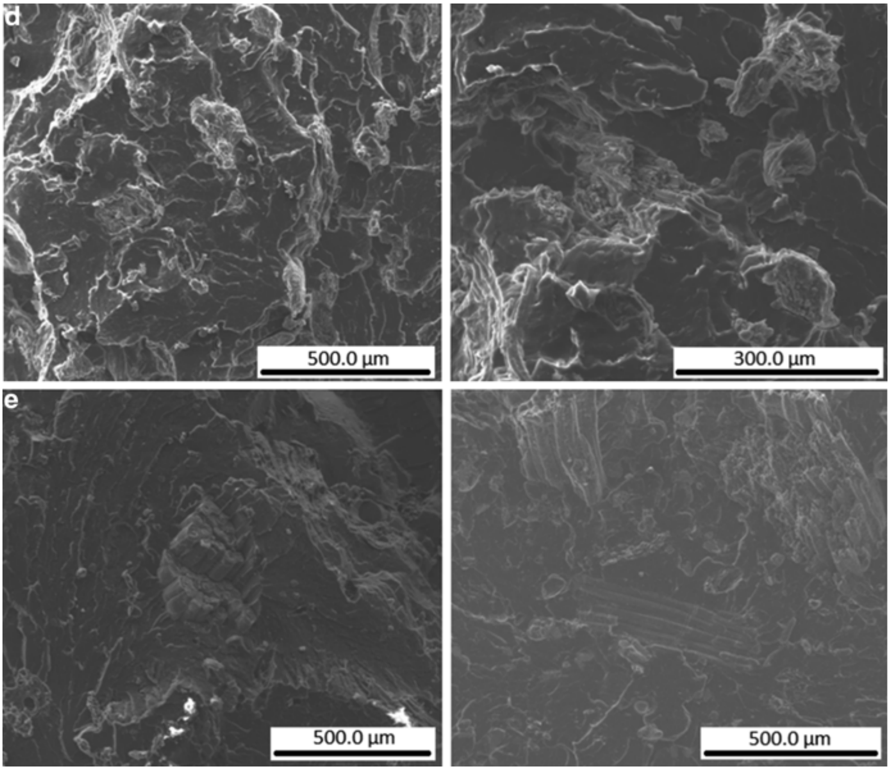

Fig. 14.6 (continued)

14.5.1 Tensile Properties

The mechanical properties for composite materials are carried out from tensile, flexural, compression, torsion, and dynamic analysis. The uniaxial tensile test is the most frequent mechanical test used for the characterization of materials. The tensile test is used to determine the following characteristics: The Young's modulus or stiffness modulus (E in MPa), the tensile strength or maximum stress (reached during the stress) (σ_M in MPa), the strain at yield (ε_M in mm/mm), and the plastic energy. Young modulus is determinated from the stress vs. strain curve, between 0.0025 and 0.005 % strain, according to ISO 527-1 (2012), which is seen to be linear for these tapes.

The mechanical properties, namely tensile and rheological properties of composites, were carried out to evaluate the effect of addition of natural fibers into the polymer matrix (PP). All tensile tests were performed at a crosshead speed of 3 mm/min using a 5 kN load.

Before compounding fibers with a polypropylene matrix at different amounts (5, 10, 15, 20, 25 wt.%), the fibers are alkali treated using sodium hydroxide to remove the amorphous materials (pectin, waxes, and non-cellulosic components) from the fibers' surface. Figure 14.7 illustrates the effects of addition of fibers (fiber source and fiber content) on the tensile properties (Young's modulus and tensile strength) of a polypropylene matrix.

Addition of fibers (Alfa, Doum, Pine cone, Hemp, Coir or Sugarcane Bagasse) to matrix yields a higher young's modulus compared to neat matrix (PP) (Fig. 14.7). It was observed for all types of fibers, a linear increase in the Young's modulus with increasing fiber content. Figure 14.7 shows the tensile strength variation as function of fiber content and fiber type. The trend of tensile strength shows a decrease with increasing fiber content. This behavior is quite characteristic of short-fiber reinforced composites. The tensile strength values of PP/Pine cone, PP/Hemp, and PP/Doum composites are higher than those of other composites; this result can be related to the morphological properties, chemical composition, and microfibrillar angle of each fiber.

14.6 Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) was performed on the natural fiber composites in order to study and establish the viscoelastic behavior. The viscoelasticity of materials is determined by applying a sinusoidal strain and measuring the stress as response (Essabir et al. 2013b). Measures of viscoelasticity can be expressed by the equation of strain and stress:

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

where ε_0 is the strain amplitude, ω is the angular frequency and δ is the angular shift between stress and strain.

The dynamic modulus or complex modulus (E^*) is given by equation:

$$E^* = \sqrt{E'^2 + E''^2}$$

where E' is the elastic modulus and E'' the viscous modulus. E' and E'' are expressed in the equation:

$$E' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\cos\delta$$

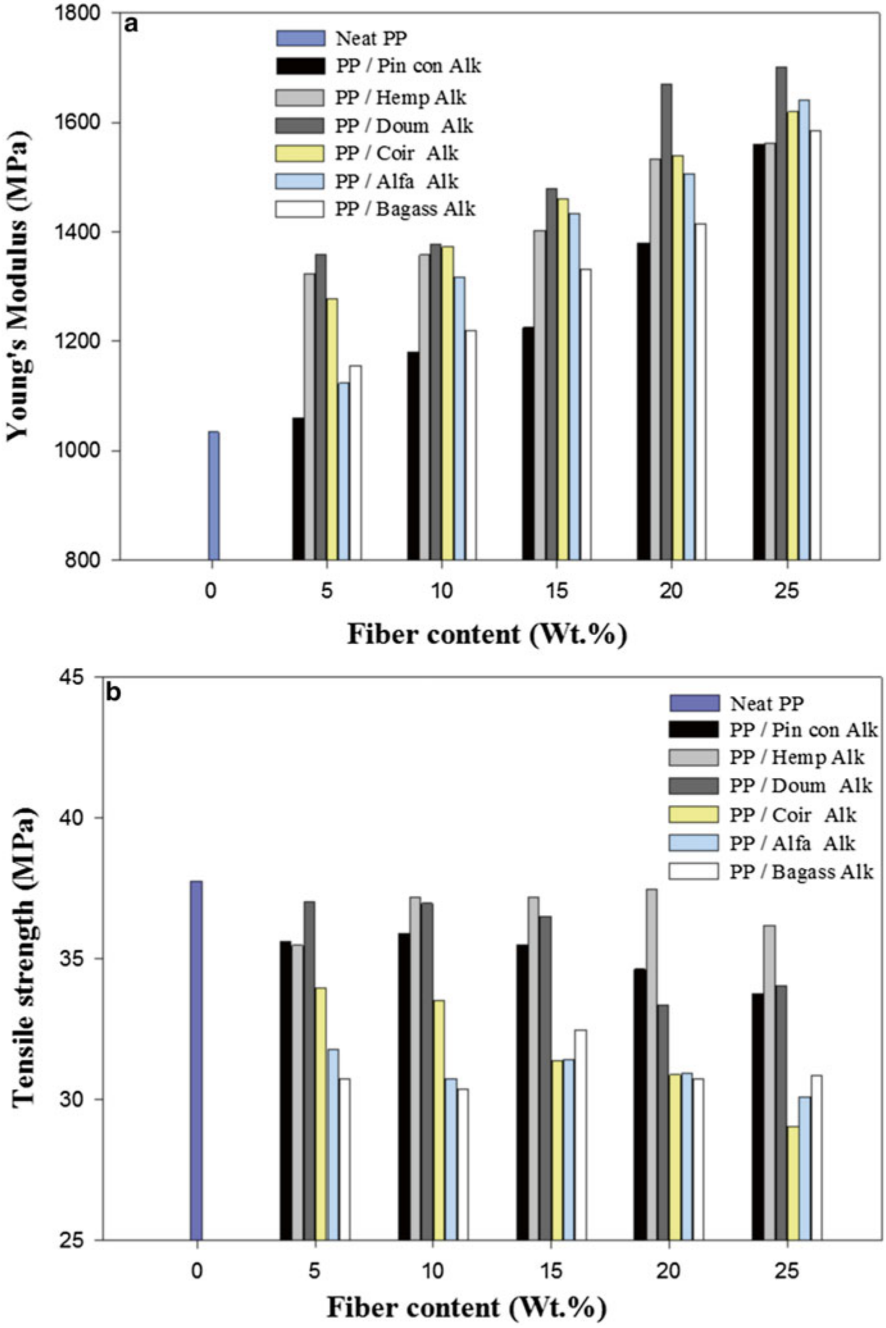

Fig. 14.7 Tensile properties of composites: (**a**) Young's modulus of composites, (**b**) tensile strength of composites

$$E'' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\sin\delta$$

where ε_0, σ_0, and ω represent respectively the amplitude of the deformation cycle, the amplitude of the stress cycle, and the pulsation in rad/s.

The elastic modulus (storage modulus), is proportional to the energy stored by cycle (elastic behavior). However viscous modulus (loss modulus), represent dissipated energy by cycle (viscous behavior). The Loss factor is the relationship between the loss modulus and storage modulus and is expressed by equation:

$$\tan\delta = E'' / E'$$

In dynamic mode, the mechanical properties of the material depend on the deformation of the excitation frequency and temperature.

The Dynamic mechanical thermal tests were performed on a rheometer Solid Analysis (RSA) operating with a dual cantilever configuration. Samples dimension were 45 mm in length, 5.5 mm in width, and 2 mm in thickness. A strain sweep test was carried out and strain from this linear regime was 0.002. After a dynamic frequency sweep tests were performed using this strain amplitude (0.002) between 0.015 and 15 Hz, finally temperature sweep tests were ranged from 30 to 120 °C with a heating rate at 5 °C/min, frequency and strain were fixed at 1 Hz and 0.002 respectively.

Figure 14.8 shows the frequencies sweep tests, complex modulus (E^*), and mechanical loss factor ($\tan\delta$), for PP/Doum composites. It was observed that the complex modulus increases with increases in frequency. This behavior is due to the molecular time response. At higher frequencies have not enough time to relax and attend permanent deformation. It was also observed that the loss factor ($\tan\delta$) was less sensitive to changes related to the fibers' content. Generally a change in the $\tan\delta$ curve indicates a relaxation process which is associated to the movement of molecular chains within the polymer structure.

The temperature at which the $\tan\delta$ peak occurs is commonly known as the glass transition temperature (T_g). The glass temperature (T_g) was determined from the derivative curves of $\tan\delta$ vs. temperature (Fig. 14.8). Figure 14.8 shows the T_g variation as function of Doum fibers content in PP matrix. It was observed that the addition of fiber improves the T_g of composites from 76.6 °C for neat PP to 90.25 °C for composite with 30 wt.% fiber content . These results show a gain of gain of 17.8 % in T_g.

14.7 Interface Fiber/Matrix

14.7.1 Techniques to Improve the Interface Adhesion

The biggest challenge in developing of material composites based on natural fibers is the incompatibility between the hydrophilic fibers and the hydrophobic matrix. This incompatibility leads to a poor homogenization between fibers and the

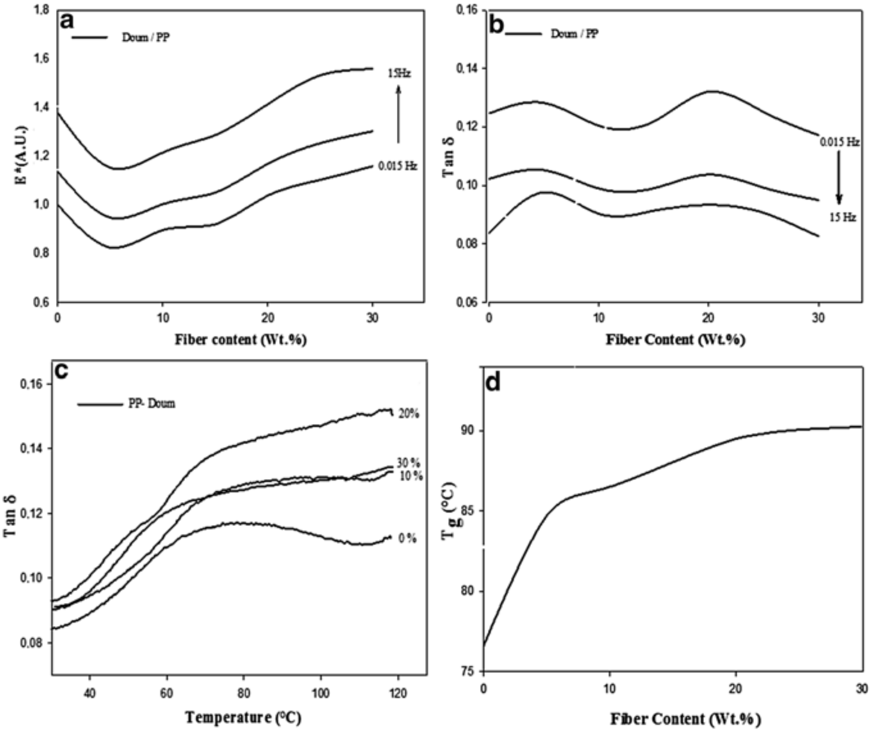

Fig. 14.8 PP/doum composites (**a**) complex modulus (*E**) vs. frequency and of fibers content, and (**b**) loss factor (tan δ) vs. frequency and of fibers content, (**c**) loss factor (tan δ) vs. temperature, (**d**) Glass temperature (T_g) vs. fiber content

polymer chains (Nazrul et al. 2010); as a result, a poor adhesion between both compounds is often seen (Pickering et al. 2007; Ku et al. 2011). Most studies refer to the modification of the interface of natural fibers or polymer matrix, to ensure compatibility between the fiber and the matrix (Huu Nam et al. 2011; Arrakhiz et al. 2012a). The treatment parameters used is a factor that influences the properties and characteristics of the result composites. Therefore, appropriate treatment techniques and parameters must be carefully selected to produce an optimal composite product. These techniques can be divided into two categories: physical and chemical methods.

The physical treatments do not alter the chemical composition of the cellulose fiber and they are expensive (Belgacem et al. 1995). Stretching, calendering, thermal treatments are considered as an example of physical treatment (Belgacem et al. 1996; Liu et al. 1998). Other types of physical treatment are also found in the literature as the electric discharge (corona, cold plasma). For example the electrical discharge treatment can modify the fiber surface from hydrophilic to hydrophobic by changing the surface energy (Belgacem and Gandini 2005; Kato et al. 1999).

The use of chemical treatments is for removing the non-cellulosic components in the fiber surface or for adding functional groups to increase connection with

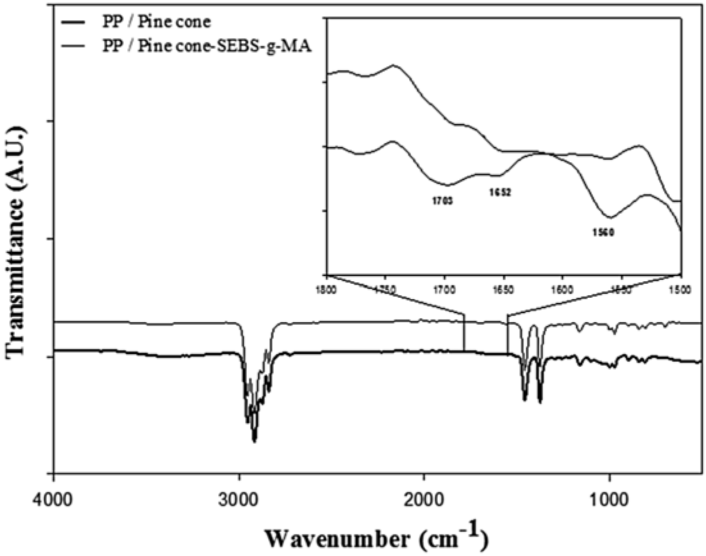

Fig. 14.9 FTIR spectra of PP/Pinecone composite with compatibilizer and without compatibilizer

polymer chains. Several chemical techniques were considered to improve the adhesion interfacial such as, grafting compatibilizer groups, addition of a coupling agent or cleaning the fiber's surface. The alkali treatment is one of the standard chemical treatments using sodium hydroxide to remove amorphous and non-cellulosic components from the fibers' surface. The estherification or etherification of the hydroxyl groups found on the fibers' surface is a possible technique to graft a functional group (Arrakhiz et al. 2012a). The use of maleic anhydride modified polypropylene (MAPP) as a coupling agent is another pathway to enhance the interface adhesion between fibers and matrix (Arrakhiz et al. 2012c). Fiber surface treatment may also increase the strength of the fiber; reduce the water absorption and surface tension between fiber and matrix.

The use of maleic anhydride grafted polypropylene; SEBS-*g*-MA as compatibilizer between fibers and matrix improves the water resistance of fibers and enhance the wettability of fibers in the polymer matrix, also the use of SEBS-*g*-MA create a strong ester bonds between polymer and hydroxyl groups of fibers. Figure 14.9 shows the FTIR curves of PP/Pine cone composites with and without coupling agent. The peaks at 1,703, 1,652, and 1,560 cm^{-1} were observed after addition of compatibilizers, these peaks are the main characteristic peaks of ester bonds formed. These formed ester bonds between matrix and hydroxyl groups of fibers enhance the thermal and mechanical properties of composites.

SEM micrographs analysis of fracture surfaces of composites with coupling agent (Fig. 14.10) confirm that the addition of coupling agent improves the interface adhesion between doum fibers by absence of decohesion zones (pull out fibers), and reduction of the fiber/fiber contact.

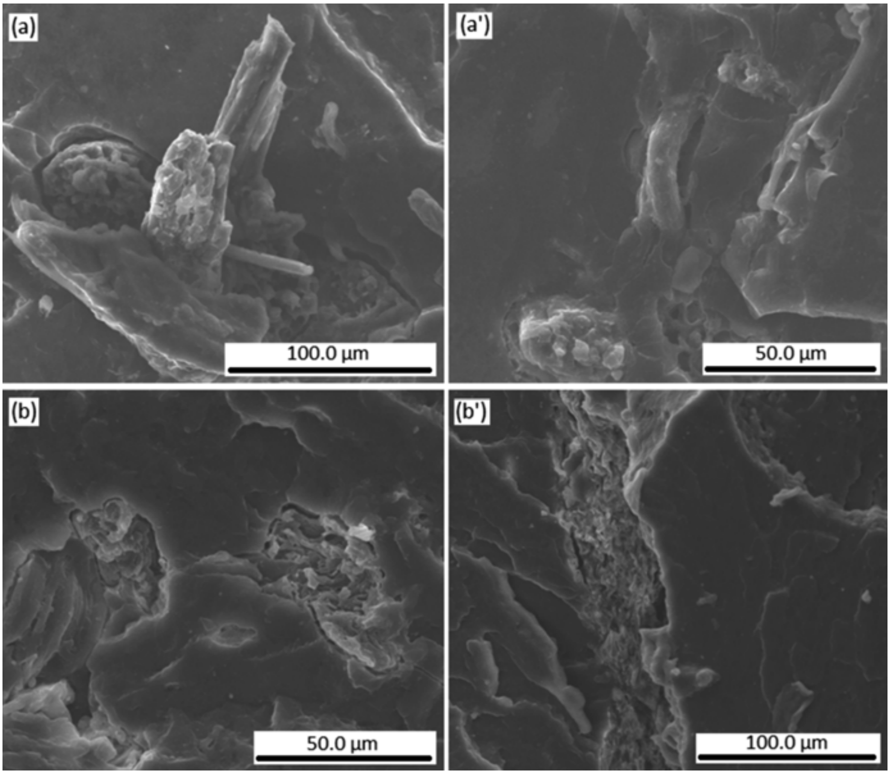

Fig. 14.10 SEM micrographs: (**a**) PP/Doum, (**b**) PP/Hemp

Table 14.1 Comparative DTG results for two fibers and their composites with and without compatibilizer (SEBS-g-MA)

				PP/fiber (wt.%)						PP-SEBS-g-MA/fiber (wt.%)					
	Neat	Raw fibers		Hemp			Doum			Hemp			Doum		
	PP	Hemp	Doum	5	15	25	10	20	30	5	15	25	10	20	30
T_{max} (°C)	351	283/426	320/420	294	364	376	360	367	380	334	344	391	363	385	400

The comparative thermal analysis between the composites with compatibilizer and without compatibilizer is found in the literature Arrakhiz et al. (2012a, b, c). Table 14.1 illustrates the comparative thermal analysis of Doum and Hemp fibers and their composites with and without compatibilizer. It was seen that the composites compatibilized exhibit a higher temperature degradation than composites without compatibilizer.

The improvement in the fiber-matrix adhesion enhances the mechanical properties of composites (Elkhaoulani et al. 2013). Figure 14.11 shows the comparative tensile properties of the fibers as Pine cone, hemp and Doum. Addition of

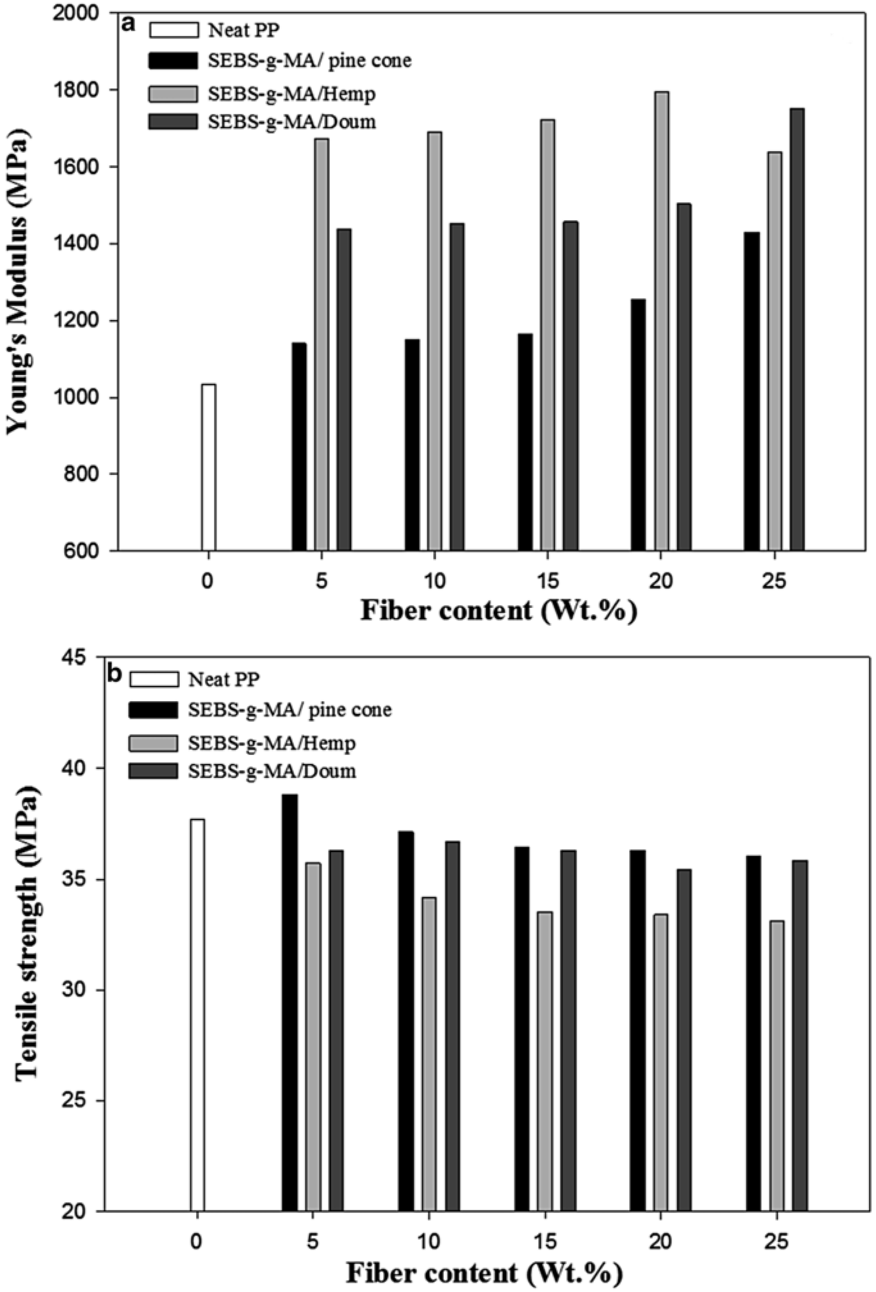

Fig. 14.11 Tensile properties of compatibilized composites: (**a**) Young's modulus of composites, (**b**) tensile strength of composites

Table 14.2 Young's modulus and tensile strength of HDPE/Coir, 20 wt.% and PP/Alfa, 20 wt.% composites made with the various chemically treated fibers

Matrix	Fibers treated		Young's modulus (MPa)	Tensile strength (MPa)
HDPE	Fiber	Chemical treatment		
	Coir	Raw fiber	1,190	24.8
		C12	1,460	26.3
		NaOH	1,300	23.5
		Silane	1,145	29
PP	Alfa	Raw fiber	1,436	29.8
		NaOH	1,838	32
		C12	1,554	32.2
		Palmitic acid *N*-succinimidyl	2,067	32.4

fibers increases Young's modulus, until it reached one maximum value at 25 wt.% (for all composites). On the other hand, the tensile strength of various composites compatibilized is stabilized at a high value, except PP/hemp which shows a slight decrease. The tensile strength properties are higher in the composites compatibilized than composites without compatibilizer, this is due to the good interfacial adhesion (fibers/matrix). The maleic anhydride molecules grafted to PP construct a strong ester bonds with the hydroxyl groups (OH) present on the fibers' surface (Elkhaoulani et al. 2013).

A good dispersion and interfacial adhesion between the matrix and fibers are both critical factors for the resulting composites to achieve improved mechanical properties. Chemical treatment of the fibers' surface was used to improve interfacial adhesion in the composite. Table 14.2 illustrates influence of chemical treatments and fictionalization on two composite systems with different fibers (Alfa and Coir), at 20 wt.%, and thermoplastics matrix (PP and HDPE). The chemical modifications used in this work, namely NaOH, etherification (C_{12} (Dodecane bromide)), Estherification (Palmitic acid *N*-succinimidyl), and silane (3-(trimethoxysilyl) propylamine) exhibit a different interaction mechanism with both fibers and polymer matrices.

The results show that chemical treatments improve the mechanical thermal proprieties of fibers, leading to improvement in properties of composites reinforced with these treated fibers. Alkaline treatment shows higher values in terms of young's modulus, also composites with fibers fictionalized with silane and C_{12} shows a significant tensile modulus when compared to raw fibers reinforced polymer.

14.8 Conclusions and Future Perspective

The improvement of mechanical and thermal properties of polymeric matrix by use of natural fibers promotes the application of resulted materials in several fields such as building materials, automotive parts, packaging, and biomedical applications.

The extrusion and injection molding techniques, which are the most used process, the choice of polymeric matrix is mandatory with processing temperature less than 200 °C to avoid the thermal degradation of the natural fiber, this constitutes the limitation of the use of the natural fibers, also the percentage of the fibers cannot exceed 25 %. More than this amount induces the processing problem and it's more difficult to wet all fibers. As second step of the use of this kind of fibers is the extraction of microfibril and nanocrystalline cellulose which can enhance the thermal and mechanical properties at small amount and the use of the matrix with relatively high processing temperature.

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Chapter 15
Lignocellulosic Materials as the Potential Source of Catalyst

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_15, © Springer International Publishing Switzerland 2014

Abstract The lignocellulosic material is most prevalently used in the production of agro based activated carbons. These catalysts have been established as benign alternatives to the heterogeneous alkaline catalysts and the unrecyclable-homogeneous acid and base catalysts heterogeneous catalyst have been considered a viable alternative since they eliminate the usual difficulties related to homogenous catalyst and can be reused several times and hence solved many problems. Biomass derived solid acid catalyst is the renewable source of energy whereas homogeneous catalyst are non-renewable and also contribute to the environmental degradation as their synthesis and production process are hazardous. The thermal inertness, good mechanical and thermal stability properties make the carbon-based solid acids as the ideal catalysts for many reactions. Heterogeneous catalyst associated with high water tolerance, high selectivity, and high activity properties. Sulfonated carbons are the most promising solid acids. In the coming future need and the demand of more biodiesel is expected to increase, this encourages to consider the use of non-edible oil seeds as reliable as a sustainable feedstock for biofuel production. This work is aimed to give an overview on the production of solid acid catalyst and the potential of non-edible oil and cake waste as an alternative feedstock for the heterogeneous acid catalyst. This study also reviewed current literature on the activities and advantages of solid acid catalysts used in biodiesel production.

Keywords Non-edible oil • Feedstocks • Activated carbon • Sulfonated activated carbon • Biodiesel

15.1 Introduction

Major issues and the priorities in the present situation are the climate change and energy security in light of the environmental problems causing increased production of bio-catalyst as important source of solid acid catalyst, in both developed and developing countries. At present the prime focus of the scientists and the researchers is the introduction of eco-friendly Green Technology. A solid acid catalyst must have the possibility to possess high activity and stability in the requirement for its utilization in low cost, renewable, and biodegradable biodiesel production. About more than 300 types of trees species are classified as oil bearing seeds and are potential source for biocatalysts generation (Subramanian et al. 2005).

Most usually all carbon-containing lignocellulosic materials are the promising materials for activated carbon preparation (Uçar et al. 2009) although the coal is the important precursor of the activated carbon but the cost of production is high, the main concept is to consider cheap and efficient materials for the production of activated carbon.

Non-edible feedstocks are easily available and are economically feasible with respect to edible feedstock. In comparison to edible feedstock, non-edible like rubber seed, jatropha, sea mango are not suitable for human consumption because of its toxic and anti-nutritional components or constituent (Kumar and Sharma 2011). In contemporary research the main commodity sources for catalyst production from the non-edible discarded parts, different agricultural biomass based wastes and raw materials derived from plant species have been presented in Table 15.1. Moreover the cost of plantation for edible oil crops is higher than the non-edible oil crops, with an

Table 15.1 Main commodity sources for catalyst production

Non-edible discarded parts	Agricultural biomass based wastes	Raw materials from plant species
Vineyard shoot	Olive seed oil cake	Esparto grass
Cassava peel	Industrial waste lignin	Tobacco residues
Tunisian deposit lignin	Safflower species seed cake	*Euphorbia rigida*
Olive mill waste water	Oil palm shell biomass	*Zizania latifolia*
Pomegranate seeds	Jordanian olive cake waste	*Ramulus mori*
Rice husks	Bamboo waste	*Mesua ferea* L.
Jatropha hull	Tea factory waste	Flamboyant (*Delonix regia*)
Coconut shell	Wool waste	*Prunus domestica* and *Jacaranda*
Grape seed	Marine maexoalgal biomass	*Eucalyptus camaldulensis* wood
Date pit	Langsat empty fruit bunch waste	*Arundo donaxcane*
Walnut shell	–	*Posidonia oceanica* (L.) dead leaves
Cherry stones	–	
Corn cob		
Chest nut wood		

exemption to palm oil plant (Kumar and Sharma 2011). Apprehension regarding environmental safety has improved over the years from a universal viewpoint. Nowadays rapidly fluctuating technologies, industrial goods and practices create waste that could impend towards public health and the environment (Shen 1995). Agricultural waste biomass presently one of the most challenging issue, which gained widespread serious attention from the past decades (Andrew et al. 2003). During the manufacture process of the olive in mills, olive mill waste water is produced in large quantities, this waste water can be used as raw materials to yield valuable product by both physical and chemical activation (Moreno-Castilla et al. 2001). Several variety of agricultural by-products (lignocellulosics) including peach stones (Molina-Sabio et al. 1995), date stones (Girgis and El-Hendawy 2002) and (Haimour and Emeish 2006), waste apple pulp in cider production (Suarez-Garcia et al. 2002), rice husks (Chuah et al. 2005), pistachio-nut shells (Yang and Lua 2006), and grain sorghum (Diao et al. 2002) have been investigated as activated carbon precursors. However, waste cakes received much less attention as a precursor lignocellulosic material for activated carbon production (Cimino et al. 2005; Baçaoui et al. 2001). Agricultural cake wastes are generated in each growing season like olive cake, some of them are used in boilers, some are dumped in the environment, and there they release harmful and toxic compounds by the action of fungi.

15.2 Potential Non-edible Feedstock

Coal, wood, and coconut shell are the most extensively used carbonaceous materials precursors for the production of activated carbons on industrial scale, although they are expensive and are often imported thus it is important to find cheap feed stocks for the activated carbon preparation and its several application in industry.

The agricultural wastes pose a disposal problem and affecting the country's very limited water resources (Aljundi and Jarrah 2008). Thus wastes obtained from

Table 15.2 Preparation of activated carbons using agricultural wastes as raw material (Diasa et al. 2007, with permission)

Raw material	Activation agent		Relevant issues	References
	ChA	PhA		
Vineyard shoot	H_3PO_4		Well-developed pore structure. In general, AC were better when raw material was impregnated and heated at intermediate temperatures	Corcho-Corral et al. (2006)
Cassava peel	KOH		Activation time showed no significant effect on the pore structure. Maximum surface area and pore volume were obtained using: impregnation ratio of 5:2 and carbonization temperature of 750 °C	Sudaryanto et al. (2006)
Olive pit	KOH		PAC adsorption capacity was the highest at 75 % (w/w) KOH	Martínez et al. (2006)
Olive cake		Steam	The best AC was obtained activating for 68 min at 1,095 K	Baçaoui et al. (2001)

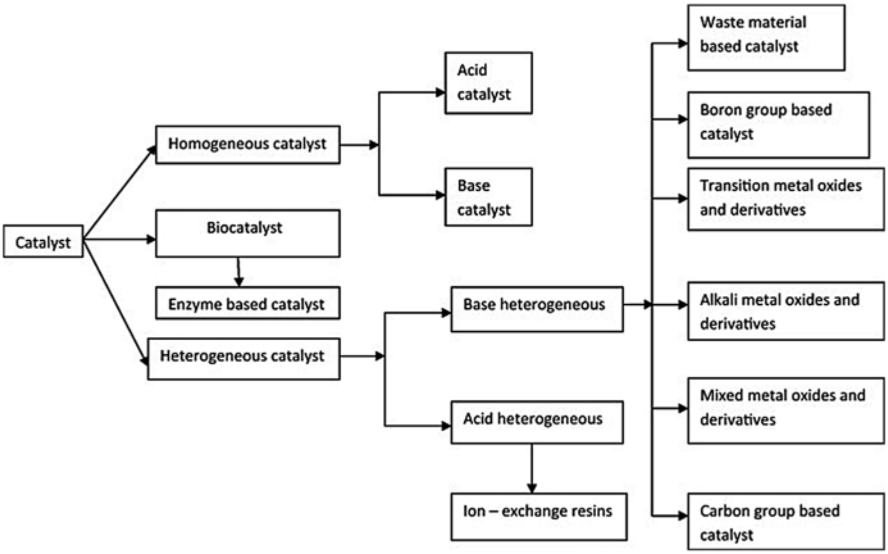

Fig. 15.1 Classification of catalyst (Chouhan and Sarma 2011, with permission)

agricultural sector are considered to be very important feedstock because of two important facts: they are low-cost materials and are renewable source of energy (Stavropoulos and Zabaniotou 2005). Both conventional (from agriculture and wood industry) and non-conventional (from municipal and industrial activities) wastes can be used to prepare AC. Table 15.2 clearly depicted the activated carbons preparation using agricultural wastes as raw material, physical or chemical activation can be used to prepare high surface areas activated carbon catalyst (Diasa et al. 2007). Catalysts can be generally classified based on several studies and research into homogeneous, heterogeneous, and biocatalysts (Chouhan and Sarma 2011) and their sub classification can be represented in the Fig. 15.1.

15.3 Homogeneous and Heterogeneous Catalyst

The rate of a chemical reaction changes due to the participation of heterogeneous catalyst. The product generally desorbs from the surface of the catalyst and diffuses away after the completion of reaction. The catalytic site determined the surface area of the catalyst and hence it is very critical and important. Adsorption and desorption are the two phenomena associated with the heterogeneous catalysts functions. The two processes help in the reaction of molecules to make them attract and attach to one another. Homogeneous catalysts are in the same phase as the reactants. When catalysis in a single liquid phases this type of catalyst is called homogeneous catalysis. Table 15.3 shows the comparison of main advantages/disadvantages of homogeneous vs. heterogeneous catalysts. A main disadvantage of homogeneous catalysts is the problem of their recovery from the reaction medium because of its hygroscopic nature along with its hazardous nature for the environment as compared to heterogeneous catalysts; this led to flourishing activity attempting to heterogenize homogeneous catalysts.

15.3.1 Types of Heterogeneous Catalyst

Homogeneous catalysts can be base catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) (Shimada et al. 2002), or acid catalysts, such as sulfuric, sulfonic, phosphoric, and hydrochloric acids (Georgogianni et al. 2009). Base catalysts possess higher catalytic efficiency, lower cost (Wen et al. 2010), and lower reaction temperature and pressure (Freedman et al. 1984) so they are preferred over acid catalysts. Heterogeneous catalysts also classified as acidic and basic. Such as sulfated metal oxide, heteropolyacids, acidic ion exchange resin, and sulfonated amorphous catalysts (Sakai et al. 2009) Ni–Ca-hydroxyapatite solid acid catalyst (Chakraborty and Das 2012) zinc oxide (ZnO), calcium oxide (CaO), strontium oxide (SrO) (Lam and Lee 2011), and Na/SiO_2 (Akbar et al. 2009) and (Yusuf et al. 2012). Researchers used calcined washed Rohu fish scale (*Labeo rohita*) as a heterogeneous base catalyst with a maximum biodiesel yield of 97.73 % and up to six reuses (Chakraborty et al. 2011). Fly-ash-supported CaO catalyst from eggshell waste shows a performance of 96.5 % for biodiesel production (Chakraborty et al. 2010). Some of the commonly used heterogeneous base catalysts are K/γ-Al_2O_3 catalyst (Alonso et al. 2007), $HTiO_2$ hydrotalcite catalyst (Barakos et al. 2008),

Table 15.3 Comparison of main advantages/disadvantages of homogeneous vs. heterogeneous catalysts

Property	Homogeneous	Heterogeneous
Catalyst recovery	Difficult and expensive	Easy and cheap
Thermal stability	Poor	Good
Selectivity	Excellent/good—single active site	Good/poor—multiple active sites

Ca and Zn mixed oxide (Ngamcharussrivichai et al. 2008), Al_2O_3 supported CaO and MgO catalysts (Umdu et al. 2009), alkaline earth metal oxides (Mootabadi et al. 2010), KF/Ca–Al, basic zeolites, alkali metal loaded alumina (Narasimharao et al. 2011). Basic heterogeneous catalysts have higher activity than acidic catalysts owing to shorter reaction times lower temperatures requirement in comparison to acidic catalyst.

15.4 Activated Carbon–Carbon-Based Acid Catalyst

An activated carbon is amorphous-based material and can be defined as "a material exhibiting a high degree of porosity and a prolonged inter-particulate surface area" (Bansal et al. 1988). A black solid substance resembling granular or powder charcoal regarded as activated carbon that possesses highly internal surface area, highly developed porosity, relatively high mechanical strength (Sahu et al. 2010). Activated carbon is the best example of heterogeneous acid catalyst. Adsorption and desorption are the process through which catalyst works. The two processes help in the reaction of molecules to make them attract and attach to one another. Activated carbon is best, effective adsorbents for the purification or recovery of different chemicals. Turnover frequency usually expresses the efficiency of a catalyst. It is a chemical reaction rate and not a rate constant. Equation 15.1 is used for calculating the TOF of a catalytic process (Boudart 1995)

$$\begin{aligned}\mathrm{TOF} = {} & \text{number of molecules of a given product} / \\ & (\text{number of active sites}) \times (\text{times})\end{aligned} \tag{15.1}$$

It is the best method of comparing the activities of different catalysts, however seldom used for the heterogeneous catalysts.

The ultimate product of an activation process of carbonaceous materials is activated carbon with carbon contents in the range 72–90 %. The activation sequence generally commences with an initial carbonization of the raw material to obtain samples with high carbon content (Daza et al. 1986). Any organic material that is rich in carbon content but with low content in inorganic matter can be used as precursor material for the preparation of activated carbon.

15.5 Chemical Activation

The physical and chemical activation are the two most common methods involved for the activated carbon preparation (Prauchner and Rodríguez-Reinoso 2012) though, mutual treatments might enhance the surface properties of the adsorbent, therefore increasing its adsorption capacity (Diasa et al. 2007). Chemical activation can be completed in a single step by carrying out thermal decomposition of raw material with chemical reagents. Dehydrating agents such as sulfuric acid (H_2SO_4), zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) and KCl (Al-Khalid 1995), and potassium hydroxide/carbonate (KOH/K_2CO_3) (Uçar et al. 2009) are the most widely used chemical agents.

Steam, nitrogen, or carbon dioxide are employed for mild oxidation of the carbonaceous matter in the physical activation. The process is usually involved two stages, carbonization stage is the first stage followed by an activation stage of the resulting char in the presence of activating agents (Haimour and Emeish 2006).

The physical activation occurs at relatively higher temperature in comparison to chemical activation, thus chemical activation results a perfect and improved pore development in the carbon structure. Generally chemical activation results higher carbon yields than physical ones (Sudaryanto et al. 2006). Table 15.4 shows the different raw materials, activating agent and their corresponding references that have been already studied. Catalytic properties of activated carbon such as acid site density and strength, crystalline structure, surface area, and pore volume greatly

Table 15.4 List of different raw materials and activating agents for preparation of activated carbon

Raw materials	Activation agent	References
Date stems	H_3PO_4	Hadoun et al. (2013)
Sour cherry stones	$ZnCl_2$	Angin (2014)
Walnut shells	$ZnCl_2$	Yang and Qiu (2010)
Rice husk ash	K_2CO_3	Liu et al. (2012)
Herb residues	$ZnCl_2$	Yang and Qiu (2011)
Esprato grass	CO_2	Nabais et al. (2013)
Grape seed	K_2CO_3, KOH	Okman et al. (2014)
Zizania caduciflora	H_3PO_4	Liu et al. (2014)
Sun flower seed oil residue	K_2CO_3	Foo and Hameed (2011a, b)
Bamboo	H_3PO_4	Liu et al. (2010)
Ramulus mori waste	Diazonium hydrogen phosphate	Tang et al. (2012)
Wools waste	H_3PO_4	Gao et al. (2013)
Acorn shell	$H_2O–CO_2$	Şahin and Saka (2013)
Albizia lebbeck seed pods	KOH	Ahmed and Theydan (2014)
Euphorbia rigida	$ZnCl_2$, K_2CO_3, NaOH, H_3PO_4	Kılıç et al. (2012)
Orange peel	K_2CO_3	Foo and Hameed (2012a, b, c)
Palm oil fronds	$KOH–CO_2$	Salman (2014)
Orange skin	CO_2	Rosas et al. (2010)
Rice bran	CO_2	Suzuki et al. (2007)
Flamboyant pods	NaOH	Vargas et al. (2011)
Almond shell	CO_2	Omri et al. (2013)
Jatropha curcas fruit shell	NaoH	Tongpoothorn et al. (2011)
Oil palm shell	$ZnCl_2$	Hesas (2013a, b)
Pistachio-nut shell	KOH	Foo and Hameed (2011a, b)
Mango steen shell	K_2CO_3	Chen et al. (2011)
Liquified Poplar bark	Steam	Zhang and Zhang (2013)

(continued)

Table 15.4 (continued)

Raw materials	Activation agent	References
Baggase fly ash	$ZnCl_2$, CO_2	Purnomo et al. (2011)
Rubber seed shell	Steam	Sun and Jiang (2010)
Cotton stalks	CO_2, steam-CO_2 mixture, $ZnCl_2$, H_2SO_4	Özdemir et al. (2011)
Durian shell	KOH	Chandra et al. (2009)
Pomegranate seeds	$ZnCl_2$	Uçar et al. (2009)
Coconut husks	KOH, CO_2	Tan et al. (2008)
Cherry stones	H_2SO_4	Olivares-Marín et al. (2012)
Barley husks	$ZnCl_2$	Loredo-Cancino et al. (2013)
Rubber wood saw dust	Steam	Kumar et al. (2006)
Agricultural waste	NaOH, H_3PO_4, steam, KOH	Hesas et al. (2013a, b)
Rice straw	$(NH_4)_2$ HPO_4	Gao et al. (2011)
Waste tea	K_2CO_3	Gurten et al. (2012)
Hemp biomass	H_3PO_4	Rosas et al. (2009)
Date palm pits	CO_2, H_3PO_4	Reddy et al. (2012)
Marine macro algal biomass	$ZnCl_2$	Aravindhan et al. (2009)
Chicken manure	CO_2	Koutcheiko et al. (2007)
Rubber seed shell	Steam	Sun and Jiang (2010)
Siris seed pods	KOH	Ahmed and Theydan (2013a, b)
Pea nut shells	CO_2	Wu et al. (2013)
Buriti shell	$ZnCl_2$	Junior et al. (2014)
Sunflower seed oil residue	K_2CO_3	Foo and Hameed (2011a, b)
Peach stones	H_3PO_4	Maia et al. (2010)
Date stones	CO_2	Sekirifa et al. (2013)
Pea nut hulls	H_3PO_4	Zhong et al. (2012)
Oil palm stones	CO_2	Lua and Guo (2001)
Macadamia nut endocarp	$ZnCl_2$	Junior et al. (2014)
Leather waste	H_3PO_4, $H_4P_2O_7$	Kong et al. (2013)
Coconut shell	H_3PO_4	Laine et al. (1989)
Coconut shell	H_3PO_4	Cazetta et al. (2013)
Vine shoots	H_3PO_4	Corcho-Corral et al. (2006)
Jacaranda mimosifolia	H_3PO_4	Treviño-Cordero et al. (2013)
Piassava fibers	$ZnCl_2$, CO_2, H_3PO_4, water vapor	Avelar et al. (2010)
Apricot stones	Steam	Şentorun-Shalaby et al. (2006)
Coconut husk	KOH, CO_2	Tan et al. (2008)
Pumpkin seed hull	KOH	Njoku et al. (2013)
Langsat EFBW	H_3PO_4, K_2CO_3, H_2SO_4, HNO_3, NaOH, KOH	Foo and Hameed (2012a, b, c)
Sugarcane molasses	KOH	Sreńscek-Nazzal et al. (2013)
Maize tassel	CO_2, H_3PO_4	Olorundare et al. (2012)
Rambutan peel	KOH–CO_2	Ahmad and Alrozi (2011)
Camellia oleifera shell	H_3PO_4	Kang et al. (2011)
Mangosten peel	CO_2	Ahmad and Alrozi (2010)
OPEFB	CO_2, KOH	Hameed et al. (2009)
Olive stones	H_3PO_4	Yakout and El-Deen (2012)

(continued)

Table 15.4 (continued)

Raw materials	Activation agent	References
Tamarind fruit seed	KOH	Foo et al. (2013)
Eucalyptus camaldulensis wood	CO_2	Heidari et al. (2013)
Rice straw	KOH	Yakout et al. (2013)
Soybean straw	$ZnCl_2$	Miao et al. 2013
Paulownia wood	$ZnCl_2$	Yorgun et al. (2009)
Coffee husks	$FeCl_3$, $ZnCl_2$	Oliveira et al. (2009)
Olive baggase	N_2 atmosphere	Demiral et al. (2011)
Chick peas husks	K_2CO_3	Hayashi et al. (2002a, b)
Argania spinosa seed shells	KOH	Elmouwahidi et al. (2012)
Arundo donaxcane	H_3PO_4	Vernersson et al. (2002)
Jack fruit peel	NaOH	Foo and Hameed (2012a, b, c)
Teak saw dust	Steam	Ismadji et al. (2005)
Bamboo waste	H_3PO_4	Ahmad and Hameed (2010)
Tea waste	Potassium acetate	Auta and Hameed (2011)
Date stones	Phosphoric acid	Yakout et al. (2013)
Jack fruit peel waste	H_3PO_4	Prahas et al. (2008)
Date stones	Steam	Bouchelta et al. (2008)
Waste tea leaves	KOH	Peng et al. (2013)
Lotus stalks	Guanidine phosphate (GPP)	Liu et al. (2013)
Waste biomass	K_2CO_3, KOH	Tay et al. (2009)
Tunisian oil cake wastes	H_3PO_4	Baccar et al. (2009)
Corn cob	H_3PO_4	Njoku and Hameed (2011)
Date stones biomass (Phoenix dactylifera)	H_3PO_4	Danish et al. (2014)
Rattan saw dust	H_3PO_4	Ahmad et al. (2009)
Olive-waste cake	H_3PO_4	Baccar et al. (2012)
Safflower seed cake	KOH	Angın et al. (2013a, b)
Saw dust of Algarroba wood	CO_2, N_2 atmosphere	Matos et al. (2011)
Wild olive cores (*oleaster*)	H_3PO_4	Kaouah et al. (2013)
Coconut shell	H_3PO_4	Laine et al. (1989)
Palm shell	K_2CO_3	Adinata et al. (2007)
Rice husk	K_2CO_3, KOH	Foo and Hameed (2011a, b)

affected by calcination temperature (Hattori 2001). As sulfonic acid groups are hydrophilic in nature its number greatly enhanced the activity of the solid acid activated carbon.

In terms of Brunauer–Emmett–Teller (BET) surface area and pore volume the activated carbons prepared under vacuum condition are better than those produced under nitrogen atmosphere (Yang and Lua 2006). Biomass derivatives are abundant and inexpensive (generally agricultural residues) obtained from renewable sources and hence they are quite remarkable raw materials (Prauchner and Rodríguez-Reinoso 2012) thus they are important to meet the growing world demand.

15.5.1 Biomass for Activated Carbon

Cost, purity, availability, the processing steps, and intended application of the product are the valuable factors for considering the precursor of ACs (Al Bahri et al. 2012). A variety of carbonaceous materials including agricultural wastes or industrial wastes can be used to prepare ACs with high surface area and pore volumes. Although the materials used as a precursor and the preparation method determines the textural properties of ACs, however a variety of natural and synthetic materials have been used as precursors (Yagmur et al. 2008). Almost half of the raw materials used are lignocellulosic ones (Duran-Valle et al. 2005; Sudaryanto et al. 2006). Agricultural wastes due to their abundance are a rich source for activated catalyst production; it also supports to elucidate environmental problems and also reduces the expenses of activated carbon preparation.

Lignocellulosic agricultural wastes considered as a perfect precursor for the production of activated carbon (Kirubakaran et al. 1991; Al-Khalid 1995; Toles et al. 1998; Shawabkeh et al. 2002; Dastgheib and Rockstraw 2001). The most widely used carbonaceous materials for the industrial production of activated carbons are coal, wood, and coconut shell (Vernersson et al. 2002; Yang and Lua 2006) although these precursors are costly and are often imported in the country from developed ones thus there is need to utilize low-cost carbonaceous materials as feedstocks. As the demand for vegetable oils for food and oleo chemicals increased recently, the contribution of discarded by product of oils and wastes will have to play a crucial rule. Nowadays both conventional (from agriculture and wood industry) and non-conventional (from municipal and industrial activities) wastes employed to prepare activated catalyst (Diasa et al. 2007). The use of OCW as starting material for catalyst production can partly address issues concerning waste disposal and it can simultaneously help to generate revenue from a potential waste (Konwar et al. 2013).

15.5.2 Methods of Preparation of Activated Catalyst

The carbon-based materials are converted to AC by thermal decomposition in a furnace using a controlled atmosphere and heat by physical activation or chemical activation (Hsieh and Teng 2000; Mohan et al. 2005) involving the following steps: (1) removal of all water (dehydration), (2) conversion of the organic matter to elemental carbon, driving off the non-carbon portion (carbonization), and (3) burning off tars and pore enlargement (activation) (Ahmadpour and Do 1997). The two common methods for the preparation of activated catalyst are physical and chemical activation, the difference between the two methods and their advantages (Table 15.5).

Different chemical activating agents and related recent studies are presented in Table 15.6. Different physical forms of AC that usually can be found, including: (1) granular activated carbon (GAC); (2) powdered activated carbon (PAC); (3) activated carbon fibers (ACF); and (4) activated carbon cloths (ACC). GAC and PAC

Table 15.5 Comparison between physical activation and chemical activation method

Physical activation	Chemical activation
A two-step method	A one-step method
It involves carbonization followed by activation	It involves activation followed by carbonization
Activation generally occurs at temperature ranging from 700 to 1,200 °C	Activation generally occurs at lower temperature relative to physical activation ranging from 500 to 700 °C
Activating agents are air, CO_2, steam etc. that can develop the porosity	Activating agents are KOH, NaOH, H_3PO_4, H_2SO_4 etc. that can act as a dehydrating agent
Lower yield comparatively and lesser development of porosity, complicated process	Results higher yield, higher development of porosity, simple process
No requirement of washing stages	Require an additional washing stage to remove the chemical agent
Relatively less preferred	Generally more preferred over physical activation
Carbon yields of physical activation are lesser	Carbon yields of chemical activation are higher

Table 15.6 Chemical activation using different activating agents

Chemical agent	References
Zinc chloride ($ZnCl_2$)	Mohanty et al. (2005)
	Yue et al. (2002)
Phosphoric acid (H_3PO_4)	Ichcho et al. (2005)
	Suárez-Garcıa et al. (2004)
	Díaz-Díez et al. (2004)
	Yue et al. (2003)
Potassium hydroxide (KOH)	Sudaryanto et al. (2006)
	Lozano-Castelló et al. (2001)
	Guo and Lua (1999)
	Otowa et al. (1997)
Potassium carbonate (K_2CO_3)	Erdoğan et al. (2005)
	Hayashi et al. (2005)
	Hayashi et al. (2002a, b)
Sodium hydroxide (NaOH)	Rahman et al. (2005)
	Lillo-Ródenas et al. (2001)
Sulfuric acid (H_2SO_4)	Guo et al. (2005)
	Rio et al. (2005)
	Guo and Lua (1999)

Diasa et al. (2007), with permission

are the most widely used activated catalyst. Hard materials are used to prepare GAC, such as coconut shells, including particles retained in an 80-mesh sieve (0.177 mm); PAC obtained when small particles are the raw materials, like wood sawdust, (includes particles <0.177 mm); ACF prepared from homogeneous polymeric raw materials and, in contrast to GAC and PAC, they show a mono dispersed pore size distribution (Kasaoka et al. 1989).

Phenolic or viscose rayon initially used to develop ACC in the early 1970s (Bailey et al. 1971). Thus the utilization of discarded materials possesses several advantages, mainly involve the eco-friendly nature and their economically feasibility.

15.6 Structure of Activated Carbon

Structurally activated carbon is a disorganized form of graphite due to impurities and the method of preparation (activation process) where the layers are held by carbon–carbon bonds. Its precise atomic structure comprised of curved fragments containing pentagons, hexagons in addition to other non-hexagonal rings. Pentagonal rings structure is naturally porous, due to the curvature of the carbon layers, and relatively hard compared to other carbons, because of the absence of parallel graphene layers, the most expected arrangement or structure of activated catalyst is represented in Figs. 15.2 and 15.3 (Harris et al. 2008).

It explains the microporosity and many other properties of the carbon. Recently it has been suggested that fullerenes structure is quite associated with the activated carbon structure, pentagonal rings are visible at 2,000 °C, showing that the carbons bear fullerene-related structure. This type of structure helps to explain the properties of activated carbon, and also gives an important implication for the modeling of adsorption on microporous carbons. Cross-links consist of domains containing sp^3 bonded atoms (Ergun and Tiensuu 1959; Ergun and Alexander 1962) however neutron diffraction studies entirely discounted that non-graphitizing carbons consist entirely of sp^2

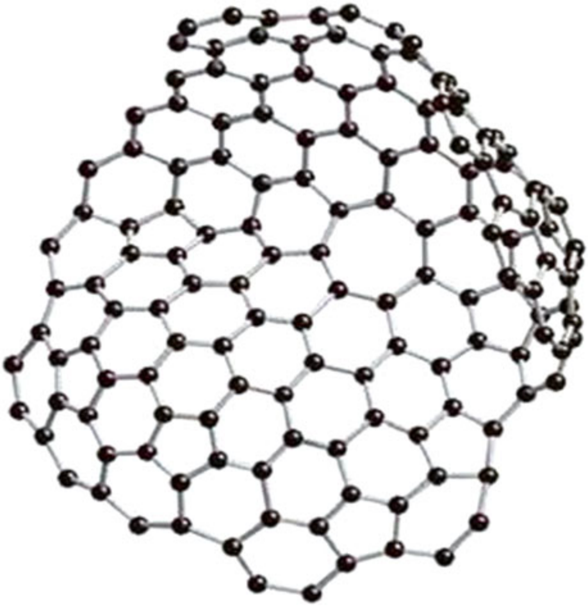

Fig. 15.2 Proposed atomic structure of activated carbon (Harris et al. 2008)

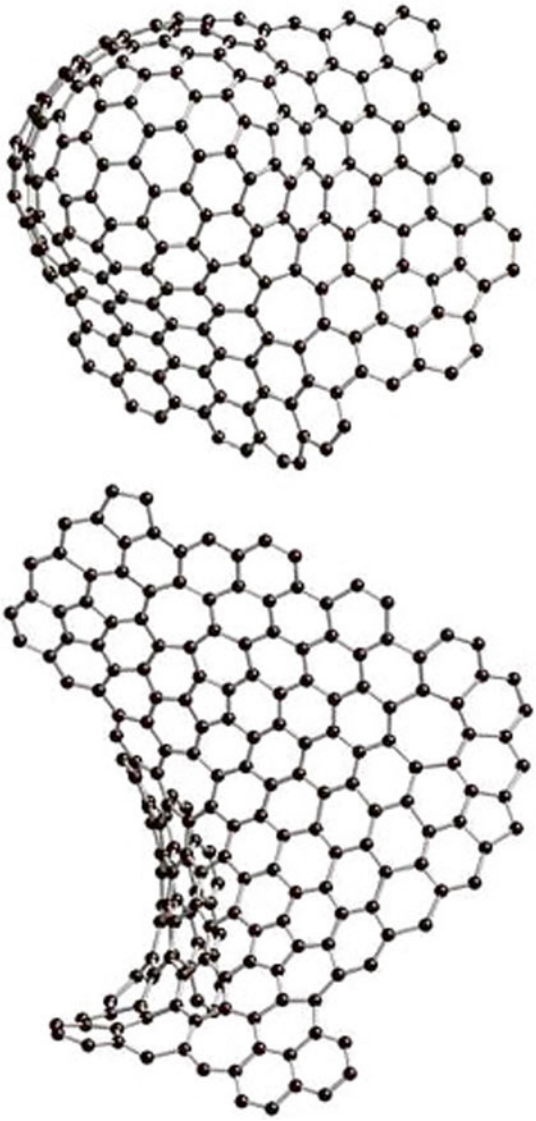

Fig. 15.3 Proposed structure of activated carbon (Harris et al. 2008, with permission)

(Mildner and Carpenter 1982). Presence of pentagonal rings in the structure leads to extremely porous, due to the curvature of the carbon layers (Harris et al. 2008).

15.6.1 Catalyst Leaching

The CBSC can be deactivated by leaching of sulfonated species, formation of sulfonic esters (Kang et al. 2013). Most usually there are five reasons behind catalyst deactivation, these are Sintering, Evaporation, Poisoning, Fouling, and Thermal degradation often occurred by mechanical damage, high temperature, and corrosion by the reaction mixture. Hence study of leaching catalyst is important for the carbon-based catalysts. Since the functional groups of the carbon based sulfonated acid catalysts consisted of SO_3H, COOH, OH, shows the leaching of SO_3H and possibly COOH and OH into the reaction medium (Adrian 2012).

15.6.2 Optimization of Parameters for Chemical Activation Reaction

The utilization of renewable and cheaper precursors to prepare activated carbon produces useful and economically feasible adsorbent but also contributes towards minimizing the solid wastes. The preparation method can be optimized to determine the effect of the main parameters associated with the process are: Impregnation ratio, activation temperature, acid concentration, activation time, the precursor materials nature, the activation type (chemical and physical activation), and pyrolysis temperature, all these affect the properties of the resulting activated carbon (Girgis and El-Hendawy 2002; Haimour and Emeish 2006; Diao et al. 2002).

The processing conditions are generally expressed in terms of some properties, among which: surface area, cation-exchange capacity (CEC), phenol and methylene blue, bulk density and adsorption efficiency towards iodine are frequently considered (Vernersson et al. 2002; Yang and Lua 2006; Haimour and Emeish 2006). However, methylene blue is the most accepted probe molecules for the determination of the ability of sorbent for the removal of large molecules whereas the iodine number shows indication on microporosity and consequently on the specific surface area of the sorbent materials (Baccar et al. 2010). Therefore, to determine the most important factor and their regions of interest it is essential to study these factors and their effects on the production of activated catalyst.

Experimental design technique is an important tool which provides statistical models in understanding the interactions among the parameters that have been optimized (Alam et al. 2007). The major benefit of using Response Surface Methodology (RSM) is to reduce the number of experimental trials required to evaluate several parameters and their interactions (Lee et al. 2000). RSM is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. RSM involves three main stages: (1) design and experiments, (2) response surface modeling through regression, (3) optimization (Myers and Montgomery 1995). Based on this central composite design (CCD), quadratic models were developed. The analysis of variance (ANOVA) on each experimental design response was recognized from them (Ahmad and Hameed 2010). Previously RSM was applied for the preparation of activated carbons using precursors such as Luscar char (Azargohar and Dalai 2005), Turkish lignite (Karacan et al. 2007), and olive-waste cakes (Baçaoui et al. 2001).

15.7 Characterization of Activated Catalyst

Raw material and activated carbons tests were performed on dry basis according to International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM) procedures to determine their main property. Fixed carbon content was determined by difference (Angın et al. 2013a, b). Acid densities of the carbons were determined by titration method using phenolphthalein indicator (Konwar et al. 2013). Textural property of the prepared activated carbon including pore size distribution, surface area (S_{BET}), and total pore volume (V_{tot}) were determined from N_2 adsorption at 77 K using an Autosorb1-Quantachrome instrument (Baccar et al. 2012). Pore size distribution, surface area, and pore volume of the activated carbons were determined by the BET equation and *t*-plot analysis software (Angın et al. 2013a, b). The carbonaceous materials porosity and irregular shapes are clearly visible by means of Scanning Electron Microscopy. Characterization also involved Elemental Analysis of the porous carbon materials before and after sulfonation, Transmission Electron Microscopy (TEM), Infrared Spectroscopy for the determination of the functional groups like sulfonic, carbonyl group in the activated carbon (KBr pellet), Raman spectroscopy, X-ray Powder Diffraction used for illustrating the amorphous nature of the carbonaceous materials and Thermo Gravimetric Analysis for the determination of the thermal stability (Konwar et al. 2013). The carbon, hydrogen, and nitrogen contents of the precursor material and activated carbon were analyzed by Elemental Analyzer. However oxygen contents were calculated by difference. The DR (Dubinin–Radushkevich) method used to determine the micropore volume accordingly. Fourier transform infrared spectra (FTIR) used extensively to determine surface functional groups (Angın et al. 2013a, b). The $–SO_3H$ densities of sulfonated carbons were estimated from elemental analysis by considering that all sulfur present in the carbon samples was due to $–SO_3H$ groups (Konwar et al. 2013).

15.8 Biomass Derived Activated Sulfonated Catalyst

Lignocellulosic materials are economically cheap, perfect precursors to produce activated carbon. Due to the abundance of cellulosic biomass in the nature they are usually used to produce activated carbon as the catalytic active site in these catalysts are chemically bound, as a result both the biodiesel and glycerol by-product will be free of catalysts contaminants (Emrani and Shahbazi 2012). For biomass derived CBSC, the body is often amorphous and owns aromatic structure. Moreover, conventional solid acids bearing single functional groups are different from the biomass derived CBSC. CBSC possess high density of nearly neutral phenolic –OH in addition to Brønsted acid sites ($–SO_3H$ and –COOH), as shown in Fig. 15.4 (Kang et al. 2013).

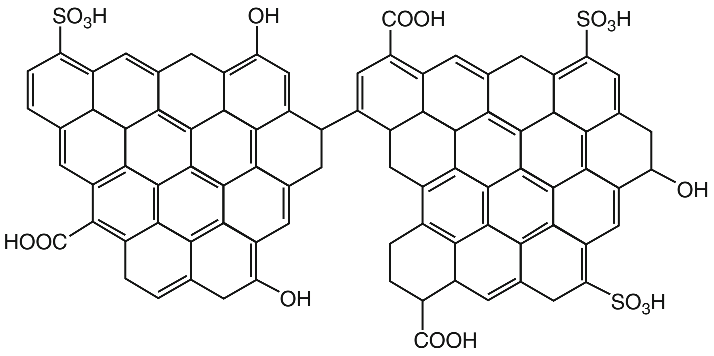

Fig. 15.4 Proposed structural model of the biomass derived carbon-based sulfonated catalyst (Kang et al. 2013, with permission)

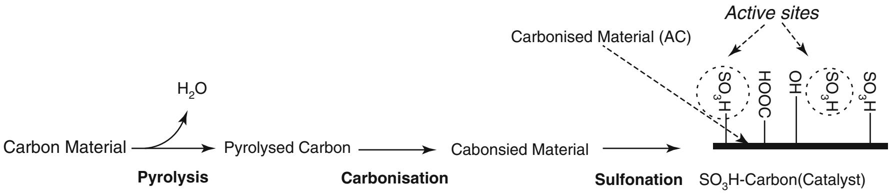

Fig. 15.5 Preparation of SO_3H-carbon (Konwar et al. 2014, with permission)

15.8.1 Sulfonation of Activated Catalyst

Some rigid carbon materials like carbon nanotubes, graphene, ordered mesoporous carbon, and activated carbon are relatively hard to be sulfonated. Concentrated H_2SO_4 and fuming H_2SO_4 are used as the sulfonating agents. However the CBSC prepared with fuming H_2SO_4 possess much higher catalytic activity (Dehkhoda et al. 2010; Kastner et al. 2012). Researchers have extensively studied the influence of different parameters like sulfonating agent, sulfonation time, and carbon precursor on the activity of such catalysts by direct sulfonation. Directly pyrolysis of the carbon precursors and sulfonation is concentrated at high H_2SO_4 temperatures, produces sulfonated carbons with low in acid density, lower specific surface area, and poor reusability (Konwar et al. 2013). Figure 15.5 shows the way for the preparation of SO_3H-carbon (Konwar et al. 2014).

Studies also indicated that the catalytic activity is primarily determined by total acid density, $–SO_3H$ density, surface functional groups, and pore structure. It is established that a high $–SO_3H$ density and pore volume favored high activity. These properties in turn are directly influenced by the carbonization temperature (Konwar et al. 2014). Apart from these there are numerous other reports on the preparation of similar sulfonated carbons catalysts, by one-step hydrothermal carbonization/

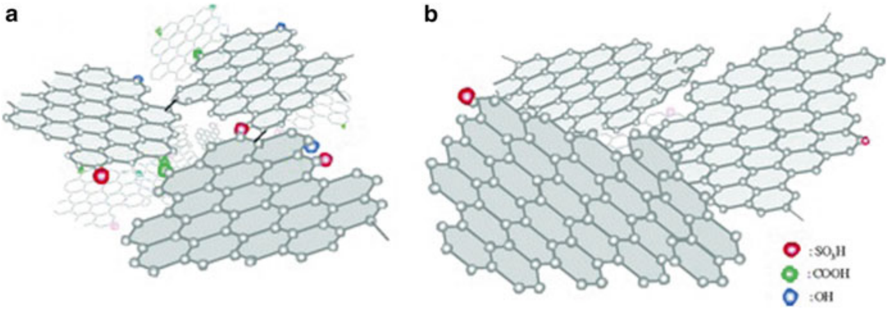

Fig. 15.6 Proposed schematic structure of the sulfonated carbon materials. Adapted from Okamura et al. (2006), with permission

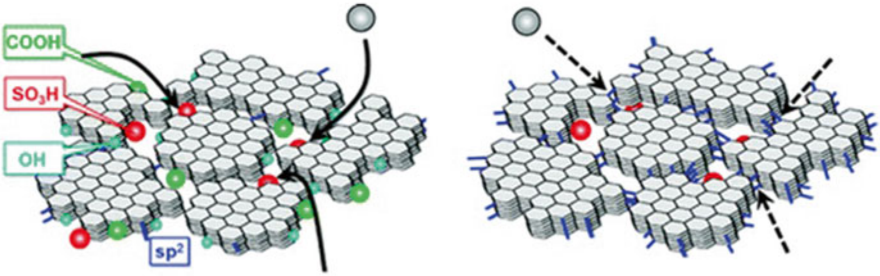

Fig. 15.7 Amorphous car bearing SO_3H groups as an insoluble Bronsted acid available for various acid-catalyzed reactions (Nakajima and Hara 2012, with permission)

sulfonation (Xiao et al. 2010), polymerization followed by sulfonation and carbonization (Zhao et al. 2010), by the thermal treatment of *p*-toluene sulfonic acid (Zhang et al. 2010) etc.

15.8.2 *Structure and Figure of Sulfonated Catalyst*

The most accepted structure of solid acid consists of a flexible carbon-based framework with highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups (Shu et al. 2010). Figure 15.6 represents the proposed schematic structure of the sulfonated carbon materials. Every sulfur atom presents in the catalyst exists as $-SO_3H$, the sulfur content obtained from the analysis was used for calculating the sulfonic acid density (Ezebor et al. 2014) while SO_3H + COOH and SO_3H + COOH + OH densities were calculated from ion exchange (Kitano et al. 2009). Figure 15.7 shows the amorphous carbon bearing SO_3H groups as an insoluble Bronsted acid available for various acid-catalyzed reactions (Nakajima and Hara 2012).

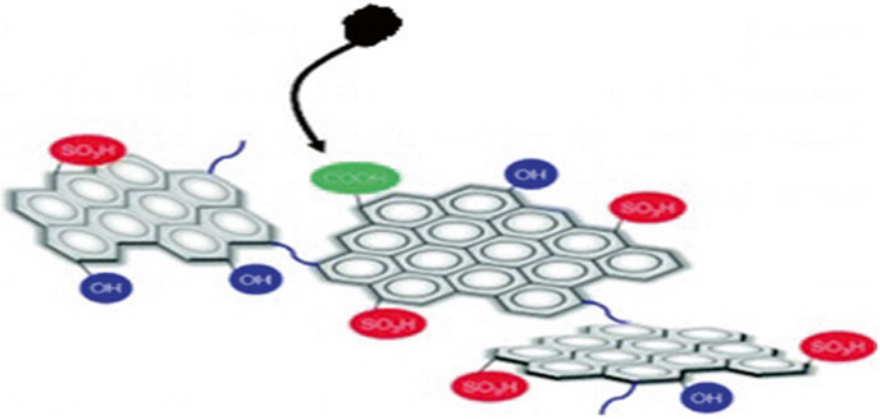

Fig. 15.8 Sulfonic acid group (SO_3H)-bearing amorphous carbon (Nakajima et al. 2008, with permission)

The large amounts of SO_3H group are present in the polycyclic aromatic groups constituting the carbon sheets of aromatic carbon. The strong hydrogen bonding to SO_3H groups results in strong acidity due to mutual electron-withdrawal and creating the reason behind their higher catalytic activity (Hara 2010). Figure 15.8 shows the sulfonic acid group SO_3H groups bearing amorphous carbon (Nakajima et al. 2008). Hydrophobicity that prevented the hydration of –OH species, its high acid site density (–OH, Brönsted acid sites) hydrophilic functional groups (–SO_3H) that gave improved accessibility of methanol to the triglyceride and FFAs, and large pores that provided more acid sites for the reactants are the factors that increase the high catalytic activity and stability of the activated carbon catalyst (Shu et al. 2010).

Sulfonic acid group (SO_3H)-bearing amorphous carbon well regarded as carbon-based solid acid catalysts. SO_3H-bearing carbon particles with large surface area inhibit intramolecular Friedel–Crafts alkylation, thus shows greater catalytic activity that are revealed from structural and reaction analyses (Nakajima et al. 2008). The hydrolysis of β-1, 4 glycosidic bonds in both cellobiose and crystalline cellulose can be catalyzed by carbon-based solid acid catalyst. The large adsorption capacity for hydrophilic reactants and the adsorption ability of β-1, 4 glucan is responsible for the high catalytic performance of the carbon catalyst, which is not adsorbed to other solid acids (Suganuma et al. 2010).

15.9 Conclusions

Activated carbons were prepared from huge variety of cellulosic resources including agricultural wastes, municipal wastes, plants residues, and non-edible oil cakes wastes considering that biomass is renewable, abundant, and low cost, either using chemical activating agent or physical agents. The effect of parameters such as activation temperature, and impregnation ratio on pore structure and surface chemistry of resulting carbons were also studied. By nitrogen adsorption the pore structure of the activated carbon was studied, however functional group analyzed by FT-IR. The surface areas of the activated carbons were strongly affected by the carbonization temperature and concentration of the activation reagent. The obtained activated carbons mainly have microporous characteristics. Consequently, obtained activated carbons from the agricultural or industrial waste biomass can be utilized for the preparation of further sulfonated activated catalyst; however the catalytic properties depend upon the nature of attached molecule/group (acidic or basic), with the possibility to be utilized as heterogeneous catalysts in different chemical reactions. However, further works on economic study, improvement of catalytic stability, and mechanical strength should be conducted.

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Chapter 16
Straw Availability, Quality, Recovery, and Energy Use of Sugarcane

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_16,

Abstract Sugarcane straw is destroyed through burning before harvest or left on the ground for decomposition. Sugarcane straw is composed of cellulose (33.30–36.10 %), hemicelluloses (18.40–28.90 %), lignin (25.80–40.70 %), ashes (2.10–11.70 %), and extractives (5.30–11.50 %). Sugarcane straw availability depends on the sugarcane variety and age of harvesting. It can be used for alternative energy production and improvement of soil properties such as soil erosion, moisture content, and soil carbon stock. The biomass of sugarcane straw can be converted into biofuel through pyrolysis. The sugarcane straw has potentiality that could produce textile fibers. Bioelectricity is environmentally friendly produced from sugarcane straw which contributes to economic development.

Keywords Sugarcane straw • Biofuel • Bioelectricity • Ethanol

16.1 Introduction

Sugarcane is the main source of sugar in the world. It is native to Southeastern Asia (Daniels and Roach 1987). Brazil is the largest sugarcane-producing country throughout the world. In 1532, it was first introduced in Brazil. Brazil has favorable climate and soil conditions for sugarcane cultivation and is considered an important sugarcane exporting country to European Union (Dinardo-Miranda et al. 2008). It may be adapted in different parts in Brazil and 85 % of sugarcane currently cultivated at Sao Paulo and adjacent states in Brazil (Goldemberg 2007). Sugarcane can accumulate vigorous biomass due to C4 photosynthesis in nature. Sugarcane is a highly productive C4 photosynthesis plant, which bestows higher light, water, and efficient nitrogen use compared to C3 pathway of plant (DeSouza and Buckeridge 2010). It is clonally propagated by stem cutting and semi-perennial with life cycle. Sugarcane takes 12–18 months for maturity from planting to harvest during cultivation. Sugarcane has been used as ratoon crops that can allow up to five harvests. About 70 % raw table sugar has been produced from sugarcane in the world (Contreras et al. 2009). Generally, sugarcane stalks are used during dry season for cattle when pastures are unavailable for grazing. The sugarcane is consisted of two parts such as stem and straw. The sugar and ethanol has been processed from stem while energy is obtained from burning the straw in industry. According to Saad et al. (2008) and Moriya et al. (2007), the thing which is removed from sugarcane is considered as straw. Sugarcane straw is composed of dried and fresh leaves as well as top of the plant, and 150 kg straw can be obtained from one ton of cultivated sugarcane (Saad et al. 2008).

The sugarcane straw is generally burnt before harvesting. The practice of burning the sugarcane residues to facilitate harvest and transport operation of straw has been widespread in the world for reducing the harvesting cost in nonmechanical area. Andrade et al. (2010) reported that sugarcane field is burnt to facilitate the manual harvesting for increasing the content of sugar content by weight. Sugarcane straw is burnt by the industry to generate local energy for producing sugar and alcohol (Costa et al. 2013).

Now the manual operation has been replaced by mechanical operation gradually for maintaining the straw on the ground under green cane management. França et al.

(2012) reported that burning practice is being reduced day by day for preventing major health problems which have been created from the cloud of smoke and ash released during sugarcane straw burning.

The collection of sugarcane straw is being improved technically that would increase the amount of sugarcane straw. Sugarcane straw can be considered as alternative energy production in the world. Carrier et al. (2011) reported that sugarcane straw can be used for energy production through pyrolysis and vacuum. On the other hand, Brazil has introduced a law to avoid the burning of sugarcane residues. Other countries like South Africa are trying to consider the application of sugarcane straw in energy production. The straw of sugarcane is composed of three main macromolecules such as cellulose, hemicellulose, and lignin. Cellulose-based fibers have mechanical and physical properties that are widely used as biodegradable filler (Toriz et al. 2005; Sun et al. 2004). Pyrolysis is an alternative way of burning in order to produce ashes, bio-oil, biogas, and charcoal by using the sugarcane straw. The sugarcane straw is used for energy production which is environmentally friendly (Cortez and Lora 2006). Biodiesel and petrochemicals can be produced through pyrolysis of sugarcane straw.

16.2 Sugarcane Straw Availability and Quality

The sugarcane straw availability depends on the sugarcane variety and age of harvesting. The sugarcane straw can be harvested from 10 to 18 tons per hectare on the dry basis ration of straw and stalk (11–17 %). The acceptable ratio of straw to stalk range is 14–18 %, and straw availability depends on sugarcane yield (Leal et al. 2013). The sugarcane straw consists of cellulose (33.3–36.1 %), hemicellulose (18.4–28.9 %), lignin (25.8–40.7 %), extractives (5.3–1.5 %), and ashes (2.1–11.7 %). Leal et al. (2013) reported that sugarcane straw would be harvested as 62 % dry leaves, 31 % green leaves, and 7 % tops. Top of sugarcane containing higher chlorine may cause corrosion in the fire boilers. The proximate and ultimate analysis of dry matter and mineral of sugarcane straw has been shown in Tables 16.1, 16.2, and 16.3.

Table 16.1 The proximate analysis of sugarcane straw (dry matter %)

Sugarcane straw	Moisture content	Ash	Fixed carbon	Volatile matter	Higher heating value
Dry leaves	13.5	2.7	11.6	84.5	17.4
Green leaves	67.7	3.7	15.7	80.6	17.4
Tops	82.3	4.3	16.4	79.3	16.4

Table 16.2 The analysis of sugarcane straw (dry matter %)

Sugarcane straw	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Chloride
Dry leaves	46.2	6.2	0.5	43.0	0.1	0.1
Green leaves	45.7	6.2	1.0	42.8	0.4	0.4
Tops	43.9	6.1	0.8	44.0	0.1	0.7

Table 16.3 Sugarcane straw mineral analysis

Sugarcane straw	P_2O_5 (g/kg)	K_2O (g/kg)	CaO (g/kg)	MgO (g/kg)	Fe_2O_3 (g/kg)	Al_2O_3 (g/kg)
Dry leaves	0.5	2.7	4.7	2.1	0.9	3.5
Green leaves	2.0	13.3	3.9	2.2	0.5	1.4
Tops	2.5	29.5	2.6	2.5	0.2	0.5

16.3 Straw Recovery

Straw recovery is one of the major challenges for sustainable sugarcane cultivation. Sugarcane straw can contribute to the improvement of soil properties such as soil erosion, incorporation of organic matter, and conservation of soil moisture and increase the biological activities in soil. On the other hand, sugarcane straw may help to increase the incidence of pest. However, straw recovery from field is not that simple due to technological and economic challenges related to handling and transportation. High investment is required for straw transportation from the field to the power plant. At present, some initiatives and developments have been done to transportation of straw. The best option for removing the straw from the field to industry has been shown in Fig. 16.1.

Sugarcane straw recovery depends on many factors especially harvesting procedure, sugarcane topping, variety, height and crop age, climatic condition, and soil. Sugarcane straw can be recovered from 24 to 95 % through mechanical harvesting (Paes and Hassuani 2005). There are some ways to recover the straw from the sugarcane field.

16.3.1 Straw Recovery Way I

Unburned chopped cane may be harvested using sugarcane straw removal harvester. Straw is baled and transported to the industry, and chopped cane is carried from the field to the sugarcane mill. Eighty-eight percent of straw can be carried from the field to the sugarcane mill, and 64 % of straw can be separated from cane stalks.

16.3.2 Straw Recovery Way II

Another way of straw recovery is harvesting unburned chopped cane without straw removal. Straw and cane stalks are transported from the field to the mill while both are separated in a dry cleaning station. About 95 % of straw can be transported in this way. But only 66 % of straw can be recovered, and 29 % of straw can be crushed with cane stalk in the mill.

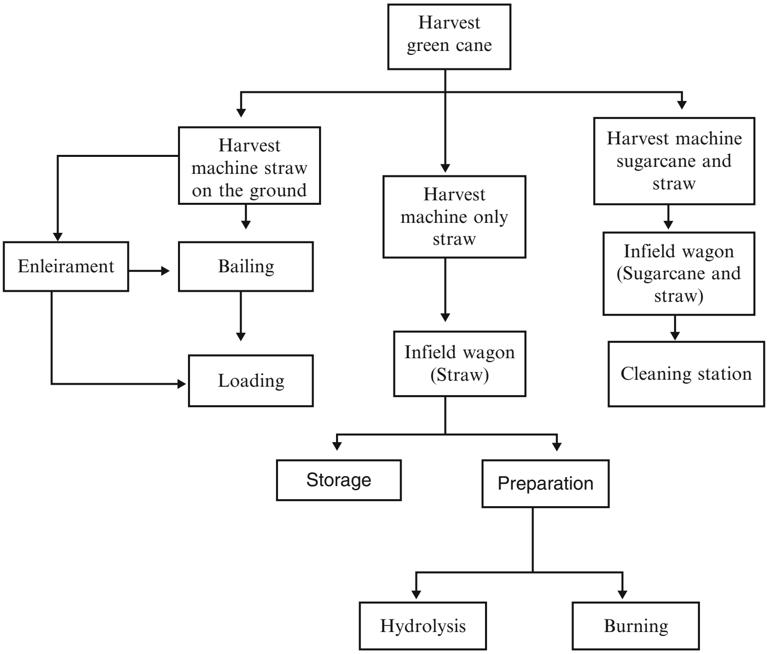

Fig. 16.1 Possible routes for sugarcane straw recovery for energy

16.3.3 Straw Recovery Way III

Unburned chopped sugarcane may be harvested with the help of partial cleaning. A specific amount of the sugarcane straw is left on the ground, and the rest of the straw is transported from the field to the mill with the sugarcane stalks. Sugarcane straw is separated from the stalk in a dry cleaning station in the sugarcane mill. 71 % of straw can be transported from the field to the mill, and 50 % of straw can be separated from cane stalks.

16.4 Improvement of Soil Properties Through Sugarcane Straw

16.4.1 Erosion of Soil

Soil erosion may be controlled by minimizing the raindrops and the speed of running water on the surface soil (Andraski et al. 1985). This involves the protection of soil surface with the help of mulching as well as preventing the rain water from striking the soil water directly and keeping away the practices such as compacting the soil or excessively pulverizing it. Soil erosion may be reduced when sugarcane straw would be harvested mechanically without straw burning resulting to mulching effect. Nutrient losses were noticed after burning the sugarcane field due to soil erosion. Izidorio et al. (2005) reported that soil nutrients such as phosphorus (1.07 kg/ha), potassium (1.59 kg/ha), calcium (10.24 kg/ha), and magnesium (1.91 kg/ha) may be reduced in the soil of sugarcane fields. Andrade et al. (2011) observed the nutrient loss through soil erosion that has economic and technical impacts in sugarcane cultivation in Brazil. On the other hand, burned sugarcane lost more soil nutrient than the unburned sugarcane.

16.4.2 Moisture Content

Sugarcane straw can help to increase the moisture content and reduce soil evaporation that improve the water use efficiency. Sugarcane has been covered by straw up to 90 days after transplantation due to the increase in the moisture holding capacity for good emergence. Tominaga et al. (2002) reported that soil moisture content was higher in sugarcane field without straw burning than other sugarcane plots burned before harvest and bare soil plots. On the other hand, higher sugarcane production was observed in the unburned management using the APSIM model in South Africa which was related to higher soil moisture content (Thorburn et al. 2002). Shrivastava et al. (2011) reported that sugarcane straw covered on interrow spaces around 0.1 m thick exhibited the highest efficient use of irrigation water by reducing the evaporation loss from the surface of soil. They found that the sugarcane straw maintained the water content of soil at maximum level for a longer duration than the uncovered soil surface. Therefore, sugarcane straw without burning enhanced around 10 % yield.

16.4.3 Soil Carbon Stock

The soil carbon stock increases when the sugarcane straw is left on the ground without burning. Wood (1991) reported that soil carbon stock was 20 % higher in the 0.0–10.00 cm depth in areas without burning than burned areas under straw management experiments in Australia. Canellas et al. (2003) reported that concentrations of carbons were 22.34 g kg^{-1} in the cane with straw management and 13.13 g kg^{-1} in the burned cane in the 20 cm soil depth in Southeastern Brazil. The soil carbon stocks increase about 15 % in the 0.1 m layer after 6 years of green cane management, compared to the burning management (Razafimbelo et al. 2006). Galdos et al. (2009) reported that soil carbon stocks increased up to 30 % after 8 years of conversion due to mechanizing harvest with crop residue management on the field. It is revealed that sugarcane straw is capable to increase the soil carbon stocks in the soil under straw management.

16.5 Ethanol Production from Sugarcane Straw

The energy production through sugarcane straw involves the liquid, gaseous, and solid fuel production. Ethanol fuel is the most important that reduces our dependence on oil. Sugarcane straw is a suitable material for the ethanol fuel production because of its higher cellulose and hemicellulose content, which can be hydrolyzed, for instance, into fermentable sugars, and its other characteristics. The processes involved in bioethanol production are appropriate pretreatment, straw hydrolysis, conversion of the cell walls to simple sugars, anaerobic fermentation to convert the sugars to ethanol, and finally distillation. Pretreatment of straw is estimated for bioethanol production to account for 33 % of the total cost of bioethanol production. Appropriate pretreatment selection technique is the major challenge for the development which is economically sustainable for bioethanol production technology from straw.

16.5.1 Pretreatment of Biomass

Several pretreatment techniques such as alkaline pretreatment, dilute acid hydrolysis, and fungal pretreatment have been used for ethanol production. The acid pretreatment was the best pretreatment for ethanol production followed by alkaline and fungal pretreatment.

16.5.1.1 Alkaline Pretreatment

Generally, the alkaline pretreatment has been used for delignification. The removal of lignin is needed for cellulose that is available for enzymes. Delignification has been tested by using different concentrations of hydrogen peroxide at different pH for various time intervals. However, 2 % hydrogen peroxide has been used at alkaline pH for the removal of lignin from sugarcane biomass (Dawson and Boopathy, 2008). Lignocellulosic biomass cannot be saccharified by enzymes without pretreatment. Proper pretreatment would reduce the lignin content of sugarcane straw. Hydrogen peroxide can play an important role for the delignification of sugarcane straw. Krishna and Chowdary (2000) reported that alkaline peroxide pretreatment was more effective for delignification of leaves. Alkaline pretreatment has an advantage for by-products which are released during lignin degradation by alkaline peroxide (Gould and Freer 1984). Suhardi et al. (2013) reported that alkaline pretreatment at pH 12 was the optimum for maximum ethanol production in variety of cane L 79-1002.

16.5.1.2 Diluted Acid Hydrolysis

Dilute acid pretreatments can free hemicellulose and cellulose at moderate temperatures and disrupt the lignin through releasing the cellulose during the enzymatic reactions (Knappert et al. 1981; Yang and Wyman 2004). Suhardi et al. (2013) reported that the highest ethanol production was obtained from 3 to 4 % sulfuric acid-treated biomass. The acid hydrolysis pretreatment and the enzymatic catalysis have been proved effectively for increasing the bioethanol production using both cellulose and pentose sugar fermenting recombinant *E. coli*. On the other hand, recombinant plasmids can be used to produce strains of *Saccharomyces* that are capable of fermenting sugars. Ho et al. (1998) reported that diluted acid hydrolysis was involved for the use of three xylose-metabolizing genes such as xylose reductase, xylitol dehydrogenase, and xylulokinase, which was converted xylose to xylitol, xylitol to xylulose, and xylulose to xylulose-5-phosphate.

16.5.1.3 Fungal Pretreatment

The sugarcane straw with pretreatment of both fungi, *Ceriporiopsis* and *Phanerochaete*, has produced the maximum ethanol in 6 days of fermentation. The fungi such as brown rot and white rot fungi are capable of decomposing the fallen leaves naturally using trees and other plants for humic and water-soluble compounds (Lynn et al. 2010). These fungi produced different types of enzymes such as lignin peroxidase, phenol oxidase, manganese peroxidase, and laccase (Kuhad et al. 1997; Lenowicsz et al. 1999; Howard et al. 2003). Osma et al. (2007) reported that these fungi can produce enzymes under both submerged fermentation (SmF) and solid-state fermentation (SSF). Suhardi et al. (2013) reported that the solid-state fermentation pretreatment showed effective removal of lignin for higher ethanol production from the fungal pretreated energy sugarcane compared to control treatment.

16.5.2 Enzymatic Hydrolysis of Cellulose

Enzymatic hydrolysis is the best procedure for degrading cellulose into reducing sugars. It depends on the temperature, time, pH, enzyme loading, and concentration of substrate during the hydrolysis. Hydrolysis and fermentation can be done together for reducing time and avoiding end product inhibition. This process is called simultaneous saccharification and fermentation. Three types of cellulolytic enzymes such as endo-β-1,4-glucanases, cellobiohydrolases, and β-glucosidases are required for enzymatic hydrolysis of cellulose. Duff and Murray (1996) reported that various types of enzymes such as xylanase, b-xylosidase, glucuronidase, acetylesterase, galactomannanase, and glucomannanase are necessary for breaking down the hemicelluloses. Bacteria and fungi are used for enzymatic hydrolysis, but *Aspergillus* and *Trichoderma* genera are widely used for enzymatic hydrolysis for cellulose production. The enzyme source is a major effect for effective hydrolysis.

16.5.3 Detoxification of Hemicellulosic Hydrolysate

There are several methods that can be used to detoxify the hydrolysates during ethanol production. These methods are membrane use, ion exchange resins, evaporation, neutralization, and activated charcoal which have been used for ethanol production. The ion exchange resins process are the most effective detoxification method that can remove lignin-derived inhibitors and acetic acid and significantly improve the yield of fermentation (Chandel et al. 2011). This method can be regenerated and reused without disturbing any treatment. On the other hand, adsorption of activated charcoal is widely used to detoxify for lower cost and efficient inhibitor compound removal. This method can remove only phenolic compounds that cannot change the fermentable sugar levels (Canilha et al. 2008). The success of this method depends on charcoal and hydrolysates ratio, contact time, pH, and temperature (Mussatto and Roberto 2004).

16.5.4 Fermentation of Biomass into Ethanol Production

Fermentation is a biological process for ethanol production. The microorganism such as yeasts is the best choice for ethanol production. There are three kinds of processes used in the ethanol production from sugarcane straw. Separate hydrolysis and fermentation is the first process of fermentation where lignocellulosic hydrolysis and ethanol fermentation have been done separately. Another two methods are simultaneous saccharification and fermentation (SSF) and simultaneous saccharification and cofermentation (SSCF). To obtain the desired ethanol yields from sugarcane straw hydrolysates, it is essential that the hemicellulose fraction should be fermented with the same conversion rate for getting the maximum ethanol production (Lin and Tanaka 2006). Hemicellulose hydrolysate contains pentose and hexose sugars. The different types of yeast, fungi, and bacteria can assimilate pentose sugar by conversion of sugarcane straw hydrolysate.

16.5.5 Distillation of Ethanol

The final medium of ethanol production is composed of water and ethanol (Huang et al. 2008). Ethanol recovery is necessary from a fermented substrate. The water and ethanol cannot be separated by conventional method. There are three steps for ethanol purification such as distillation, rectification, and dehydration. The dehydration method can be used for producing high concentrated ethanol. Huang et al. (2008) reported that a dehydration process can be realized through azeotropic distillation, extractive distillation, liquid–liquid extraction, adsorption, or some complex hybrid separation methods.

16.6 Bio-Oil Production from Sugarcane Straws

Bio-oil from straw is a complex mixture that contains different organic compounds formed by the thermal degradation of cellulose, hemicelluloses, lignin, and other biomolecules which are presented in sugarcane straw biomass. Biofuel can be obtained from pyrolysis method from sugarcane straw. Pyrolysis is one kind of thermo-degradation technique that can be used for transformation of the biomass in bio-oil. The biomass has been converted into a liquid product such as bio-oil through pyrolysis which can be used as feedstock for fuels and valuable chemicals (Maiti et al. 2006; Li et al. 2011). Thermal pyrolytic conversion is the promising method that can be used for biomass conversion (Strezov et al. 2008). The medium temperature (550 °C) leads to the production of a pyrolysis gas composed by H_2 and CO (Morf et al. 2002). Mesa-Perez et al. (2013) investigated on biofuel production through pyrolysis using sugarcane straw. They obtained 35.5 % bio-oil at 470 °C temperature that has low oxygen content and high heating value. The pyrolysis of sugarcane straw is an environment-friendly method for the production of bio-oil because it does not have another important use (Cortez and Lora 2006). The development of biorenewable agro-industry needs to integrate the coproducts obtained through pyrolysis process (Arbex et al. 2004). Bio-oil is a good coproduct of pyrolysis and an energy carrier and feedstock for biodiesel and petrochemical production. Bio-oil is a complex nature that requires the usage of high-resolution chromatographic techniques. The multidimensional chromatography specially GC x GC/TOFMS is a powerful technique for analysis of bio-oil. This technique has some advantages for separation capacity, resolution, sensitivity, and selectivity. Sfetsas et al. (2011) have used the GC x GC/FID and GC x GC/TOFMS for quantification of bio-oils. Fullana et al. (2005) reported that 70 % chromatogram could be obtained using GC x GC.

16.7 Sugarcane Straw as Textile Fiber Production

The natural cellulosic fibers using agricultural by-products have become more urgent and currently used due to higher price and availability of natural and synthetic fibers (Reddy and Yang 2009). These agricultural by-products can be used for the development of novel cellulose, protein, and synthetic fibers for textile, composite, and biomedical applications (Huda et al. 2007). Research groups have been encouraged to develop suitable technologies such as the use of raw material for textile fiber production due to the availability and composition of sugarcane straw which would give innovative and nonpolluting destination. Lu et al. (2009) reported that sugarcane straw has three main macromolecular components: cellulose, polyoses, and lignin. The physical, biological, and chemical processes can be used for separation of the macromolecular fractions of lignocellulosic materials. The sugarcane straw cellulose fiber could be produced by a wet-spinning method that can show tensile strength compatible with lyocell fibers in the textile market.

16.8 Sugarcane Straw for Bioelectricity

Bioelectricity has been produced by burning the sugarcane straw in high-efficiency broilers. The production of bioelectricity could reach 11,500 MW by 2015 which would cover 15 % of Brazilian electricity. Brazilian sugarcane mills are self-sufficient for energy to produce more bioelectricity to cover their own necessary demand. Sugarcane bioelectricity offers environmental and economic benefits and a guarantee of electrical energy. Sugarcane bioelectricity is outstanding due to costs competitiveness and reduction of greenhouse grass emissions.

16.9 Conclusion

Brazil is the main sugarcane-producing country and tries to use sugarcane straw as an alternative energy production. The main challenge is the recovery of sugarcane straw from the field. Mechanical technology can help to recover the straw from the field. Scientists are trying to develop the suitable technology for maximum recovery of sugarcane straw and production of energy.

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Chapter 17
Jatropha curcas: A Prospective Energy Crop

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_17, © Springer International Publishing Switzerland 2014

Abstract Declining reserves of fossil fuels, climate change issues, aim to reduce dependence on fossil fuels and CO_2 emissions has inspired global interest in *Jatropha curcas* L. as an alternate energy biosystem. *J. curcas*, an underutilized, robust energy plant belonging to family Euphorbiaceae has ability to grow in wastelands and semi-arid areas with low nutrient requirements and produces wood, fruit shells, seed husks, seed oil, and press-cake which are potential sources of renewable energy. *J. curcas* seed contains 35 % oil which is an eco-friendly renewable energy resource and has properties highly suited for making biodiesel which emits less greenhouse gases (GHG) than fossil diesel fuel and if well exploited can help most of the countries in the world to meet their fuel requirements. However, several issues such as energy versus food, energy and environmental impacts need to be addressed.

Keywords *Jatropha curcas* • Fossil fuel • Global warming • Alternate energy

17.1 Introduction

Global energy reserves and their use have been and still are most debated and researched issues worldwide for a long time. Globally there is rapid multiplication of energy demand as a result of greater than ever increasing population and development rate. Patently current global trends of energy supply and consumption are economically, socially, and environmentally unsustainable which has stimulated the necessity of finding alternatives. Recognition of the facts that fossil-fuel-based can hardly sustain the same outsize share which once they occupied in global energy consumption and that growing green house gas (GHG) emissions from their use are driving climate change and impacting global warming have focused world attention on the need to reduce fossil fuel dependence and stimulated the necessity to look for alternatives. The depletion of fossil fuels reserves has reached to such an extent that they are unlikely going to fulfill future needs (Dowlatabadi 2006) and also wide spread awareness about harmful impacts their use have on environment can no longer be neglected (IPCC 2007). In order to deal with the world energy crisis, both in developing and developed countries, reduction in energy consumption and search for alternatives to fossil fuels are gaining serious attention (FAO 2008) so that affordable, reliable, low-carbon efficient, and environmentally benevolent energy supply system can be secured. As such switching to such renewable energy has been provoked which can reduce global warming and curb current trends (IEA 2006). There are several renewable alternative energy sources to fossil fuels such as wind, sun, water, nuclear and biomass. The pursuit for alternate energy source, poses momentous question that which choice could alleviate successfully current fossil energy crisis and allied climatic problems importantly global warming mitigation, and improve life quality globally. Numerous solutions which may vary according to regional peculiarities taking into account economic, environmental, and social spheres, seem available nowadays to countenance worldwide energy hunger, without compromising the health of the planet.

Biofuels as renewable energy substitutes to fossil fuels have attracted great attention worldwide because of their production ease, environmental benefits and sustainable supply advantages (Jingura et al. 2010). Over 14 % of world's energy demand is catered by biomass resources (McKendry 2002; Demirbaş and Demirbaş 2003). For many years now, biofuels have been a theme of lot of claims. FAO has classified biofuels into two groups; First-generation and Second-generation biofuels. Those biofuels which are mainly derived from food crops, including starch and sugar based bioethanol and oilseed are termed as First-generation biofuels (Pramanik 2003; Bozbas 2008); while biofuels derived from non-food crop forestry and agricultural products are termed as second-generation biofuels (FAO 2008, Jinguara et al. 2010). On one hand, biofuels from both from first and second generation provide an option to reduce dependence on fossil fuel and combat adverse climate change, but directly or indirectly at the same time can affect food security. The main concerns which looms with fuels coming from food crops is that apart from competition for land, soil nutrients and water, they can goad increase in food price. Also repeated monoculture can lead to biodiversity loss, reduction in soil resources that are of vital importance as well as water use efficiency, which at present is the concern in non-industrialized countries, where for introduction and cultivation of bioenergy plantations, demand for large land area is increasing (Demirbaş and Demirbaş 2003; Daey Ouwens et al. 2007; von Braun and Meinzen-Dick 2009).

As far as second-generation biofuels are concerned, their use seems difficult owing to lack of technology knowledge (FAO 2008). Though second-generation biofuels represent a viable option to tone down fossil fuel dependence, reduce global warming, and also might not affect food availability; the selection of the fuel crop, their competition for land, mineral resources and water, and its management in the cultivation and processing steps are the major concerns. Moreover less efficiency or usefulness of some bioenergy crops have rendered their use controversial while some others call for more research before being used as an energy feedstock.

Fortunately, some shrubs and spermophytic trees offer an option to be utilized as biofuels. With no competing food uses, this characteristic turns attention to *Jatropha curcas*, as one of the potential renewable energy source, which thrives in subtropical and tropical climates across the world (Martin and Mayeux 1985; Jones and Miller 1991; Openshaw 2000, Daey Ouwens et al. 2007; Achten et al. 2008). Since without detoxification, *Jatropha* oil cannot be used for nutritional purposes, its use becomes more attractive as energy source.

17.2 *Jatropha curcas*: Occurrence and Morphology

J. curcas L., a potential bioenergy crop 70 million years old, is a monoecious, deciduous perennial small tree or shrub belonging to family Euphorbiaceae, to the tribe Jatropheae of the subfamily Crotonoideae. In 1737 Karl von Linne first described and in 1753 classified *J. curcas*. The genus name *Jatropha* comes from the Greek words "iatros" meaning doctor and "trophe" meaning food. It is commonly known as "Physic nut" in English and "Ricino d'inferno" in Italy. Southern Mexico and parts of central America are believed to be centers of origin of *Jatropha* (Dehgan and Webster 1979). The plant was later spread by the Portuguese settlers to other continents of the world (Gubitz et al. 1999). However in some parts of the world, including the United States, Australia, South Africa, and Puerto Rico, *Jatropha* is recognized as an invasive species (Global Invasive Species Programme 2008).

The plant initially develops five roots; one thick deep primary taproot and four lateral roots, followed by many straight secondary roots (Heller 1996). The stem arises from perennial root stock, has reddish or grey bark which exudates latex white in color. Generally, the tree attains a height between 6.0 and 18.0 ft but under favorable conditions can grow up to 30.0 ft. Leaves are green, simple, petiolated, having 3–5 lobed ovate lamina and are alternate in arrangement. Inflorescence is terminal bearing unisexual flowers. The fruit is ellipsoid capsule, containing three seeds. Seeds are 1–2 cm long, granular, and black in color. Agents of pollination are beetles, honeybees, and moths (Bhattacharya et al. 2005; Henning 2007). In flowering, the male flowers open 1 or 2 days after opening of female ones, with former lasting only for 1 day. Plants bear fruits from midsummer to late winter. In indoor cultivation seed never sets unless the flowers are pollinated by hand.

The seeds become mature in 2–4 months with the capsule changing from green to yellow. Upon seed maturity, fleshy exocarp dries and three bivalved cocci are formed. The seeds contain oil which contains 21 % saturated and 79 % unsaturated fatty acids (Heller 1996; Gubitz et al. 1999; Deng et al. 2010). Linoleic and oleic acids are the main components of oil (List and Horhammer 1979). The seeds also contain fructose, glucose, galactose, raffinose, saccharose, stachyose, and protein. Arachidic, curcasin, myristic, stearic, and palmitic acids are also present in *Jatropha* (Perry 1980). *Jatropha* also contains toxic compounds such as curcin and phorbolester.

17.3 Plantation and Ecological Requirements of *Jatropha curcas*

The main inputs for *J. curcas* production are land, local climatic conditions, plantation establishment, and management practices. The outputs are the fruits, seeds, wood, and other biomass elements (Achten et al. 2008).

17.3.1 Soil Requirement

J. curcas is adapted to wide range of soils and can thrive on degraded, sandy, saline soils and even on rock cervices, but shows luxurious growth on drained soils with good aeration (Dagar et al. 2006). Although the plant can grow on low nutrient content marginal soils, such as along streams, canals, river embankments, coastal lines, along roads and railway lines, the crop however requires phosphorus and nitrogen fertilization in order to support a high biomass production (Daey Ouwens et al. 2007). *Jatropha* grows best on loamy soil while as clay soils become unsuitable, if climatic conditions cause water logging. Soil pH between 5.5 and 9.0 is considered optimal for growth (Foidl et al. 1996). Nutrient availability is affected significantly by soil proprieties such as EC, pH, $CaCO_3$, organic C, and clay.

17.3.2 Climate

Jatropha thrives well in warm weather in temperature range of 20–27 °C and can tolerate severe heat. Although vulnerable to freeze damage, *Jatropha* can withstand short duration light frost. In extreme cold conditions, the plant drops its leaves. Tolerance to cold temperature increases with increase in age with older trees being more tolerant. Black frost severely damages older plants and can kill young plants (Nahar and Ozores-Hampton 2007). Little rain in summers favors proper seed germination. A decrease in temperature on onset of rainy season induces flowering. *Jatropha* can be cultivated successfully in areas with sparse to heavy rainfall (Gubitz et al. 1999). *Jatropha* can be grown in subtropical/tropic areas, with 200–1,500 mm rainfall per annum (The Biomass Project 2000).

17.3.3 Propagation

Seeds and plant cuttings are means of propagation. Seeds or cutting twigs can be planted directly in the field. Germination is quick and better if seeds are soaked in cold water for 24 h (Kaushik et al. 2007). Nursery-grown seedlings produce seeds earlier than direct seeded ones and also have survival rate higher than later (Daey Ouwens et al. 2007). Seedlings can be planted in the field at the onset of the rains (Heller 1996). Taproot development in seed raised plants confers more drought resistance to them in comparison to plants raised from cuttings (Achten et al. 2007) as it enables plant to extort moisture from deeper soil stratum. In intercropping systems, the tap root also reduces competition for nutrients and water between the different crops.

17.3.4 Irrigation

Irrigation largely depends on local climatic conditions. *Jatropha* is well adapted to dry soils and can stand without water for long periods (as long as 2 years) and can resume growth once rains return (Nahar 2011). *Jatropha* with high-quality seeds has an average 1 L/plant/day water consumption rate throughout the growing season (PSO 2010). Although *J. curcas* by shedding its leaves, can survive on precipitation as low as 300 mm, but under such conditions it does not produce well. To produce healthy fruits, an indicative of economically sustainable oil production, minimum and optimal rainfalls are 600 mm ha^{-1} y^{-1} and 1,000–1,500 mm ha^{-1} y^{-1} (Henning 2007). The crop should be artificially irrigated during dry period whenever required.

17.3.5 Fertilization

Jatropha is adapted to low soil fertility, however organic or artificial fertilization might be required for plantations aiming at oil production. Application of N-P-K and cow manure annually is highly recommended (PSO 2010). *Jatropha* plantations on poor-quality soils when fertilized with phosphorus (P), nitrogen, calcium (Ca), potassium (K), magnesium (Mg), and sulfur (S) rich fertilizers produce higher yield than *Jatropha* planted on soils without fertilizers (Achten et al. 2008; Mohapatra and Panda 2011; Moore et al. 2011).

17.3.6 Pruning

Pruning should be done once a year. Lateral shoots are requisite for maximum sprouting flowers and seed production (Gour 2006). Pruning is very essential as it determines seed yield to a large extent and can facilitate mechanical and manual harvesting of fruits. Number of flowering branches is determined by canopy size. Sufficient flowering branches can result apparently from smaller plants on high densities and large plants on a low planting density (Daey Ouwens et al. 2007). Ideal time for pruning is during dry season when the tree enters a period of dormancy and sheds its leaves (Kaushik et al. 2007).

17.3.7 Weed Control

Weeding is an important issue particularly during early stages of plant growth as it reduces competition for acquiring nutrients. Weeding can be done either by applying herbicides or by soil surface plowing. The most common herbicides used are oxyfluorfen and pendimethalin (Rocha 2010). Number of times weeding should be performed mainly depends on the season and field conditions with four times a year being ideal. Fertilization, pruning, and regular weeding are hence important cultural practices in new plantations (Henning 2007).

17.3.8 Harvesting

Jatropha becomes highly productive in 4–5 years time. Flowering mainly depends on agro-climatic conditions and location. Generally, flowers are produced in first 16–17 weeks by cloned *Jatropha* seedlings. Once mature, *Jatropha* fruits can be harvested mechanically which has several benefits, such as continuous and selective harvesting, labor reduction, cost control, on demand harvest ability and reliability and efficiency.

17.4 Energy Constituents of *Jatropha curcas*

The energy constituents of *J. curcas* are wood, fruit as whole and parts of fruit such as shells, seed husks, and kernel (Singh et al. 2008) which are direct sources of fuel. All these products have different energy values. The energy value of these products increases upon processing, but unless a use for by-products is found a decrease in overall energy availability occurs. A schematic illustration of these energy components is shown in Fig. 17.1.

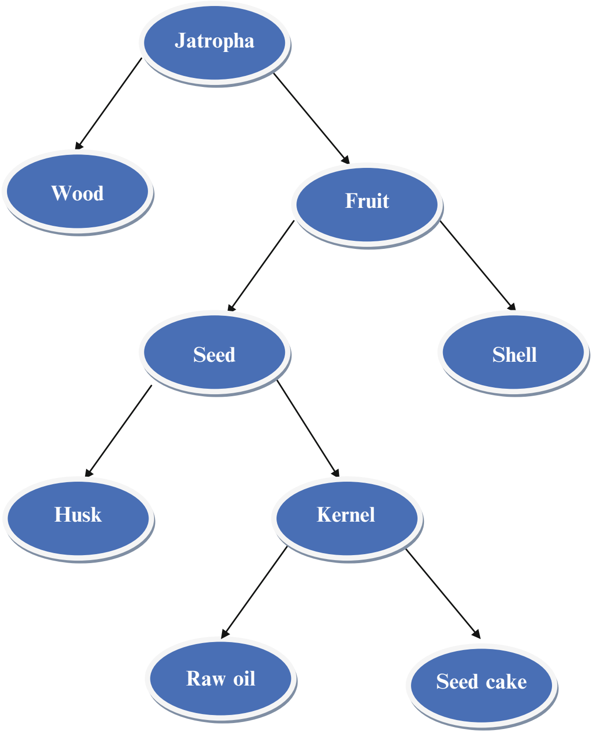

Fig. 17.1 Energy components of *Jatropha curcas*

17.4.1 The Fruit

The fruits of *J. curcas* are about 2.5 cm long and are ovoid in shape. Average fruit yields are about 3.5 tons ha^{-1}, and, yields of 1–1.25 tons ha^{-1} are common when grown in wastelands under rain-fed conditions (Kumar et al. 2003). The fruit is made up of the shell and seeds. Two to three seeds are present in each fruit. It has nearly 400–425 fruits per kg and 1,500–1,600 seeds per kg weight (Singh et al. 2008). In dry *J. curcas* fruit, shell accounts for 35–40 % and seed for 60–65 % of weight (Vyas and Singh 2007). All these components of the *J. curcas* fruit have been used as sources of bioenergy.

17.4.2 The Shell

The shell is removed mechanically during oil extraction from the fruit. One hectare of land under *Jatropha* plantation produces about one ton of shell material which can be used as energy source. The shell contains 34 % cellulose, 12 % lignin, and 10 % hemicelluloses. The shells have 16 % fixed carbon content, 15 % Ash, and 69 % volatile matter respectively (Singh et al. 2008). The *J. curcas* shell has caloric value of 16.9 MJ kg^{-1} (Vyas and Singh 2007) to 17.2 MJ kg^{-1} (Openshaw 2000) implying one hectare plantations can supply energy of 16.9–17.2 GJ vice shells alone. *J. curcas* shells owing to their chemical composition are also a good feedstock for briquetting, bio-methanation and pyrolysis (Singh et al. 2008; Manurung et al. 2009; Sotolongo et al. 2009).

17.4.3 Seeds

The seed accounts for 70 % weight of the fruit and is made of about kernel and husk (Singh et al. 2008). The seed is about 17.5 mm in length and 11.5 mm width and contains oil which is about 34 % of its total weight (Singh et al. 2008). The *Jatrpoha* fruit seeds have an energy value of 24 MJ kg^{-1}, which is higher than coal (Augustus and Jayabalan 2002). Seed kernel represents 70 % of seed weight and has calorific value of 29.8 MJ kg^{-1} (Openshaw 2000) to 31.6 MJ kg^{-1} (Martinez-Herrera et al. 2006). *J. curcas* seed contains about 42 % seed husks. The seed husks contain 4 % ash, 25 % fixed carbon, and 71 % volatile matter (Vyas and Singh 2007; Singh et al. 2009). The seed husk has calorific value of 16 MJ kg^{-1} (Vyas and Singh 2007). Seed husks have a high bulk density (223 kg m^{-3}) which makes them acquiescent to briquetting and hence an energy source. Syngas is obtained from *J. curcas* seed in an open core down draft gasifier (Vyas and Singh 2007).

Table 17.1 Fuel properties of Jatropha raw oil and fossil diesel

	Jatropha oil	Fossil diesel	References
Calorific value	39.77	42.4	Rosenblum (2000)
Cetane number	45–62	45–55	Nahar and Sunny (2011)
Density	884	840	Basker (1993), Heller (1996)
Flash point (°C)	235–240	50	Islam et al. (2011)
Specific gravity	0.87	0.91	–
Sulfur weight (%)	0.04–0.13	1.2	Heller (1996)
Viscosity	49.93	4.59	Basker (1993)

17.4.4 Seed Oil

Seed contains about 35–40 % oil (Kandpal and Madan 1995; Jongschaap et al. 2007), which can be extracted by pressure, heat, or solvents. One hectare of *Jatropha* plantation can produce about 900 kg of oil. Raw seed oil of *J. curcas* has been extensively studied because of its promising potential to substitute fossil diesel (Achten et al. 2008). *J. curcas* raw oil is cost effective, environmentally safe, renewable nonconventional source of energy and has fuel properties comparable to fossil diesel (Table 17.1).

These properties, particularly calorific value of *J. curcas* oil which is akin to fossil diesel and greater than coal (Gubitz et al. 1999; Rosenblum 2000; Sotolongo et al. 2009), vindicates its use both in unmodified and modified diesel engines as a substitute for petro-diesel.

However the high kinematic viscosity of raw oil 49.93 $mm^2 s^{-1}$ compared to diesel fuel which is 1.3–4.1 $mm^2 s^{-1}$ results in less satisfactory use of raw oil in diesel engines (Shahid and Jamal 2008; Kywe and Oo 2009) as it causes several problems in diesel engines such as increasing fuel spray and reduction in fuel atomization, which causes choking of injectors, engine deposits, thickening of lubricating oil, and piston ring sticking (Shahid and Jamal 2008; Kywe and Oo 2009). Notwithstanding these problems, raw oil is used with success in slow-speed stationary diesel engines such as generators and pumps (Tomomatsu and Brent 2007). Prasad et al. (2000) reported that use of raw *J. curcas* oil in diesel engine results in lower GHG emissions than fossil diesel which is beneficial for environment. To improve the use of raw *Jatropha oil* as fuel, its viscosity is reduced by either blending raw oil with fossil diesel or preheating it (Achten et al. 2008). Apart from transportation fuel, raw oil also finds its use in lamps and cooking stoves. Thus, the most common uses of raw *J. curcas* oil are lighting lamps combustion, in stationary diesel engines and cooking stoves; however to counter low absorbance capacity and high viscosity of oil, they have to be modified slightly.

17.4.4.1 Production of Biodiesel from *J. curcas* Seed Oil

Jatropha seed oil in raw form without any modification can be used directly in agricultural machinery. However, conversion to biodiesel first, will result in very little long-term problems (Harwood 1984). High content of unsaturated fatty acids (78–84 %) makes *J. curcas* seed oil suitable for biodiesel production (Salimon and Abdullah 2008). Pure biodiesel and its blends with petro-diesel can be used in any petroleum diesel engine without the need for modification. The oil can be used in machines and engines as a direct replacement for fuel, in addition to many other commercial and industrial uses (Cerrate et al. 2006; Ndong et al. 2009).

The most common technology to produce biodiesel *J. curcas* oil is Trans-esterification (Meher et al. 2006). The *J. curcas* oil in trans-esterified form gives comparable results to fossil diesel (Prasad et al. 2000). The suitability of *Jatropha* oil for trans-esterification into biodiesel has been demonstrated (Achten et al. 2008; Shahid and Jamal 2008). In trans-esterification process, under heat using alcohol and a strong base usually NaOH as catalyst, *J. curcas* oil is converted to esters and glycerine. The ester usually formed is methyl esters (Singh et al. 2008). The process involves three successive reversible reactions. In the first reaction diglycerides are formed from triglycerides, and then former is converted to monoglycerides which finally forms glycerine. In all the three reactions, esters are produced. Raw oil type, temperature of reaction, alcohol to ratio, catalyst type and quantity, and mixing intensity are different variables in process of trans-esterification (Marchetti et al. 2007). Acids, alkali, lipases, or supercritical alcohol all can be used as catalysts. The stoichiometric ratio of oil and alcohol is usually 1:3 (Marchetti et al. 2007). Ethanol is preferred usually as it is CO_2 neutral and also renewable. Trans-esterification transforms 92–98 % of the original oil to biodiesel and also reduces its viscosity from 49.93 to 4.59 $mm^2\ s^{-1}$. Thus one hectare of *Jatropha* plantation can produce about 828 kg biodiesel, representing about 32 GJ ha^{-1} energy. The economic evaluation showed that the production of biodiesel from *Jatropha* oil is profitable provided the by-products of production process are also commercialized as valuable energy products (Eisa 1997; Foidl and Eder 1997).

17.4.5 Press-Cake

Press-cake is residue matter which remains as a by-product after oil extraction from the *Jatropha* seeds. The cake is made up of the seed husks and kernel and contains mainly proteins and carbohydrates. About 50–75 % of seed weight remains as press-cake (Staubmann et al. 1997; Singh et al. 2008). Press-cake contains oil which is about 9–12 % of its weight (Achten et al. 2008). Press-cake has about 18.2 MJ kg^{-1} gross energy value (Achten et al. 2008). Press-cake contains 6 % nitrogen 2.8 % phosphorus, and 0.9 % potassium respectively (Del Greco and Rademaker 1998). Out of total 94 % solids present in press-cake, 93 % are volatile solids. One hectare

Jatropha plantation can produce about one ton of press-cake which can supply about 18.2 GJ of energy.

The press-cake has high organic content making it a good potential entity for production of biogas that can be used to supply electricity, process steam, heat, and methanol. Biogas is produced by digestion of adequate amounts of carbohydrates and proteins present in press-cake by anaerobic bacteria (Staubmann et al. 1997; Singh et al. 2008). Staubmann et al. (1997) using pig manure as inoculums, obtained 0.446 m^3 of biogas containing 70 % methane per kg of dry seed press-cake. Singh et al. (2008) observed *J. curcas* press-cake produced 60 % higher biogas than cattle dung and contains 66 % methane. *Jatropha* press-cake via pyrolytic processes can be materialized for biofuel production (Demirbaş 2002). Cellulose, hemicellulose, and lignin, which are major components of press-cake during pyrolysis are broken down to produce char, bio-oils, and gas which are important energy carriers. Press-cake if present in large quantities can be as a fuel for steam turbines to generate electricity.

17.4.6 Woody Products

Wood is far and wide being used as energy source. Pruning is used to prop up lateral branching in *Jatropha*. On average, one hectare land has about 2,500 *Jatropha* trees (Gour 2006) which on pruning produces substantial amounts of wood. One hectare of *Jatropha* plantation produces about 20 tons of woody biomass over a period of 6 years (Sotolongo et al. 2009).

Each *Jatropha* plant at about 7 years of growth produces about 200 kg of biomass with about 25 % dry matter content (Benge 2006). This yields about 80 ton ha^{-1} dry matter content of wood from cuttings done once every 10 years. The wood has an energy value of 15.5 MJ kg^{-1} (Openshaw 2000; Sotolongo et al. 2009). With this value it can supply 1.2 PJ of energy.

17.5 Net Energy Output

Net energy gain (NEG) one of the accepted indices for analyzing biofuel energy efficiency is the difference between the total energy outputs and total energy inputs (Nguyen et al. 2007). Net energy ratio (NER), an indicator for comparing the energy efficiency of biofuels is the ratio of total energy outputs to total energy inputs. Energy balance of *J. curcas* biodiesel is found to be positive. Life cycle analysis of *J. curcas* has shown that it has positive NEG (Prueksakorn and Gheewala 2008; Preuksakorn et al. 2010). The NER ratio of *J. curcas* depends on whether the plantation is annual or perennial. Preuksakorn et al. (2010) reported NER values for annual and perennial plantations are 7.5 and 6, respectively. The total energy output is 121.2 GJ for annual plantation and 101 GJ for perennial plantation.

17.6 *Jatropha curcas* and Environmental Concerns

The impact of biofuels on environment cannot be neglected. The main issues concerning environmental impacts of *J. curcas* production system are the impact on global warming, biodiversity, and land use. GHG emissions from biodiesel are found to be less compared to fossil diesel (Tobin and Fulford 2005; Prueksakorn and Gheewala 2006; Silitonga et al. 2011) and hence have less negative impact on environment. In comparison to fossil diesel production and use (Sheehan et al. 1998), GHG emissions from biodiesel production and use (Wenzel et al. 2000; IPCC 2001) have 73 % less global warming potential (Prueksakorn and Gheewala 2006; Tiwari et al. 2007) (Fig. 17.2). Over 90 % of GHG are emitted during use phase from both diesel and biodiesel.

Biodiesel produced by *Jatropha* emits 100 % less SO_2 than fossil diesel. Since biodiesel is of biomass origin, carbon dioxide emissions from its use in engines are considered GHG neutral as *Jatropha* plants during growth absorb them from the atmosphere. Furthermore, every year around 7.9 kg of CO_2 is absorbed by a full-grown *Jatropha* plant (PSO 2010). Thus one hectare *Jatropha* plantation can potentially sequester about 18.1 ton of GHG from environment per year (Nhar and Homptan 2011).

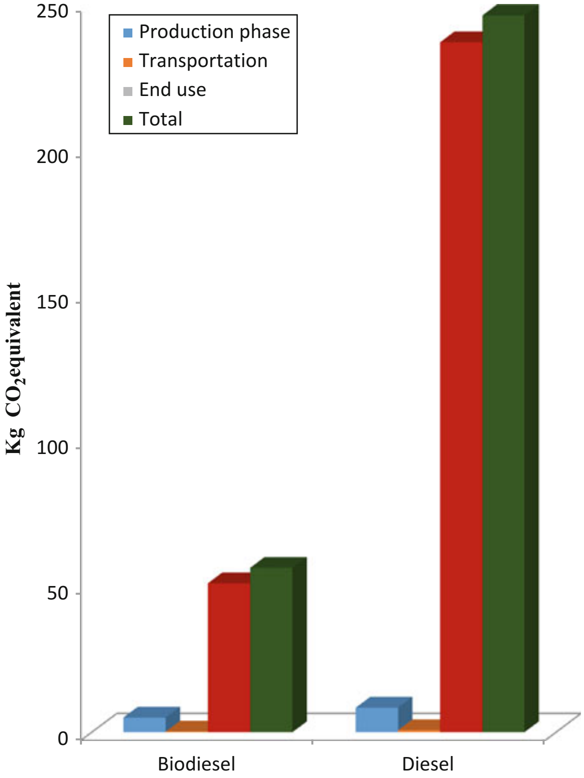

Fig. 17.2 Comparison of GHG emission from life cycle of biodiesel and diesel (*source*: Prueksakorn and Gheewala 2006)

Although as compared to fossil diesel, biodiesel production from *J. curcas* showed a reduction of GHG emissions but reallocating of (semi-) natural forest for *J. curcas* cultivation will result in negative effect on the overall GHGs balance.

Since at most growing areas *Jatropha* is an exotic species, introduction and cultivation of *J. curcas* is expected to have negative impact on biodiversity (Achten et al. 2008). As *Jatropha* is believed to sequestrate carbon, reduce/prevent soil erosion and hence leading to soil structure improvement, its land impact on soil due to *Jatropha* land occupation is expected to be positive.

17.7 Non-energy Uses of *J. curcas*

J. curcas apart from its use as a biofuel can be put to different uses (Fig. 17.3) (Shanker and Dhyani 2006; Kumar and Sharma 2008). The extract from oil has been used as an insecticide in the control of pests of potato, pulses, and cotton such as cotton bollworm (Kaushik and Kumar 2004). The glycerin, a by-product of the trans-esterification process, can be used to make high-quality soap. Press-cake derived from *J. curcas* can be used as animal and human feed after isolating toxic phorbol esters. The physic nut seed once boiled and roasted is eaten as food in Mexico (Delgado and Parado 1989). Press seed cake can be used as fertilizer owing to its high organic content. *Jatroph*a since ages have found its use in medicine (Dalziel 1955). Seeds are used to treat jaundice, gout, eczema, arthirits, and dermatomucosal diseases. Plant extracts are used to treat cuts, burns, allergies, scabies, leprosy, leco-derma, and small pox. Curcacycline A and some alkaloids such as jatrophine, curcain, and jatropham obtained from *Jatropha* are believed to have antitumor properties (Van den Berg et al. 1995; Thomas et al. 2008) and are used in treatment of HIV and tumor. The roots are reported as an antidote for snake-bites. *J. curcas* is also used as hedging plant in agricultural fields for protection against damage by livestock.

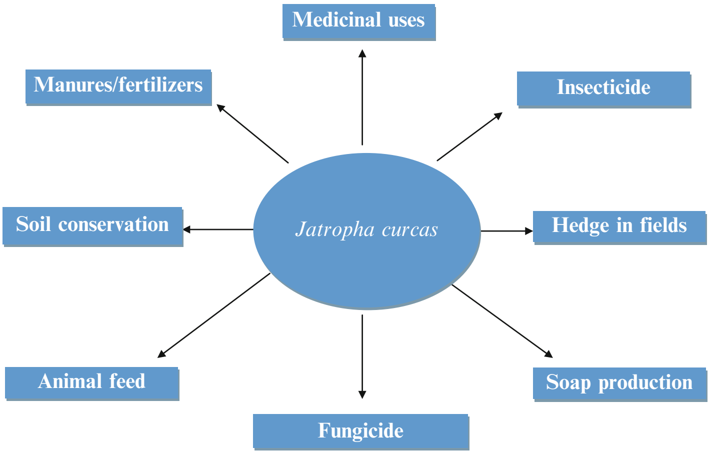

Fig. 17.3 Some essential uses of *J. curcas*

17.8 Conclusions & Future Endeavor

J. curcas owing to its remarkable features appears to be a suitable valuable option to meet energy demands world. Low technology inputs are requirements during cultivation step, where most of the management actions are done manually (pruning and harvesting, mainly), to harness oil reduces the investment required to generate a unit quantity of biofuels.

Multiple energy carriers of *Jatropha* plants and oil expelled from its seeds are not only useful in mitigating the environmental pollution but also support for employment generation and entrepreneurship development. Apart from *Jatropha* use as potential energy crop, industrial application and soil conservation measures can also promote its cultivation on the barren and unused land. As energy crop, blending with petro-diesel and proper processing has already demonstrated its use as an alternative fuel in motive and stationary diesel engines. Proper commercialization and utilization of by-products of biodiesel such as press-cake and glycerine oil cake can make *Jatropha* cultivation and oil production economically more feasible.

A better overall efficient development of *J. curcas* production system can be achieved, if knowledge gulf regarding fundamental agronomic characteristics, employment of best cultivation and management practices, the improvement of energy carriers and processing of oil protocols and the input/output balances at all these stages are addressed into. A deep analysis of cultivation processes will help in understanding intercropping and monoculture growth variables as well as looking for sustainability indicators in these two production systems.

A better in-depth understanding of the eco-physiology of the plant is required so to gain insight into its nutrient requirements for maximum net primary productivity and oil production, nutrient cycling, impact on biota of soil (Achten et al. 2008), plant-soil relationship, and foliar nutrient content of *Jatropha* (Daey Ouwens et al. 2007; Chaudhary et al. 2008) which is essential for domestication of the plant, its water use efficiencies, its potential and actual energy.

Apart from these mentioned concern, also environmental impact assessments have not been carried out exhaustively yet (Achten et al. 2008). Impacts on soil structure and its water-holding capacity, organic content and soil biological activity needs detailed investigation as well. Research for understanding plant energy efficiency under different agro-climatic condition and to improve its yield needs to be carried out (Daey Ouwens et al. 2007).

Jatropha bioenergy development has many potential benefits although having some negative impacts also. Development of this sector calls for execution of well balanced policies which can reduce the negative effects and maximize positive ones. Of positive effects some are:

1. Agricultural output diversification
2. Higher income for farmers
3. Poverty reduction
4. Rural development stimulation,
5. Employment in rural areas

6. Infrastructure development
7. Increased investment in land rehabilitation
8. Lower GHG emissions
9. Generation of new revenues from agricultural residues, wood use, and from carbon credits

On the other hand, some potential negative effects are:

1. Replacement of subsistence farmland with energy crops will result in reduction in local food availability.
2. Increase in deforestation to meet land demand for energy crops will lead to forest ecosystems degradation and decrease in biodiversity as well.
3. Degradation of soil fertility and quality due to intensive cultivation of bioenergy crops.
4. Pollutants as well as GHG emissions will register an increase.
5. Modifications to requirements for vehicles and fuel infrastructure.

Nonetheless, with the current emphasis on alternative renewable fuels due to the soaring fossil energy prices as their reserves continue to dwindle and the perspective on global climate change, the potential role of *Jatropha* to meet energy services of world will warrant it beyond doubt to be one of the energy plants of future.

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Chapter 18
Algal Biomass Production Using Waste Water

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_18,

Abstract Microalgae have emerged as a potential feedstock for sustainable energy in recent years because of their higher biomass productivity and ability to eradicate air and water pollutants via bio-extraction. Augmentation of lipid contents through metabolic pathway engineering and growth conditions optimization along with the efficient harvesting and processing technologies are leading goals of today's microalgae research. Although microalgae have huge potential for biodiesel production yet there are several challenges for making it commercially available. Among several others, extensive water requirement for microalgae cultivation is a major challenge because water is one of the basic requirements for algal cultivation. This chapter describes the current status of algal biomass production and its biotechnological potential as well as exploitation for biofuel production using waste water. The key challenges to algal biomass production on commercial scale, biorefinery concept, and future perspective of the technology are also discussed.

Keywords Microalgae • Biomass • Biofuel • Waste water • Bioremediation • Biorefinery

18.1 Microalgae as a Potential Feedstock

Petroleum-based fuels are no more sustainable for industrial and transportation purposes due to emission of green-house gases (GHGs) and other poisonous gases from their burning, increasing demand and depleting natural resources. Moreover, CO_2 (a GHG) buildup due to their combustion, is a serious environmental threat. These facts are leading towards the development of alternative energy sources for ensured environmental sustainability. Therefore, renewable raw materials which include edible plants/seeds (mustard, corn, canola, palm oil, soybean, sunflower, coconut) and non-edible plants/seeds oils (jojoba, castor, jatropha, pongame, *Citrus reticulate*, *Cucumis melo*, *Moringa oleifera*) and waste oils have been explored for the biodiesel production (Rashid et al. 2008, 2011, 2012, 2013; Sharma et al. 2009; Yadav et al. 2009; Diaz and Borges 2012). However, there are several limitations with these resources; (1) competition with human food demand, (2) use of arable land, (3) requirements of huge amounts of fresh irrigation water, (4) lower yield of biofuel molecules, (5) long cultivation periods and low seasonal production (e.g., once a year). Alternatively, microalgae have received massive attention as an alternative, among the many options. They are presumably the cheapest source among all other renewable sources for biodiesel production (Chisti 2007; Petkov et al. 2012).

Microalgae are tiny (unicellular or filamentous) photosynthetic factories and their photosynthetic competence is remarkably higher than terrestrial plants. Growth rate and oil productivity of microalgae is considerably higher (Fig. 18.1) than the oil productivity of the best available oil producing crops (Chisti 2007; Wu et al. 2012). They are believed to produce up to 300 times more oil than traditional energy crops on the basis of acreage usage (Chisti 2007; Schenk et al. 2008). The average lipid

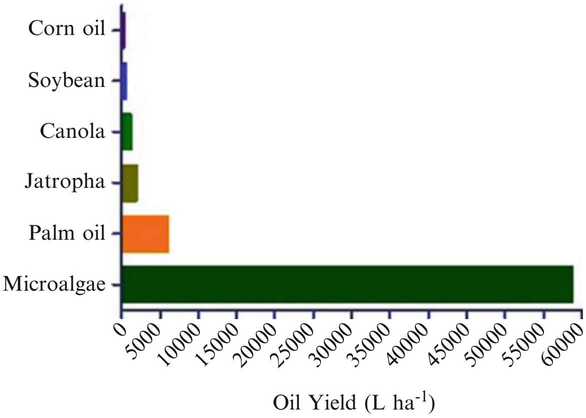

Fig. 18.1 Comparison of oil productivity of traditional energy crops with microalgae [we have considered 30 % oil contents in microalgae because of lower lipid contents in waste water] (Wu et al. 2012)

Table 18.1 Microalgae producing >30 % lipids contents (Wu et al. 2012)

Sr. #	Microalgae	% Lipid contents (dry mass basis)
1.	*Botryococcus braunii*	25–80
2.	*Chlorella emersonii*	28–32
3.	*Chlorella protothecoides*	57.9
4.	*Cylindrotheca* sp.	16–37
5.	*Dunaliella tertiolecta*	35.6
6.	*Hormidium* sp.	38
7.	*Isochrysis* sp.	25–33
8.	*Nannochloris* sp.	30–50
9.	*Nannochloropsis* sp.	31–68
10.	*Neochloris oleoabundans*	35–54
11.	*Nitzschia* sp.	45–47
12.	*Phaeodactylum tricornutum*	20–30
13.	*Pleurochrysis carterae*	30–50
14.	*Prymnesium parvum*	22–38
15.	*Scenedesmus dimorphus*	16–40
16.	*Schizochytrium* sp.	50–77

contents of microalgae range between 1 and 70 % (~30 %, when grown in waste water) but under the optimized conditions some species (*Botryococcus braunii*) can yield up to 80 % of oil (Table 18.1) on dry biomass basis (Schenk et al. 2008; Wu et al. 2012). Moreover, they lack lignin in contrast to higher plants, so are easily degradable. Most importantly, they do not compete with food crops and can be cultivated using non-arable (saline, sodic, water-logged soils) lands, saline/waste water, and artificial beds, e.g., compact bioreactors (Musharraf et al. 2012). They produce remarkable quantity of polysaccharides (sugars) and proteins along with the lipids, so the left-over biomass (after oil extraction) may be exploited for production of bio-ethanol, biogas, bio-fertilizers as well as to enhance to protein and mineral contents of the animal feed (Gill et al. 2013). Microalgae have potential to sequester the atmospheric CO_2 at the rate as high as 1.8 kg of CO_2 per kg of dry biomass (Wang et al. 2008). This makes the algal fuels carbon neutral and in certain cases algal fuel production may earn salable carbon credits to meet Kyoto targets.

18.2 Biomass Production Systems

Here we discussed different system of microalgal biomass production, their problems and future considerations, which is summarized in Table 18.2.

18.2.1 Open Pond Production

Open pond production is achieved through using a special type of pond called "raceway pond" that is a shallow artificial pond and is commonly used for the cultivation of microalgae. The pond is formed into a rectangular grid, containing an oval channel resembling to an automotive raceway circuit. From an aerial view, many ponds look like a rounded-corner maze (like a puzzle in which we find the way in a closed circuit). It contains a paddle wheel to make the water flow continuously around the circuit (Fig. 18.2).

Raceway ponds (RP) have been used for mass culture of microalgae (Acien Fernandez et al. 1999) since last six decades. A best suited RP for microalgal cultivation is usually 0.3 m deep. Paddle wheel provides mixing and circulation of water in the pond. They are built with solid concrete to avoid water seepage and the floor is lined with a white sheet for enhanced light reflection (to improve the light use efficiency in photosynthesis). Culture is fed continuously in front of paddle wheel during day light and broth is harvested on completion of the loop behind the paddle wheel. The continuous (24/7) operation of paddle wheel prevents the culture sedimentation (Spolaore et al. 2006). Evaporation of water from the RP is a necessary evil, because it is source of water loss but also helps to maintain temperature. Because, in summer cooling effect of evaporation lowers the temperature and in winter heat-retaining capacity of water does not allow the temperature to go too low. Overall, mitigation of water loss in raceway ponds due to seepage and evaporation is an engineering challenge.

Contamination of heterotrophic microbes is another offending challenge in open cultivation systems since it may strongly influence microalgae productivity as the contaminant microbes (bacteria, fungi etc.) become parasite on microalgae. Moreover, RPs may have poor mixing of atmospheric CO_2 and least penetration of sunlight (because waste water has a dark color) keeping most of the cells in dark zone. Subsequently, low biomass is produced as compared to the theoretical yield calculated for a raceway pond based on its engineering dimensions. The mixing may be improved by using an aeration system and light penetration may be enhanced by decreasing the depth of pond (maybe 0.2 m instead of 0.3 m). Despite these facts,

Table 18.2 Comparison of algal cultivation systems

Cultivation system	Type of bioreactor	Advantages/benefits	Challenges/problems	Considerations/future prospects
Open Cultivation system	Raceway ponds	• Cheaper (both construction and running)	• Biomass productivity may be low	• Although biomass productivity is low yet comparatively they are still the cheapest way, so overall cost benefit ratio may be considered
		• Easy maintenance and cleanliness	• Poor mixing of light and CO_2 utilization may be inefficient	• Bio-preservative microalgae strains may be isolated or engineered to put contamination risk at bay
		• Non-arable land may be used	• Contamination risk	
		• Feasible for massive cultivation	• Difficult harvesting	
			• Seasonal variations threat	
			• Environment is not controlled	
	High rate algal ponds	• Lower input cost because several nutrients are provided by waste water	• Higher contamination risk (may be covered by using a pre-disinfection step)	• Selection or improvement of algal strains capable to cope with contamination by producing antimicrobial agents to avoid pre-disinfection steps
		• Gaseous mixing is efficient because CO_2 is produced	• Growth productivity may be low, but considering biomass production as a by-product of waste water treatment, overall system is efficient	• Instead of using unicellular microalgae, filamentous microalgae or macro-algae may be preferred for biomass production in HRAPs for easy harvesting
		• O_2 is consumed by microbial activity • Economically feasible as a biorefinery approach • Consortia of microalgae may be used	• Biomass harvesting is expensive but may be covered because treatment of waste water and by choosing suitable harvesting method or using filamentous microalgae	

(continued)

Table 18.2 (continued)

Cultivation system	Type of bioreactor	Advantages/benefits	Challenges/problems	Considerations/future prospects
Closed Cultivation systems	Tubular photo-bioreactor	• Efficient light utilization	• Difficult to clean in case of growth of microalgae on walls	• The investment cost of the closed photo-bioreactors may be covered by cultivating microalgae capable of producing high-value products
		• Suitable for outdoor cultures	• Expensive installation	• Use of synthetic biology and metabolic pathway engineering may be used to address the problems such as wall growth, temperature sensitivity
		• Relatively cheap	• Requires large land space	
		• Biomass productivity is higher	• Gradients of pH, dissolved oxygen and CO_2 along the tubes	
		• Relatively controlled environment	• Inside temperature may rise in summer due to glass-house effect	
	Flat-panel photo-bioreactor	• Biomass productivities are higher	• Scaling up requires many compartments and is difficult	
		• Low oxygen buildup	• Difficult temperature control especially day-night variation	
		• Readily tempered	• Hydrodynamic stress on walls	
		• Efficient light utilization	• Wall growth may occur	
		• Relatively cheap		
		• Easy cleaning and maintenance		
	Column photo-bioreactor	• High mass transfer	• Light use efficiency may be low	
		• Low energy consumption	• Expensive as compared to open ponds	
		• Efficient mixing	• Sophisticated construction makes commercialization difficult	
		• Low shear stress		
		• Easy to sterilize		
		• Good for immobilization		
		• Reduced photo-inhibition		
		• Photo-oxidation threats		

Brennan and Owende (2010), Ugwu et al. (2008), Singh et al. (2011), Park et al. (2011a), Santiago et al. (2013), Saqib et al. (2013)

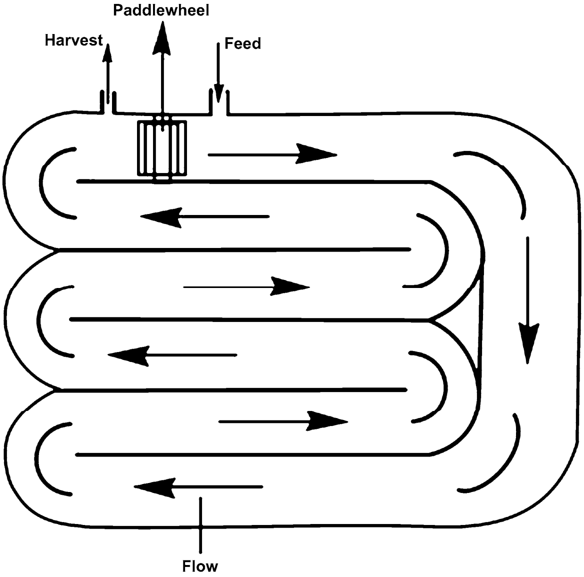

Fig. 18.2 Schematic diagram of raceway pond (RP) for algal biomass production

production of microalgal biomass for making biodiesel has been extensively studied in RPs (Sheehan et al. 1998). Although RPs have a low biomass productivity compared with photo-bioreactors yet they balance the equation by lowering the cost of production (Terry and Raymond 1985).

18.2.2 Closed Photo-Bioreactors

Unlike open raceway ponds, where risk of contamination is distressing, single specie culture may be grown in closed photo-bioreactors (CPBs) without any contamination risk. Huge quantities of algal biomass have been produced using CPBs for fuel production previously using different types of CPBs, including tubular, column, and flat-panel (Fig. 18.3) (Sánchez Mirón et al. 1999; Pulz 2001; Carvalho et al. 2006).

A tubular photo-bioreactor comprises of an array of straight transparent (plastic or glass) tubes. This tubular array also called as a solar collector captures the sunlight. The solar collector tubes are generally ≤0.1 m in diameter. Tube diameter is limited because light does not penetrate too deeply in the dense culture broth that is essential to ensure higher biomass productivities in the CPB. Microalgal broth is circulated from a reservoir to the solar collector and back to the reservoir making it a continuous operation. Capturing of sunlight may be enhanced through the orientation of the collector facing sun pathway and through the use of transparent pipes or flat panels as solar collectors. Alternatives of tubular photo-bioreactors exist in considering flaws related to tubular photo-bioreactors (Carvalho et al. 2006; Pulz 2001)

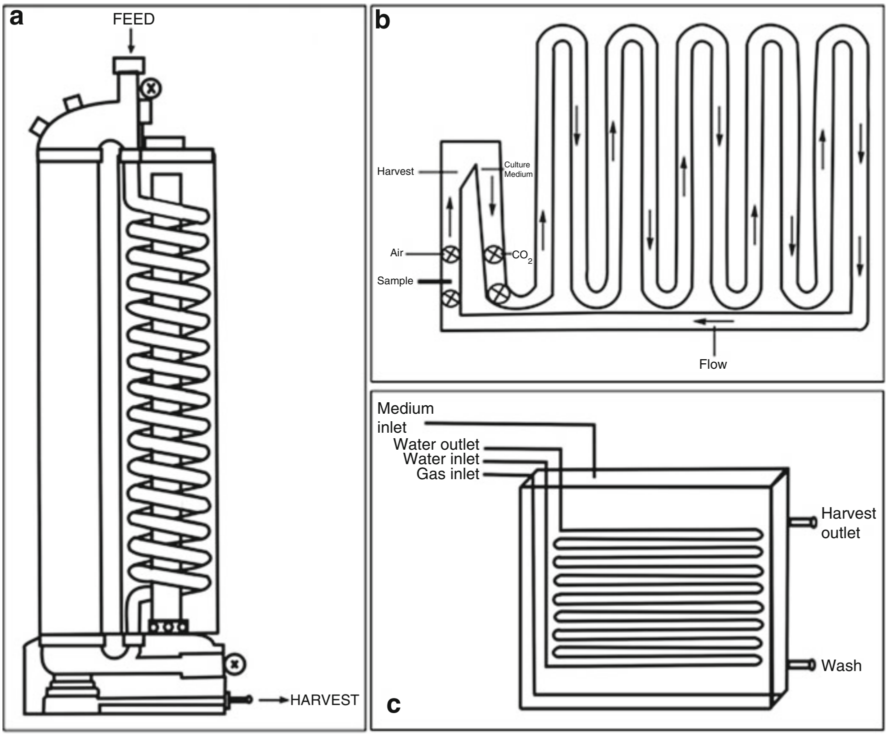

Fig. 18.3 Schematic diagrams of closed photo-bioreactors (CPBs) for algal biomass production a; (**a**) column (**b**) tubular (**c**) flat-panel

but these alternatives are not commonly used for mass culture. Technically, achievability of tubular photo-bioreactors is maximum by artificial illumination (Pulz 2001) but costly than natural source of light (sun).

The CPBs require cooling during day-light hours; temperature control at night is also useful, in a way. For example, the loss of biomass due to respiration at night may be reduced by lowering the temperature at night. Outdoor tubular photo-bioreactors are effectively and inexpensively cooled using heat-exchangers. This may be achieved by placing a heat-exchange coil in the degassing column. Evaporative cooling by water sprayed on tubes (Terry and Raymond 1985) is also used and has demonstrated successfully in dry climates. Large tubular photo-bioreactors have also been sited within temperature controlled green-houses (Pulz 2001), but doing so is not worthwhile for economical production of biodiesel.

18.3 Microalgae Cultivation Using Waste Water

Here we discuss the nuts and bolts of microalgal biomass production using waste water.

18.3.1 Fresh Water Versus Waste Water

Extensive requirement of fresh water is the basic challenge to produce algal biomass. For instance, approximately 1.5 L of water per kilogram of biofuel produced. In CPBs, water use may be much larger due to losses either in the form of evaporation in open cultivation systems or for water usage for cooling (Wijffels and Barbosa 2010). In open systems, the annual water consumption in RPs for microalgae biomass production is in the range of 11–13 million L ha^{-1} (Chinnasamy et al. 2010). This highpoints the significance of reusing waste water (sourced from industrial, municipal effluents) that enables nutrient recycling, subsequently lowering the cost of production (Santiago et al. 2013).

18.3.2 Microalgae Based Bioremediation

Microalgae based bioremediation have been widely studied to remove pollutants (bio-extraction) from water in the last four decades (Ryther et al. 1972; Kuyucak and Volesky 1988; Romero-Gonzalez et al. 2001; Fu and Wang 2011). Several studies have been conducted to present this proof-of-concept in this scenario (Table 18.3). Three microalgal species were cultivated in heavy metal contaminated water, either nutrient addition or without nutrients. All species accumulated heavy metals concentration as high as up to 8 % of their dry mass. Interestingly, growth rates were also increased by two folds, when cultured in contaminated water as compared to fresh water (Saunders et al. 2012). In another study, two algal species, including *Scenedesmus* sp. and *Chlorella* sp. were cultivated favorably on anaerobic sludge centrate representing the higher nutrient uptake (phosphorous and ammonia) and average growth rate obtained was 3.3 ± 1.5 g dry biomass m^{-2} day^{-1} in this case (Dalrymple et al. 2013). Algae grown on anaerobic sludge centrate showed growth productivity rate of 12.8 g dry biomass m^{-2} day^{-1} (Zhou et al. 2012b). Similarly, growth rate of 3 g dry biomass m^{-2} day^{-1} for *Chlorella* sp. grown on wastewater was reported by Woertz et al. (2009). In addition, an unusually higher growth rate (13 g of dry biomass m^{-2} day^{-1}) was reported in a batch culture study. It was shown that at the end of 14-day batch culture 94 % ammonia, 89 % total nitrogen, and 81 % total phosphorous were removed by algal species from municipal waste water (Li et al. 2011a).

Although *Chlorella* sp. can produce lipid contents up to 30 % yet lipids contents decrease by two folds when grown in high strength nitrogen media (usually waste water contains high nitrogen). It is believed that lipid production is considerably reduced under such situations because of low C:N ratio. In general, high lipid contents are achieved when the microalgae are "starved" of nitrogen (Illman et al. 2000; Chisti 2007). So, nitrogen is the key nutrient to be considered while we are interested to enhance the lipid productivity of our test microalgae.

Table 18.3 Overall global trend of algal biomass production using waste water

Sr. no	Laboratory	Country	Algae used	Type of waste water used	Findings	References
1	Advanced Manufacturing Cooperative Research Centre	Australia	*Hydrodictyon* sp., *Oedogonium* sp., *Rhizoclonium* sp.	Waste water derived from coal-fired power generation	Accumulation of heavy metals up to 8 % dry mass	Saunders et al. (2012)
2	Department of Civil Engineering, Federal University of Viçosa	Brazil	*Chlorella* sp. *Desmodesmus* sp. *Scenedesmus* sp., *Chlorococcum* sp., *Coelastrum* sp., *Pinnularia* sp., *Micractinium* sp.	Municipal waste water	Biomass productivity 11.4 g VSS m^{-2} day^{-1}	Santiago et al. (2013)
3	Biochemical Engineering Research Unit and BV Sorbex, Inc. Chemical Engineering Department, McGill University	Canada	*Sargassum natans*, *Ascophyllum nodosum*	Industrial waste	Metal uptake and recovery	Kuyucak and Volesky (1988)
4	Department of Environmental Science and Engineering, Tsinghua University	China	*Scenedesmus* sp.	Secondary effluents	0.11 g L^{-1} dry weight	Xin et al. (2009)
5	Botany Department; Faculty of Science; Cairo University	Egypt	*Phormidium ambiguum* (*Cyanobacterium*), *Pseudochlorococcum typicum* and *Scenedesmus quadricauda var quadrispina* (*Chlorophyta*)	Industrial and sewage water bodies	Bio-extraction of 97 % Hg^{2+}, 86 % Cd^{2+} and 70 % Pb^{2+}	Shanab et al. (2012)
6	Karlsruhe Institute of Technology KIT, Institute for Geoecology and Geography	Germany	Microalgae	Municipal waste water	Turning waste water treatment plants into energy producers	Menger-Krug et al. (2012)

7	Department of Biotechnology & Environmental Sciences, Thapar University	India	*Chlorella* sp.	Domestic wastewater	The maximum uptake (q_{max}) by live Biomass for both Zn^{2+} and Pb^{2+} was 34.4 and 41.8 mg g^{-1}, respectively	Kumar and Goyal (2010)
8	Department of Chemical Engineering, University of Rome	Italy	*Scenedesmus dimorphus*, *Arthrospira platensis*	Olive mill wastewater	Reuse and valorize the ultra- and nano-filtration membrane Concentrates as media for biomass production	Cicci et al. (2013)
9	Laboratory of Biomass, National Institute for Resources and Environment	Japan	*Botryococcus braunii*	Secondarily treated sewage (STS) from domestic waste-water	High hydrocarbons contents, STS a suitable media for biomass production,	Orpez et al. (2009)
10	Department of Chemical Engineering, Sungkyunkwan University, Suwon	Korea	*Botryococcus braunii* UTEX 572	Piggery wastewater	Growth rate >7 g L^{-1} day. wt, Nitrogen and phosphorus removal	An et al. (2003)
11	Department of Civil and Environmental Engineering, Pusan National University	Korea	*Chlorella* sp. *227*	Effluent water, secondary municipal wastewater	UV radiation treatment for increasing algal growth, high lipid productivity	Cho et al. (2011)
12	National Institute of Water and Atmospheric Research Ltd. (NIWA)	New Zealand	*Micractinium* sp. *Desmodesmus* sp.	Average waste water	Growth rate; 8 g m^{-2} day^{-1}	Craggs et al. (2012)

(continued)

Table 18.3 (continued)

Sr. no	Laboratory	Country	Algae used	Type of waste water used	Findings	References
13	Civil & Environmental Engineering Department, University of South Florida	USA	Consortium	secondary effluent from the City of Lakeland	Biomass produced; 71 metric tons ha^{-1} $year^{-1}$	Dalrymple et al. (2013)
14	Department of Bioproducts and Biosystems Engineering, University of Minnesota	USA	*Chlamydomonas reinhardtii*	Waste water at different level of treatment	Dry mass up to 2.0 g L^{-1} day^{-1} Removal of nitrogen and phosphorus up to 55.8 and 17.4 mg L^{-1} day^{-1}	Kong et al. (2010)
15	Department of Biological and Agricultural Engineering, The University of Georgia,	USA	*Chlorella minutissima*	Municipal wastewaters	Mixotrophic growth, Anaerobic survival, High growth rate	Bhatnagar et al. (2010)
16	Department of Biological and Agricultural Engineering, The University of Georgia, Athens	USA	Consortium	Industrial untreated wastewater	Biomass Productivity 21.1 g m^2 day^{-1}, Estimated biomass productivity of 51 and 77 tons ha^{-1} $year^{-1}$	Chinnasamy et al. (2010)
17	Department of Bioproducts and Biosystems Engineering, University of Minnesota	USA	*Chlorella* sp.	Municipal wastewater	Biodiesel yield of 0.12 g-biodiesel L^{-1} algae culture	Li et al. (2011a)
18	Department of Bioproducts and Biosystems Engineering, University of Minnesota	USA	*Chlorella* sp., *Haematococcus* sp., *Scenedesmus* sp., *Scenedesmus* sp., *Chloroccum* sp.	Municipal centrate wastewater	Biomass produced; 2.01 g L^{-1}	Li et al. (2011b)

19	Department of Civil & Environmental Engineering, University of South Florida	USA	*Chlorella* spp.	General Wastewater	>91 % recovery of multivalent ions	Udom et al. (2013)
20	Research Engineer, Department of Civil and Environmental Engineering	USA	Consortium	Dairy and Municipal Wastewater	Lipid productivity 2.8 g m^{-2} day^{-1}	Woertz et al. (2009)
21	Bioproducts and Biosystems Engineering Department, University of Minnesota	USA	*Chlorella*, *Scenedesmus*, *Botryococcus*, *Ankistrodesmus*, *Tetraadron*, *Tetracystis*, *Nannochloris*, *Crucigenia*, *Dictyochloris*, *Chlamydomonas*	Animal Wastewater, digested swine manure wastewater	High growth rate coupled with nutrient uptake	Zhou et al. (2012a, b)

18.3.3 High Rate Algal Ponds

Algal biomass can be produced as a by-product of high rate algal ponds (HRAPs) running for waste water treatment (Park et al. 2011). The HRAPs are raceway-type open ponds with depths in the range of 0.2–0.5 m, retention times (HRT) ranging from 3 to 10 days (that depends on growth rate of test algae), and paddle wheel to provide mixing (Park and Craggs 2010; Craggs et al. 2012). In such systems algal photosynthesis releases oxygen which is required for degradation of organic matter by heterotrophic bacteria.

The concept of using HRAPs for waste water treatment and algal biomass production for purposes of energy production (biofuel) was presented by Rupert Craggs and his colleagues working at National Institute of Water and Atmospheric Research Ltd. (NIWA), New Zealand. The HRAPs keep the advantages of simplicity and economy, overcoming the disadvantages of other systems including poor effluent quality and limited nutrient and pathogen removal (Craggs et al. 2012).

18.3.4 Pretreatment of Influent

The pathogen load during algal cultivation using waste water is another major challenge. A large number of bacteria present in waste water can impede microalgae growth by competing for space and nutrients, and bacteria grow faster than microalgae. To cope with that, pre-disinfection steps have been devised by the scientists. Using ultraviolet (UV) radiation is one of the options, because UV may be used to dis-infect the influent (in-coming waste water) to achieve the desired microbial load. Moreover, it is believed that the UV disinfection as a pretreatment prior to the HRAP does not only ensure the microbiological quality of the effluent but also increase the microalgae productivity (Cho et al. 2011). After a pre-disinfection step, the loads of bacteria and protozoa which negatively affect microalgae growth are reduced.

Based on this concept, a recent study was conducted in a collaborative research project between Federal University of Viçosa, Brazil and National Laboratory of Energy and Geology, Lisbon, Portugal (Santiago et al. 2013), using HRAPs. The study included pretreatment methods with the objective to evaluate the influence of UV pre-disinfection on algal productivity in HRAPs waste water treatment performance. *Chlorella* sp. was used in this study as a test microalga. The use of UV in HRAPs indicated that pre-disinfection may cause dominance of certain species; however, the recycling of settled biomass seems to be more effective for that purpose. Pre-disinfection is then responsible for maintaining high algae/bacteria ratios. It was shown that pre-disinfection by UV radiation increased algal biomass productivity. The percentage of chlorophyll "a" in relation to total biomass (VSS) was greater in the UV-irradiated HRAP. However, if total biomass productivity is considered, the system without pre-disinfection (HRAP) was more efficient. Treatment efficiencies were similar for both ponds, despite the greater photosynthetic activity in the UV-HRAP, as shown by the higher dissolved oxygen (DO) and pH values and greater percentage of chlorophyll "a." Similar studies may be planned under different climatic conditions across the globe to evaluate the worldwide potential of the concept.

18.3.5 Selection of Efficient Strains

Selection of efficient strains is a continuous process and it should never stop to fulfill the commercialization needs. It needs to launch a massive strain selection program across the globe. Different microalgae species have been studied under various experimental designs with respect to nutrient starvation and heterotrophic conditions to evaluate their lipid contents and the lipid productivity. The *Chlorella* sp. has been reported to be the most suitable for such systems (Chu et al. 2009; Bhatnagar et al. 2010). Among these, *C. kessleri* was shown to produce a very high biomass density (2.01 g L^{-1}) when cultivated using municipal waste water (Li et al. 2011a). Naturally, a consortium of microalgae (*Chlorella* spp., *Micractinium* spp., *Actinastrum* spp.) may be established when cultivated in waste water for treatment purposes. A maximum lipid productivity of 24 mg L^{-1} day^{-1} has been reported (Woertz et al. 2009) in such cases. Other microalgae, for instance, *Botryococcus braunii* is widely distributed in freshwater, brackish, and saline lakes and is capable to accumulate unsaturated long-chain hydrocarbons at a concentration of 15–75 % of its dry biomass (An et al. 2003; Orpez et al. 2009) but still needs optimization of growth conditions for each water source. An efficient strain of *Scenedesmus* sp. LX1 showed biomass yield @ 0.11 g L^{-1}, lipid contents ranging from 31 to 33 % with a lipid productivity @8 mg L^{-1} day^{-1} in a batch culture study using secondary effluent as growth medium (Xin et al. 2009). Moreover, LX1 was shown to remove total nitrogen and phosphorous as high as 90.4 % and nearly 100 %, respectively. When ammonium was used as the nitrogen source, LX1 reached a very high specific growth rate of 0.82 day^{-1} (Xin et al. 2010). Similar findings have been reported in literature (Zhou et al. 2012a, b). *Chlamydomonas reinhardtii* is another microalga with the potential to treat waste water along with oil production. It was cultivated in waste water collected at three different stages (influent, effluent and centrate) of a municipal waste water treatment plant. In this case, a lipid productivity of 505 mg $L^{-1}day^{-1}$ was achieved, which may be the highest lipid productivity reported for microalgae production in waste water (Kong et al. 2010). The use of olive mill waste water as media for biomass production from *Scenedesmus dimorphus* and *Arthrospira platensis* was reported to be another hopeful strategy, recently (Cicci et al. 2013).

18.3.6 Lower Input for Economical Production

Keeping in view the bio-extraction potential of microalgae along with biomass production, such integrated systems that use microalgae for treating waste water and producing oil for biodiesel and chemical products are gaining interests globally. It has demonstrated that dual-use of microalgae cultivation for waste water treatment coupled with biofuel generation is an attractive option for reducing energy, fertilizer, and freshwater costs of production along with reduced GHG emissions (Pittman et al. 2011; Park et al. 2011; Menger-Krug et al. 2012). A group of researchers have claimed that microalgae-mediated CO_2 fixation coupled with biofuel production is more sustainable if we integrate biomass production with wastewater treatment (Kumar et al. 2010). Actually, cultivation of microalgae consumes more fertilizers as compared to the most common oleaginous plants. For instance, N-fertilizer consumption in the range of 0.29–0.37 kg kg^{-1} oil is reported, which is higher than that for Jatropha and palm oil where 0.24–0.048 kg of fertilizer is required per kg oil production, respectively (Lam and Lee 2012). So, use of waste water enriched with nutrients will undoubtedly decrease the cost of production.

Moreover, although microalgae grow in an aquatic medium yet they require less water than terrestrial oleaginous crops while making use of saline, brackish, and/or coastal seawater (Kliphuis et al. 2010; Rodolfi et al. 2009). This allows the production of algal biomass without competing for valuable resources such as arable land, landscapes, and freshwater. The microalgae *Nannochloropsis* sp., *Dunaniella salina*, *Chlorella* sp., and *Etraselmis* sp. were found suitable for a multiple-product algae crop. The tropical and sub-tropical microalgae display a variety of fatty acid profiles making algal biomass production more attractive to obtain oil-based bio-products, including biodiesel and omega-3 fatty acids (Lim et al. 2012). Conclusively, a biorefinery approach (integration of waste water treatment and algal biomass production) for microalgae would make the process economically feasible but challenges remain there regarding the efficient harvesting and extraction processes for some species.

18.4 Challenges in Using Waste Water as Growth Media

Although algal biomass production using waste water as a growth media seems attractive, we face several challenges thereof. One problem with such system is the availability of production sites (Slade and Bauen 2013) because we can only integrate biomass production with city waste water treatment plants. Overall, it is clear that reducing the inputs (energy and fertilizer) of the process makes algae an ideal feedstock in such integrated systems as compared to any other biofuel feedstocks, such as canola, corn, and switch grasses (Clarens et al. 2010). The requirement of fresh water and nutrients may decrease up to 100 % by using waste water as source nutrients (Li et al. 2010; Udom et al. 2013).

Presence of potentially toxic compounds in municipal waste water is another problem, especially when industrial waste water is being mixed. Heavy metals are believed to inhibit the important enzymes involved photosynthetic pathways of microalgae (Kumar et al. 2010). A noteworthy reduction in specific growth rate and biomass productivity of *B. braunii* was observed when cultivated in secondary effluents of a municipal sewage treatment plant and it was shown that it was due to the presence of phenolic compounds and heavy metals in the waste water (Orpez et al. 2009). Very fortunately some microalgae (*Scenedesmus* and *Pseudochlorococcum.*) have displayed tolerance to higher concentrations (80–100 mg mL^{-1}) of heave metals such as Pb^{2+}. On the other hand, mercuric ions (Hg^{2+}) inhibited chlorophyll biosynthesis even at lower concentrations (5–10 mg mL^{-1}) and a complete destructed algal cells at concentration >20 mg mL^{-1} (Shanab et al. 2012). It is believed that it is related to the amount of heavy metal ions bound to the cell surface, and to the amount of up-taken heavy metal ions (Franklin et al. 2001). However, the growth inhibition may due to extracellular ions concentration, for instance in the case of zinc (Wilde et al. 2006). In the algal stabilization ponds, the heavy metal ions, Zn^{2+} and Pb^{2+} were removed up 72 % and 73 % respectively, by *Chlorella* sp. (Kumar and Goyal 2010). These studies have shown that there are important benefits to be derived from integrating algal production systems with nutrient-rich waste water streams (Dalrymple et al. 2013).

Although, people argue that using waste water for algal biomass production may pose contamination risks yet Life Cycle Analysis (LCA) studies have confirmed that it is a very productive approach and ensure the viability and sustainability of the complete biofuels production process in monetary terms (Kumar and Goyal 2010). An LCA study was carried out to evaluate the energy balance and environmental impacts from biomass to biodiesel production and combustion. It was shown that substantial (>50 %) cost reductions may be achieved if CO_2, nutrients, and water can be provided at lower cost, i.e., sourced from waste water (Lardon et al. 2009).

18.5 Conclusion and Future Prospects

The use of algal biomass costs approximately US$70 L^{-1}, which is far away to attract the commercial production of algal biofuels (Ahrens and Sander 2010). So, cost effective approaches for the algal biofuel production is a dire need. One of promising alternatives is the use of waste water for biomass production, providing a readily available medium for the production of algal biomass at very low cost. Not only the municipal waste water, the microalgae cultivation may be integrated with fish-farms, food processing facilities, and industrial waste water. It will not only be waste remediation through recycling of organic matter but will provide low-cost nutrient supply required for the biomass production, simultaneously.

Cultivation of algae removes nutrients from the waste water and reduces the environmental pollution. Large-scale biomass production systems may be linked to existing infrastructures running for waste water treatment (proposed in Fig. 18.4). It will not only provide the raw materials for the growth, such as CO_2 and nutrients but also convert wastes into useful resources (Wagner 2007). The most obvious opportunity for such integration is with the power-plants in order to take advantage of CO_2 along with a possibility to utilize the waste-heat from the power-plant.

None of the algal species studied may be considered as “the best” for biomass production on large scale using waste water. So, selection process should be continued to isolate new potential strains with desired features.

Consortia of microalgae may be established instinctively while waste water is used as growth media. Thus, evaluation of oil extracted from the biomass produced in consortia, and the bio-compatibility of the algal species in the consortia need further evaluation based studies.

Higher biomass production may be achieved using heterotrophic or mixotrophic growth systems using waste water and biodiesel-derived glycerol. But, more detailed studies may be conducted to evaluate the sustainability of such systems.

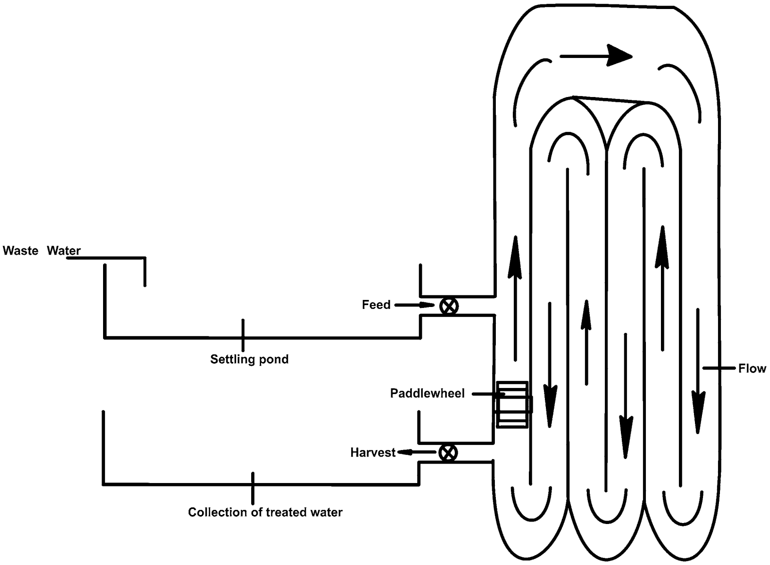

Fig. 18.4 A proposed integration of waste water treatment with algal biomass production

Although total lipid contents of microalgae cultivated in waste water may be lower than the one observed in synthetic medium and biomass may not be suitable for biodiesel production yet the biomass may be characterized for its use in biogas production. It may be used directly applied as bio-fertilizers or may be used as a career for bio-fertilizers. Bio-char production and mixing with animal feed (especially biomass with higher protein contents) are other options for the biomass with low lipid contents.

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Chapter 19
Biomass Steam Gasification for Hydrogen Production: A Systematic Review

Abrar Inayat, Murni M. Ahmad, Suzana Yusup, M.I. Abdul Mutalib, and Zakir Khan

Contents

Abstract The production of hydrogen as a clean and sustainable fuel is becoming attractive due to the energy crisis and increasing environmental issues associated with fossil fuel usage. Biomass steam gasification with in situ carbon dioxide capture has good prospects for the production of hydrogen-rich gas. Furthermore, hydrogen yield can be enhanced using catalyst steam gasification. This chapter comprises the literature review on both the approaches, i.e., experimental and modeling used to study the hydrogen production from biomass gasification specifically using pure steam as gasification agent. There were several modeling approaches for

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_19, © Springer International Publishing Switzerland 2014

gasification process based on the kinetics, equilibrium, and the fluid dynamics behaviors. A detailed discussion has been carried out in this chapter on modeling and simulation for hydrogen production from biomass based on kinetics modeling. Experimental studies have been published on steam gasification and steam gasification with CO_2 capture and catalytic steam gasification has been discussed. Gasification for hydrogen production from oil palm empty fruit bunch has also been discussed.

Keywords Biomass • Steam gasification • CO_2 capture • Hydrogen • Kinetics modeling

19.1 Introduction

Hydrogen is one of the potential alternative energy sources that could be used to replace the existing fossil fuels. Besides the zero carbon footprints, hydrogen is expected to become a prominent energy carrier for stationary and mobile power generation applications such as in transport, industrial, commercial, and residential applications (Clark Ii and Rifkin 2006; Solomon and Banerjee 2006). The utilization of renewable sources including the biomass of forestry, agricultural, and municipal waste has become a new source of energy due to the abundance of these wastes. Consequently, producing hydrogen from biomass not only offers a zero net carbon emission and burning to get electricity and heat which is clean, it can also be stored and transported and be used in existing technology and infrastructure (Jacobson 2009). Biomass gasification is considered as one of the potential alternatives for the production of hydrogen, but the quality of hydrogen and product gas varies with the different gasification agents used (Holladay et al. 2009; Kalinci et al. 2009; Kumar et al. 2009). Biomass gasification can be performed using different gasification agents such as air, air–steam and oxygen–steam mixtures, or pure steam. It is reported that the use of pure steam is more economical and in favor of producing more hydrogen yield compared to the other conventional gasification agents (Gil et al. 1999; Balat 2008; Corella et al. 2008a, b; Balat et al. 2009). This chapter comprises the literature review on both the approaches, i.e., experimental and modeling used to study the hydrogen production from biomass steam gasification. Studies have been published on steam gasification (Ptasinski 2008) and steam gasification with CO_2 capture (Florin and Harris 2008) and catalytic steam gasification has been discussed (Guo et al. 2010; Tanksale et al. 2010; Serrano-Ruiz and Dumesic 2011). Furthermore, the availability of palm oil empty fruit bunch (EFB) is abundant in Malaysia (Sumathi et al. 2008; Mohammed et al. 2011a, b), so the work reported on EFB gasification for hydrogen production has also been discussed. There were several modeling approaches for gasification process based on the kinetics, equilibrium, and the fluid dynamics behaviors (Nemtsov and Zabaniotou 2008; Wang and Yan 2008; Gómez-Barea and Leckner 2010; Puig-Arnavat et al. 2010; Ahmed et al. 2012; Guo et al. 2012). A detailed discussion has been carried out in this chapter on modeling and simulation for hydrogen production from biomass based on kinetics modeling. Finally, chapter comprises a short summary to identify the gap of study in the specific fields.

19.2 Steam Gasification for Hydrogen Production

Several scientific studies have been carried out using steam gasification for higher yield of hydrogen from different biomasses. Gil et al. (1999) have analyzed the effect of gasification agents on the product gas obtained from biomass gasification in fluidized bed using small chips of pine as biomass. Air, Steam-O_2 mixture, and pure steam have been studied for hydrogen production. They conclude their results for hydrogen purity as follows in this order:

Pure steam (53–55 vol.%) > Steam-O_2 (25–30 vol.%) > Air (8–10 vol.%)

Their results show that for hydrogen production the steam gasification is the best option. But on the other hand the steam gasification produced maximum tar yield compared to other gasification agents.

Franco et al. (2003) have studied the biomass steam gasification in fluidized bed reactor at atmospheric pressure. They operated gasifier with three different types of biomass, i.e., soft wood, hard wood, and globules. Temperature and steam/biomass were studied on the product gas composition, energy conversion, and higher heating value. They reported that both temperature and steam are in favor of more hydrogen yield. They predict that water gas shift is dominant in the biomass gasification with pure steam in the main five reactions of biomass gasification as follows.

Char gasification

$$C + H_2O \rightarrow CO + H_2$$

Boudouard

$$C + CO_2 \rightarrow 2CO$$

Methanation

$$C + 2H_2 \rightarrow CH_4$$

Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Water gas shift

$$CO + H_2O \rightarrow CO_2 + H_2$$

They reported that the rise in temperature forecast increase in hydrogen and decreases in carbon monoxide. Furthermore, they also proved that hydrogen amount through biomass steam gasification is higher compared to pyrolysis. The maximum of hydrogen purity was obtained at 1,073 K and steam/biomass ratio of 0.5, i.e., 45 mol%.

Ahmed and Gupta (2009) studied experimentally both pyrolysis and steam gasification using paper as biomass within the temperature range of 873–1,273 K. They investigated the syngas flow rate, hydrogen flow rate, yield, and thermal efficiency of the product gas. They reported that hydrogen yield is much higher in gasification compared to pyrolysis. They obtained around 60 vol.% of hydrogen at 1,173 K. They reported that gasification process has advantage due to mainly char gasification reaction.

Weerachanchai et al. (2009) investigated the effect of steam gasification on the product gas composition using larch wood as biomass in fluidized bed reactor. Along with the temperature they also investigated the different types of bed materials. The maximum hydrogen was obtained at 1,023 K with 55.68 vol.%, 96 % of carbon conversion efficiency, 75.88 % cold gas efficiency, and 14.76 of lower heating value of product gas.

Umeki et al. (2010) have studied high temperature steam gasification process for hydrogen-rich product gas from wood as biomass. Both temperature and steam/carbon ratio have been investigated on the product gas composition, carbon conversion efficiency, H_2/CO ratio, cold gas efficiency, higher heating value, and total gas yield. In the experiment results they reported that the most dominant reaction is water gas shift reaction in steam gasification. The highest cold gas efficiency was predicted 60.4 % with the hydrogen of 55 vol.% at the outlet of the updraft fixed bed gasifier.

19.3 Steam Gasification with In Situ CO_2 Capture for Hydrogen Production

Several studies have been published on steam gasification using CaO as sorbent. Acharya et al. (2009) worked on the hydrogen production from sawdust using steam gasification and CaO as CO_2 sorbent in bubbling fluidized bed reactor. Furthermore, they proposed the regenerator along the gasifier for the regeneration of calcium carbonate in the system. They predict through experimental setup around 71 vol.% of H_2 with 0 vol.% of CO_2 at 853 K, steam/biomass ratio of 1.0, and Ca/C ratio of 1. They also proved that using CaO as sorbent the purity of hydrogen increased more than 30 vol.% compared to the process without CaO. Moreover, CaO not only captures CO_2 from the system, but also increases the efficiency of the system due to the exothermic nature of carbonation reaction as follows.

Carbonation reaction

$$\mathrm{CaO} + \mathrm{CO_2} \rightarrow \mathrm{CaCO_3} - 178.3\,\mathrm{kJ/mol}$$

They also reported that in steam gasification with in situ CO_2 capture, the water gas shift reaction moves in the forward direction due to the low partial pressure of CO_2 in the system, as CaO absorbs the CO_2.

Pfeifer et al. (2009) used duel fluidized bed gasifier to study the effect of CaO on the product gas composition from biomass steam gasification. The hydrogen content in the product gas achieved 40 vol.% without CaO, but with the CaO the hydrogen content increased to 75 vol.%. They named this concept as "absorption enhanced reforming—AER concept."

Furthermore, they presented a simplified flow sheet for power generation using AER process for 100 kW at Vienna University of Technology, Austria.

Guoxin and Hao (2009) studied hydrogen production using pine tree sawdust as wet biomass in quartz reactor. They investigated the effect of temperature, Ca/C ratio, and the moisture content of the biomass on hydrogen production. They predicted that the CaO not only acts as sorbent but also acts as catalyst. Furthermore, CaO has strong impact on watergas shift reaction rather than steam reforming of methane. Moreover, the high temperature is not in favor of carbonation reaction. They reported that the optimum temperature for biomass steam gasification with CaO as sorbent is 923–973 K. Their results showed more than 55 vol.% of hydrogen in the product gas at 923 K with Ca/C ratio of 0.5.

Acharya et al. (2010) have reported biomass steam gasification using sawdust as biomass and CaO as sorbent. They investigated the effect of variables (temperature, steam/biomass ratio, and CaO/biomass ratio) on the hydrogen purity and hydrogen yield. They predicted 54.43 vol.% of hydrogen at 943 K, steam/biomass ratio of 0.83, and CaO/biomass ratio of 2. Furthermore, they have reported that hydrogen yield increased by increasing temperature.

Han et al. (2011) studied on biomass steam gasification in the presence of CaO. They investigated the effect of temperature (762–1,013 K), steam/C ratio (1.2–2.18), and CaO/C ratio (0–2) on the hydrogen purity and yield. Taking sawdust as biomass they performed experiments in the fluidized bed gasifier.

They reported that all three factors, i.e., temperature, steam/C ratio, and CaO/C ratio, are in favor of hydrogen production. The addition of steam along with CaO is in favor of more hydrogen as it shifts the thermodynamic equilibrium of char gasification and water gas shift reaction to product side. They have predicted the maximum hydrogen concentration 62 vol.% with yield of 72 g/kg of biomass at 1,013 K, steam/C ratio of 2.18, and CaO/C ratio of 1. In addition, they observed that carbonation reaction temperature range is 753–1,043 K best for the gasification process in order to get more pure hydrogen by absorbing CO_2 from the system. They reported that within these temperature ranges not only the carbonation reaction moves in forward direction but also water gas shift reaction moves to product side due to the lower partial pressure of CO_2 in the system. In addition the results showed that by increasing temperature H_2 and CO_2 increase while CO and CH_4 decrease.

A detailed comparison of the literature based on the operating conditions, optimized parameters, and results based on optimum conditions is given in Table 19.1.

Table 19.1 Comparison of literature for the steam gasification with in situ CO_2 capture for hydrogen production

			Operating parameters range					Optimum conditions at optimized product gas			Optimized gas compositions (max H_2 and Min CO_2) mol% or vol.%					
References	Feed	Flow rate	Particle size	Temp (°C)	P (atm)	St/b	Sb/b	Temp	St/b	Sb/b	H_2	CO_2	CO	CH_4	H_2 yield	Scale/reactor
Guoxin and Hao (2009)	Pine tree saw dust	–	<150	650–700–750	1	0.9	0–0.1–0.3–0.5–0.7–1 (Ca/C)	650	0.9	0.5 (Ca/C)	55	5	25	18	400 (mL (NTP)/g of b)	Lab/Fixed Bed
Acharya et al. (2010)	White fir	–	425–500	600–670–710	1	0.58–0.83–10.8–1.58	0–1.0–1.5–2.0	670	0.83	2	54	2	23	22	375 (ml/g of b)	Lab/Cylinder Tube
Hanaoka et al. (2005)	Japanese oak	–	106–250	600–650–700	3–6–13–20–64–84	–	1–2–4 (Ca/C)	700	–	2 (Ca/C)	–	–	–	–	840 (ml (STP)/g of b)	Lab/Autoclave
Mahishi and Goswami (2007)	Pine bark	5 g	–	500–600–700	1	1	–	700	1	–	65	26	4	3	780 (ml/g)	Lab/Fixed Bed
Wei et al. (2008)	Pine sawdust	1 g	600–900	650–700–750–800	1	0.35–0.38–0.42–0.46–0.56–0.59	8–19–20–21–26–39	800	0.56	26	68	22	5	4.8	–	Lab/Fixed Bed
Acharya et al. (2009)	Sawdust	0.5 kg/h	–	500–580	1	1.5	1 (Ca/C)	580	1.5	1 (Ca/C)	72	1	7	20	–	Bench/Fluid Bed
Koppatz, Pfeifer et al. (2009)	Wood chips	–	–	650–660–670–680–700	1	0.83–1.24–1.62	–	700	1.62	–	60	11	18	11	–	Bench/Dual Fluid Bed
Weerachanchai et al. (2009)	Larch wood	0.21 g/min	250–600	650–750	1	–	–	750	–	–	40	25	5	5	–	Lab/Fluid Bed
Pfeifer et al. (2009)	Wood pellets	25 kg/h	–	645–841	1	0.63–0.79	–	645	0.81	–	73	6	6	11	3.264 kg/h	Pilot/Dual Fluid Bed
Xu et al. (2005)	Coffee grounds	475 g/h	–	722–795	1	1.26 (St/C)	–	722	1.26 (St/C)	–	25	8	4	6	–	Bench/Fluid Bed
Marquard-Möllenstedt et al. (2004)	Wood	15 kg/h	100	630–650–680	1	–	–	640	–	–	67	10	3	13		Bench/FICFB

19.4 Catalytic Steam Gasification for Hydrogen Production

Different kind of catalyst used in biomass gasification using different kind of reactors has been published in the literature. Corella et al. (2008a, b) used small pine wood chips as biomass in fluidized bed gasifier along with steam reformer reactor and two shift reactors for hydrogen production. They have reported 73 vol.% of hydrogen with 140 g/kg of biomass yield using N_i-based commercial catalyst. Furthermore, they stated that 90 % CO conversion to H_2 via water gas shift reaction due to using of catalyst in the shift reactors. Along with the high production rate they have stated that not only the system is very complex with fluidized bed, steam reformer, and two shift reactors but also the hydrogen production cost is very high. Along with this they stated that the overall process is technically feasible, meaning that there are no technical major problems.

Li et al. (2009) studied the palm oil waste (mixture of EFB + fiber + shell) for hydrogen production. They used fixed bed reactor with pure steam as gasification agent and tri-metallic catalyst, i.e., $N_iL_aF_e/\gamma\text{-}Al_2O_3$. They have investigated the effect of steam/biomass ratio, temperature, and particle size on the hydrogen production. They reported 59 vol.% hydrogen with yield of 133.25 g/kg of biomass at 1,173 K and steam/biomass ratio of 1.33. Their results showed that hydrogen is increased by increasing temperature. For steam/biomass ratio, initially hydrogen increased by increasing steam/biomass ratio, but at high steam/biomass ratio hydrogen decreased. This is due to the decrease of temperature at high steam/biomass ratio in fixed bed reactor. Furthermore, the smaller biomass particles produced more hydrogen compared to the bigger particle size. They have reported that the catalyst has a strong impact on the hydrogen yield in steam gasification of biomass. Hydrogen yield without catalyst was reported 39.75 g/kg of biomass and by using catalyst hydrogen yield increased till 101.78 g/kg of biomass under the same conditions. Furthermore, the type of catalyst also plays important role for hydrogen production in biomass steam gasification.

He et al. (2009) studied the catalytic steam gasification of municipal solid waste in bench scale fixed bed gasifier using calcined dolomite as catalyst. They reported that the catalyst not only increased the hydrogen yield but also completed decomposed tar in the system in the presence of steam at high temperature. The highest hydrogen concentration was obtained 53.29 mol% with the yield of 84 g/kg of biomass. Furthermore, they reported that the system has potation to produce 140 g/kg of biomass hydrogen yield at high temperature. The use of catalyst has proved that there is remarkable increase in the hydrogen yield and concentration and decrease of CO and CH_4 due to the water gas shift reaction and steam reforming of the hydrocarbons. They did not detect any tar during the catalytic steam gasification.

Xiao et al. (2010) utilized large amount of animal waste (livestock manure compost) as biomass. They investigated the effect of temperature, steam, and catalyst using fluidized bed gasifier and $Ni\text{–}Al_2O_3$ as catalyst. They reported that the both temperature and steam are in favor of hydrogen concentration and yield in catalytic steam gasification, as the methane reforming and water gas shift reaction moves to the product side. Furthermore, catalyst simultaneously promotes tar cracking and steam reforming reactions.

19.5 EFB Gasification for Hydrogen Production

The work on biomass gasification using EFB as biomass is limited in the literature. Ogi et al. (2013) investigated EFB gasification in entrained flow gasifier using steam and steam-O_2 as gasification agent. They reported that pure steam gasification is in favor of more hydrogen production compared to steam-O_2 for EFB gasification. Because of using steam-O_2 the amount of CO_2 increased while H_2 and CO decreased in the system. Furthermore, TG analysis shows that EFB decomposed easily to the gases in the presence of steam and there is very low amount of tar in steam gasification of EFB. Furthermore, they observed that the EFB well gasified in the presence of steam compared to the cedar wood under same operating conditions and predicts high gasification rate as well.

Lahijani and Zainal (2011) investigated EFB air gasification in pilot scale fluidized bed gasifier. They studied the effect of temperature and equivalence ratio on the product gas composition. They predicted maximum of 20 vol.% hydrogen at 1,323 K. The maximum carbon conversion and cold gas efficiency was predicted 93 % and 72 %, respectively.

Mohammed et al. (2011a, 2011b) studied for hydrogen-rich gas from EFB as biomass in fluidized bed gasifier using air as gasification agent. They investigated the effect of temperature, particle size, and equivalence ratio on the hydrogen production using bench scale system. They predicted maximum 38.02 vol.% of hydrogen at 1,273 K. They reported that lower particle size of EFB is in favor of more hydrogen.

Ismail et al. (2011) investigated the effect of CaO on EFB gasification in the presence of O_2 and H_e. They reported that CaO played a very good catalyst for the gasification of EFB. The H_2/CO ratio was increased by increasing temperature in the presence of CaO. Furthermore, nanosize of CaO increased 56 % more hydrogen compared to the bulk CaO. Their results showed that the high production of hydrogen can be obtained at 973 K using EFB in dry conditions via O_2–H_e gasification.

19.6 Kinetics Modeling for Hydrogen Production via Biomass Gasification

There are several studies being carried out on kinetics modeling for biomass gasification using air–steam gasification, but limited studies on pure steam gasification. Corella and Sanz (2005) developed a reaction kinetics model based on pyrolysis and gasification in circulating fluidized bed gasifier. Several reactions have been considered in the modeling including fast pyrolysis reaction, oxidations reactions, steam reforming of methane, tar reforming, char reforming, and water gas shift reaction. The char gasification reaction is presented as follows:

$$\text{char}\left[CH_{0.20}O_{0.13}\right] + 0.38H_2O \rightarrow 0.54CO + 0.45H_2$$

The kinetics for all reactions has been considered first order based on the easiest or simplest kinetics available in the literature. For example the kinetics for the char gasification reaction was selected from the literature (Gonzalez-Saiz 1988) as follows:

$$r_{10} = k_{10} C_{\mathrm{char}\,2} C_{\mathrm{H_2O}} \quad k_{10} = 2.0 \times 10^{5} \exp\left(-6{,}000/\mathrm{T}\right)$$

Furthermore, the all rate equations for all reactions were solved using Chemical Reaction Engineering rules. For example the overall volumetric rate equation for hydrogen was presented as follows:

$$R_{\mathrm{H_2}} = \mathrm{eq.}1 + d_8.r_8 + d_9.r_9 + d_{10}.r_{10} - r_4$$

Nikoo and Mahinpey (2008) have presented a comprehensive model for biomass air–steam gasification in fluidized bed using pine saw dust as biomass. Both kinetics and hydrodynamics parameters have been considered with few assumptions.

For the reactions kinetic model, the reaction equations for combustion (CO) and steam gasification (SG) given by Lee et al. (1998) were chosen as follows:

$$\frac{\mathrm{d}X_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{CO}} \exp\left(\frac{-E_{\mathrm{CO}}}{\mathrm{RT}}\right) P_{\mathrm{O_2}}^{n} \left(1 - X_{\mathrm{CO}}\right)^{2/3}$$

$$\frac{\mathrm{d}X_{\mathrm{SG}}}{\mathrm{d}t} = k_{\mathrm{SG}} \exp\left(\frac{-E_{\mathrm{SG}}}{\mathrm{RT}}\right) P_{\mathrm{H_2O}}^{n} \left(1 - X_{\mathrm{SG}}\right)^{2/3}$$

$$r_{\mathrm{c}} = \left(\frac{\mathrm{d}X_{\mathrm{CO}}}{\mathrm{d}t} + \frac{\mathrm{d}X_{\mathrm{SG}}}{\mathrm{d}t}\right) \times \frac{\rho_{\mathrm{C}} \varepsilon_{\mathrm{S}} Y_{\mathrm{C}}}{M_{\mathrm{C}}}$$

Furthermore, the model was validated with the experimental data taken from the literature and the mean error calculated between the experimental value and the predictions. The parametric studies have been done with temperature, steam/biomass ratio, equivalence ratio, and particle size on the product gas composition and carbon conversion efficiency.

Lü et al. (2008) considered fluidized bed reactor for kinetics model of biomass air–steam gasification using assumptions of isothermal and steady state conditions. Furthermore, pyrolysis has been considered as instantaneous process. The wood powder has been taken as biomass and the following eight reactions (adopted from Lü et al. (2008)) have been solved in MATLAB.

$$\mathrm{C} + \mathrm{O_2} \xrightarrow{k_0} \mathrm{CO_2}$$

$$\mathrm{C} + \mathrm{CO_2} \xrightarrow{k_1} 2\mathrm{CO}$$

$$\mathrm{C} + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{CO} + \mathrm{H_2}$$

$$\mathrm{C} + 2\mathrm{H_2} \xrightarrow{k_3} \mathrm{CH_4}$$

$$CO + H_2O \xrightarrow{k_4} CO_2 + H_2$$

$$CO_2 + H_2 \xrightarrow{k_5} CO + H_2O$$

$$2CO + O_2 \xrightarrow{k_6} 2CO_2$$

$$CH_4 + H_2O \xrightarrow{k_7} CO + 3H_2$$

The all kinetics constants (k_0–k_7) have been chosen from the literature. Furthermore, the model has been validated with experimental data of pine sawdust taken from the literature.

Ji et al. (2009) presented a kinetics model for steam gasification of biomass for enriched hydrogen gas production from biomass. A simplified flow sheet has been also presented to get pure hydrogen based on fluidized bed gasifier, steam reformer, and H_2 membrane water gas shift reactor. Several reactions have been considered in all reactors. The rate of reactions for all reactions has been solved using the kinetics data from the literature. Furthermore, the model has been validated with the experimental data taken from the literature. The effect of temperature and steam/biomass ratio has been studied on the hydrogen purity and yield. The temperature and steam/biomass range was taken 960–1,120 K and 0.5–3.0, respectively. The hydrogen purity was predicted more than 60 mol% at 1,023 K and steam/biomass ratio of 3.0. Furthermore, they reported that the lower heating value of the product gas decreased by increasing both temperature and steam/biomass ratio due to the increase of hydrogen in the product gas.

19.6.1 Kinetics Modeling Along with Kinetics Parameters Determination

There are very limited literature on kinetics modeling for biomass gasification supported by kinetics parameters determined using experimental data. Sheth and Babu (2009) estimated kinetics parameters for biomass pyrolysis process using kinetics modeling approach. The kinetics constant of two reactions involved in the pyrolysis was calculated by minimization of least square error between the model results and the experimental data. The experimental data were chosen from the literature. The values of activation energy and pre-exponential factor of Arrhenius constants for both reactions were calculated by the minimization of the objective function as follows:

$$k_i = A_i \exp\left(\frac{-E_i}{\mathrm{RT}}\right)$$

$$F\left(A_1,E_1,A_2,E_2\right)=\sum_{j=1}^{n}\left(W_{\exp,j}-W_{\mathrm{cal},j}\right)^2$$

Wang and Kinoshita (1993) developed a reaction kinetics model for biomass O_2-steam gasification. The wood was taken as biomass and the generalized equation was presented as follows:

$$\begin{aligned}&\mathrm{CH_{1.4}O_{0.59}}+y\mathrm{O_2}+z\mathrm{N_2}+w\mathrm{H_2O}=x_1\mathrm{C}+x_2\mathrm{H_2}\\&+x_3\mathrm{CO}+x_4\mathrm{H_2O}+x_5\mathrm{CO_2}+x_6\mathrm{CH_4}+x_7\mathrm{N_2}\end{aligned}$$

Furthermore, four main reactions were considered including char gasification, boudouard, methanation, and methane reforming reaction as follows:

Char Gasification

$$\mathrm{C}+\mathrm{H_2O}\rightarrow\mathrm{CO}+\mathrm{H_2}$$

Boudouard

$$\mathrm{C}+\mathrm{CO_2}\rightarrow 2\mathrm{CO}$$

Methanation

$$\mathrm{C}+2\mathrm{H_2}\rightarrow\mathrm{CH_4}$$

Steam Reforming

$$\mathrm{CH_4}+\mathrm{H_2O}\rightarrow\mathrm{CO}+3\mathrm{H_2}$$

The rate constant of all these reactions was calculated by the minimization of the difference between the experimental data and calculated data. The equation used was as follows:

$$\mathrm{Min}\,\mathrm{f}\left(k_{a1},k_{a2},k_{a3},k_{a4}\right)=\mathrm{Min}\sum_{j=1}^{m}\sum_{j=1}^{6}\left(x_{ij}-x_{\exp,ij}\right)^2$$

The experimental data were taken from their previous work on O_2-steam gasification using sawdust as biomass (Wang and Kinoshita 1992). Moreover, the modeling results were validated with the experimental work. In addition, residence time, temperature, pressure, equivalence ratio, and moisture have been investigated on the product gas composition.

Resende and Savage (2010) described the kinetics model for the supercritical steam gasification for hydrogen production. The model consists of 11 reactions. The rate equations of each reaction were taken as first order for each species. The final concentration was calculated using mole balance equations; for example, the concentration of CO_2 was calculated using the equitation as follows:

$$\frac{\mathrm{dC_{CO_2}}}{\mathrm{d}t}=xk_4\mathrm{C_1C_W}+k_6\mathrm{C_1}+k_{10}\mathrm{C_{CO}C_W}+k_{10r}\mathrm{C_{CO_2}C_{H_2}}$$

where k_{10} is for forward water gas shift reaction and $k_{10\mathrm{r}}$ is for reversible water gas shift reaction. The equilibrium constant for the water gas shift reaction was calculated as follows:

$$K_{10} = \frac{\mathrm{C_{H_2}.C_{CO_2}}}{\mathrm{C_{CO}.C_{H_2O}}}$$

The kinetics parameters were calculated by the minimization of the objective function which is the sum squared difference between the model results and experimental values. The experimental data were taken from their previous work based on the supercritical steam gasification of lignin and cellulose (Resende and Savage 2009). Furthermore, the model was validated with the experimental data and the results showed good agreement.

Salaices (2010) developed a reaction kinetics model for catalytic steam gasification of biomass surrogates using as model compounds. The kinetics model was based on the coherent reaction engineering approach. The reaction rates were based on the dominant reactions. The reactions like methanation and boudouard reactions were neglected. So the rate of each species was calculated as follows;

$$r_i = \sum r_{ij} = r_{\mathrm{WRG}} + r_{\mathrm{SR}} + r_{\mathrm{DRM}}$$

There are only dominant reactions, i.e., water gas shift, steam reforming, and dry methane reforming considered. For example, the rate of formation of hydrogen was calculated as follows:

$$\begin{aligned}\frac{\mathrm{dp_{H_2}}}{\mathrm{d}t} = {} & \frac{k_{\mathrm{WGS}} K^{A}_{\mathrm{CO_2}} \mathrm{p_{CO} p_{H_2O}}}{1 + K^{A}_{\mathrm{CH_4}} \mathrm{p_{CH_4}} + K^{A}_{\mathrm{CO_2}} \mathrm{p_{CO_2}}} \left[1 - \frac{\mathrm{p_{CO_2} p_{H_2}}}{K_{\mathrm{WGS}} \mathrm{p_{CO} p_{H_2O}}} \right] + \\ & + \frac{k_{\mathrm{SR}} K^{A}_{\mathrm{CH_4}} \mathrm{p_{CH_4}}}{1 + K^{A}_{\mathrm{CH_4}} \mathrm{p_{CH_4}}} \left[1 - \frac{\mathrm{p_{CO} p^{3}_{H_2}}}{K_{\mathrm{SR}} \mathrm{p_{CH_4} p_{H_2O}}} \right] + \\ & - \frac{k_{\mathrm{DRM}} K^{A}_{\mathrm{CO_2}} K^{A}_{\mathrm{CH_4}} \mathrm{p_{CO_2} p_{CH_4}}}{1 + K^{A}_{\mathrm{CH_4}} \mathrm{p_{CH_4}} + K^{A}_{\mathrm{CO_2}} \mathrm{p_{CO_2}}} \left[1 - \frac{\mathrm{p^{2}_{CO} p^{2}_{H_2}}}{K_{\mathrm{DRM}} \mathrm{p_{CO_2} p_{CH_4}}} \right]\end{aligned}$$

Furthermore, the kinetics constants have been calculated using experimental data with best parameter estimations and minimizing the least squares objective function via optimization toolbox of MATLAB.

19.7 Conclusion

The literature review on the experimental work of biomass steam gasification showed that the pure steam is best gasification agent for hydrogen production. Steam gasification with CaO as sorbent improved the concentration of hydrogen in the system and also acts as catalyst. Catalytic steam gasification showed higher yield of hydrogen. So, there is need to integrate steam, CaO, and catalyst together for high purity and higher yield. Furthermore, EFB has potential for hydrogen production, so there is also need to study the biomass steam gasification using EFB as biomass for hydrogen production. The literature review on the modeling and simulation of biomass gasification showed that there are several works published on kinetics modeling for conventional gasification but limited work on biomass steam gasification specifically for hydrogen production. So there is a need to develop reaction kinetics model including the carbonation reaction along with the main steam gasification reactions. As kinetics model provides important data regarding the conversion of biomass to hydrogen which is essential to improve the process. The predictions from the kinetics model are more accurate compared to the thermodynamic equilibrium models, so the process can be simulated better with the experimental data. In addition, there is also need to work on the determination of the Arrhenius kinetic constant for all reactions involved in steam gasification with CaO for hydrogen production from biomass.

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Chapter 20
Bioethanol G2: Production Process and Recent Studies

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Contents

Abstract The demand for ethanol as a substitute of gasoline is rapidly increasing due to the recent increase of imbalance in oil market and interest in environmental issues. First-generation (G1) bioethanol which is currently derived mainly from food crops generate many problems such as net energy losses, greenhouse gas emission, and increased food price. On the other hand, biofuel produced from lignocellulosic materials, so-called second-generation (G2) bioethanol, shows environmental advantages in comparison to G1. The development of bioethanol G2 from lignocellulosic materials possesses many advantages from energy and environmental aspects. Efficient conversion of lignocellulosic biomass to ethanol and value-added biochemicals is still today a challenging proposition. Basically, four steps are included in the production process of bioethanol G2, composed of pretreatment, saccharification, fermentation, and product separation/purification. In each step, there are several ideas to improve its productivity and benefitability. In this chapter,

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*,
DOI 10.1007/978-3-319-07641-6_20,

we describe some details about the production process selection or ideas. New studies such as catalytic conversion of lignocellulosic biomass are also rapidly developing, although they are not yet mature to be utilized for industrial purposes.

Keywords Bioenergy • Lignocellulosic biomass • Pretreatment • Enzymatic saccharification • Catalytic conversion • Fermentation • Bioethanol

20.1 Introduction

Bioethanol, as a liquid fuel by the fermentation of renewable biomass, is important from viewpoint of global environmental protection. Biomass which includes animal and human waste, trees, shrubs, yard waste, wood, grasses, and agriculture residue is a renewable resource that stores energy from sunlight (McKendry 2002). Biofuel produced from lignocellulosic biomass, so-called second-generation (G2) bioethanol, shows environmental advantages in comparison to first-generation (G1) bioethanol from starch or sugar. However the conversion of lignocellulosic biomass to ethanol is more challenging due to the complex structure of the plant cell wall. The physical and chemical barriers caused by the close association of the main components of lignocellulosic biomass hinder the hydrolysis of cellulose and hemicellulose to fermentable sugars. Pretreatment is needed to alter the structural and chemical composition of lignocellulosic biomass to facilitate the rapid and efficient hydrolysis of carbohydrate to fermentable sugars (Chen et al 2005). The subject of this chapter emphasizes the lignocellulosic biomass in preparation for pretreatment, enzymatic saccharification, and fermentation for bioethanol G2 production and related studies on their catalytic conversion.

20.2 Lignocellulosic Biomass

Lignocellulose is a class of biomass that consists of three major compounds: cellulose, hemicellulose, and lignin. Lignocellulose is the most abundant renewable biomass; its annual production has been estimated in 1×10^{10} MT worldwide (Sánchez and Cardona 2008). Inside the lignocellulose complex, cellulose is a major structural component of cell walls, and it provides mechanical strength and chemical stability to plants; cellulose is found in both the crystalline and the noncrystalline structure and resistant to hydrolysis.

Hemicellulose is a copolymer of different C5 and C6 sugars that also exist in the plant cell wall. Important aspects of the structure and composition of hemicellulose are the lack of crystalline structure, mainly due to the highly branched structure, and the presence of acetyl groups connected to the polymer chain (Kirk-Otmer 2001a, b). Hemicellulose is positioned both between the micro- and the macrofibrils of cellulose.

Lignin is a complex polymer and is the binding of the matrix in which cellulose and hemicellulose are embedded. Considering that cellulose is the main material of the plant cell walls, most of the lignin is found in the interfibrous area, whereas a smaller part can also be located on the cell surface (Kirk-Otmer 2001a, b).

Apart from the three basic chemical compounds that lignocellulose consists of water and inorganic component are also present in the complex. Among inorganic contents, ash is one of the largest constituent. Ash typically comprises of calcium, potassium, magnesium, manganese, and sodium oxides, and lesser amount of other oxides of iron, aluminum, etc.

The cellulosic ethanol feedstock can be broadly categorized into agriculture residue, waste product, woody biomass, and energy crops. The composition of lignocellulose highly depends on its source. The composition of lignocellulose encountered in the most common sources of biomass is summarized in Table 20.1.

Bioethanol production from this feedstock could be attractive for disposal of these residues. Importantly, lignocellulosic feedstock does not interfere with food security. Moreover, bioethanol is very important for both rural and urban areas in terms of energy security reasons, environmental concern, employment opportunities, agricultural development, foreign exchange saving, socioeconomic issues, etc.

Since different lignocellulosic biomass have different physicochemical characteristics, it is necessary to adopt suitable pretreatment technologies based on the lignocellulosic biomass properties of each raw material.

20.3 Processing of Lignocellulose to Bioethanol

Lignocellulosic biomass consists mainly of lignin and the polysaccharides cellulose and hemicellulose. Compared with the production of ethanol from G1 feedstocks, the use of lignocellulosic biomass is more complicated because the polysaccharides are more stable and the pentose sugars are not readily fermentable by *Saccharomyces cerevisiae*. In order to convert lignocellulose to biofuels the polysaccharides must first be hydrolyzed, or broken down into simple sugars using either acid or enzymes.

Production process of lignocellulosic biomass to ethanol mainly consists of four steps: pretreatment, saccharification of cellulose to simple sugars, fermentation of simple sugars to ethanol, and product separation/purification to fuel grade ethanol. Schematic flow sheet for the production process of bioethanol from lignocelullosic biomass is shown in Fig. 20.1.

20.3.1 Pretreatment

The first step in lignocellulose conversion to bioethanol is size reduction and pretreatment. Pretreatment of biomass is technically challenging and is a large part of the process cost and therefore will need to be optimized prior to commercialization.

Table 20.1 Composition of representative lignocellulosic feedstocks

	Carbohydrate composition (% dry wt)		
Feedstocks	Cellulose	Hemicellulose	Lignin
Barley hull	34	36	19
Barley straw	36–43	24–33	6.3–9.8
Bamboo	49–50	18–20	23
Banana waste	13	15	14
Corn cob	32.3–45.6	39.8	6,7–13.9
Corn stover	35.1–39.5	20.7–24.6	11.0–19.1
Cotton	85–95	5.1–15	0
Cotton stalk	31	11	30
Coffee pulp	33.7–36.9	44.2–47.5	15.6–19.1
Dauglas fir	35–48	20–22	15–21
Eucalyptus	45–51	11.1–18	29
Hardwood stems	40–55	24–40	18–25
Rice straw	29.2–34.7	23–25.9	17–19
Rice husk	28.7–35.6	11.96–29.3	15.4–20
Wheat straw	35–39	22–30	13–16
Wheat brain	10.5–14.8	35.5–39.2	8.3–12.5
Grasses	25–40	25–50	10.2–30
News paper	40–45	24–39	18–30
Sugarcane bagasse	25–45	28–32	15–25
Sugarcane tops	35	32	14
Pine	42–49	13–25	23–29
Poplar wood	45–51	25–28	20–21
Olive tree biomass	25.2	15.8	19.1
Jute fibers	45–53	18–21	21–26
Switchgrass	35–40	25–30	15–20
Winter rye	29–30	22–26	16.1
Oilseed rape	27.3	20.5	14.2
Softwood stem	45–50	24–40	18–25
Oat straw	31–35	20–26	10.1–15
Nut shells	25–30	22–28	30–40
Sorghum straw	32–35	24–27	15–21
Tamarind kernel	11–15	55–56	–
Water hyacinth	18.2–22.1	48.7–50.1	3.5–5.4

Menon and Rao (2012)

The purpose of the pretreatment step is increasing the surface area and porosity, lignin removal, depolymerization of hemicellulose, hemicelluloses removal, and disruption of lignocelluloses structure. Thus the cellulose component is accessible to hydrolyzing agents and reduces the crystallinity of cellulose to further facilitate hydrolysis (Balat et al. 2008).

A successful pretreatment must meet the following requirements: (1) improve formation of sugars or the ability to subsequently form sugars by hydrolysis, (2) avoid degradation or loss of carbohydrate, (3) avoid formation of by-products inhibitory to subsequent hydrolysis and fermentation processes, and (4) minimize energy input

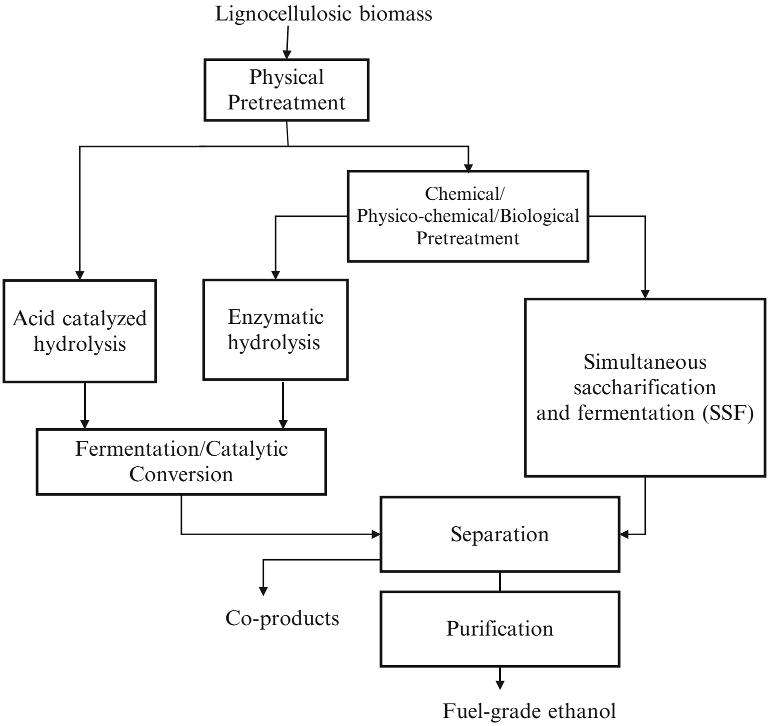


Fig. 20.1 Ethanol production from lignocellulosic biomass

and be cost-effective. The pretreatment stage promotes the physical disruption of the lignocellulosic matrix in order to facilitate acid- or enzyme-catalyzed hydrolysis. Pretreatments can have significant implications on the configuration and efficiency of the rest of the process and, ultimately, also the economics (Hamelinck et al. 2005). The goal of pretreatment of lignocellulosic biomass to biofuel is depicted in Fig. 20.2.

The most pretreatments are done through physical or chemical means. In order to achieve higher efficiencies, both physical and chemical pretreatments are required. Physical pretreatment is often aimed to reduce size of the biomass. Chemical pretreatment is aimed at removing chemical barriers so that the enzyme can access cellulose for microbial destruction. Each type of feedstock requires a particular combination of pretreatment methods to optimize the yield of that feedstock, minimize degradation of the substrate, and maximize the sugar yield.

20.3.1.1 Physical Pretreatment

Physical pretreatment processes employ the combination of mechanical and irradiation processes to change only the physical characteristics of biomass. Physical pretreatment is usually carried out before a following processing step which is often needed

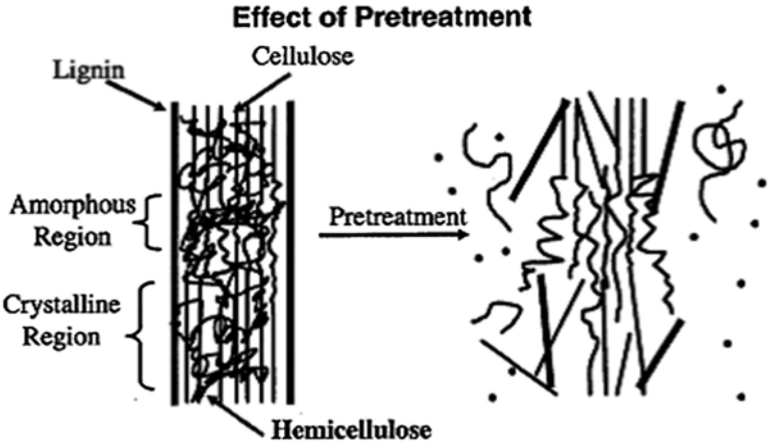


Fig. 20.2 Schematic representation on biomass pre-treatment (Mosier et al. 2004)

to reduce the particle size, make material handling easier, reduce volume, and increase surface area. This can be done by a combination of chipping, grinding, or milling depending on the final particle size of the lignocellulose biomass (10–30 mm after chipping and 0.2–2 mm after milling or grinding) (Sun and Cheng 2002). Different milling processes (ball milling, two-roll milling, hammer milling, colloid milling, and vibro energy milling) can be employed to improve the enzymatic hydrolysis of lignocelullosic biomass (Taherzadeh and Karimi 2008). Mechanical pretreatment factors such as operating costs and depreciation of equipment are very important.

20.3.1.2 Chemical Pretreatment

Chemical pretreatment was originally developed and have been extensively used in the paper industry for delignification of cellulosic materials to produce paper products. Chemical pretreatment to date has primary goal to improve the biodegradability of cellulose by removing lignin and hemicellulose and to lesser degree of crystallinity of the cellulose component. Chemical pretreatment is the most studied pretreatment technique among pretreatment categories. The various commonly used chemical pretreatment are acid, alkali, organic acids, pH-controlled liquid hot water, and ionic liquids.

Acid pretreatment uses dilute sulfuric acid (H_2SO_4), the most common chemical pretreatment which has been commercially used for a wide variety of biomass types. Other acids also have been studied such as hydrochloric acid (HCl) (Wang et al. 2010), phosphoric acid (H_3PO_4) (Zhang et al. 2007; Marzialetti et al. 2008), and nitric acid (HNO_3) (Himmel et al. 1997). Concentrated acids such as H_2SO_4 and HCl have been widely used for lignocellulosic material pretreatment because they are powerful agents for cellulose hydrolysis (Sun and Cheng 2002). Due to its ability to remove hemicellulose, acid pretreatment has been used in fractionating the components of lignocellulosic biomass. In this sense, sulfuric acid can resolve hemicelluloses and activate the enzymatic activity to cellulose.

Alkaline pretreatment uses base compounds like sodium hydroxide, potassium, calcium, and ammonium hydroxides. The major effect of alkaline pretreatment is the removal of lignin from the biomass, thus improving the reactivity of the remaining polysaccharides. NaOH causes swelling, increasing the internal surface of cellulose and decreasing the degree of polymerization and crystallinity, which provokes lignin structure disruption (Taherzadeh and Karimi 2008). NaOH has been reported to increase hardwood digestibility from 14 to 55 % by reducing lignin content from 24 to 55 % to 20 % (Kumar and Wyman 2009). In the case of pretreatment of corn stover by aqueous ammonia, 70–85 % lignin was removed, and 40–60 % of hemicelluloses were solubilized (Kim et al. 2003). Whereas pretreatment of Oil palm EFB using 6 % sodium hydroxide can remove 60–70 % lignin (Sudiyani et al. 2013). The characteristic of alkaline pretreatment is that it can remove the lignin without having big effects on other components (McMillan 1996). Some other alkaline processes reported were alkaline peroxide which combined sodium hydroxide and hydrogen peroxide or alkali and microwave. Some reports mentioned that pretreatment using alkali is one of the processes close to commercialization. Alkaline-based methods are generally more effective at solubilizing a greater fraction of lignin while leaving behind much of the hemicellulose in an insoluble polymeric form. The alkaline process involves soaking the biomass in alkaline solutions and mixing it at a target temperature for certain amount of time. A neutralizing step to remove lignin and inhibitors (salts, phenolic acid, furfural, aldehydes, others) is required before enzymatic hydrolysis. Alkaline pretreatment are more effective on agriculture residue and herbaceous crops than on wood materials (Hsu 1996).

20.3.1.3 Combination Physicochemical Pretreatments

Several pretreatment processes combine physical and chemical elements. The most common of *physicochemical pretreatments* used are steam explosion: SO_2-steam explosion, Liquid hot water, ammonia fiber explosion (AFEX), Microwave pretreatment, Ultrasound pretreatment, and carbon dioxide (CO_2) explosion.

Steam explosion is the most widely employed physicochemical pretreatment for lignocellulosic biomass. It is a hydrothermal pretreatment in which the biomass is subjected to pressurized steam for a period of time ranging from seconds to several minutes, and then suddenly depressurized. This pretreatment combines mechanical forces and chemical effects due to the hydrolysis (autohydrolysis) of acetyl groups present in hemicellulose. Autohydrolysis takes place when high temperatures promote the formation of acetic acid from acetyl groups; furthermore, water can also act as an acid at high temperatures.

Addition of dilute acid in steam explosion can effectively improve enzymatic hydrolysis, decrease the production of inhibitory compounds, and lead to more complete removal of hemicellulose.

The most important factors affecting the effectiveness of steam explosion are particle size, temperature, residence time, and the combined effect of both temperature and time (Alfani et al. 2000). Higher temperatures result in an increased removal of hemicelluloses from the solid fraction and an enhanced cellulose digestibility; they also promote higher sugar degradation.

AFEX involves liquid ammonia and steam explosion. A typical AFEX process is carried out with 1–2 kg ammonia/kg dry biomass at 90 °C pH values (<12.0) during 30 min. It reduces the lignin content and removes some hemicellulose while decrystallizing cellulose. The important advantages of AFEX include: (1) producing negligible inhibitors for the downstream biological processes, so water wash is not necessary (Mes-Hartree et al. 1988); and (2) requiring no particle size reduction. However, ammonia must be recycled after the AFEX pretreatment based on the considerations of both the ammonia cost and environmental protection. Therefore, both ammonia cost and the cost of recovery processes drive up the cost of the AFEX pretreatment (Holtzapple et al. 1992).

Carbon dioxide (CO_2) explosion acts similar to steam and ammonia explosion: high-pressure CO_2 is injected into the batch reactor and then liberated by an explosive decompression. It is believed that CO_2 reacts to carbonic acid (carbon dioxide in water), thereby improving the hydrolysis rate. The glucose yields in the later enzymatic hydrolysis are low (75 %) compared to steam and ammonia explosion. Overall however (CO_2) explosion is more cost-effective than ammonia explosion and does not cause the formation of inhibitors as in steam explosion.

20.3.1.4 Biological Pretreatment

Biological pretreatments use microorganisms viz. fungi to solubilize the lignin. Biodelignification is the biological degradation of lignin by microorganism. Fungi have distinct degradation characteristics on lignocellulosic biomass. In general, brown and soft rots mainly attack cellulose while imparting minor modifications to lignin, and white-rot fungi more actively degrade the lignin component (Sun and Cheng 2002). Several white-rot fungi such as *Phanerochaete chrysosporium*, *Ceriporia lacerata*, *Cyathus stercoreus*, *Ceriporiopsis subvermispora*, *Pycnoporus cinnabarinus*, and *Pleurotus ostreatus* have been examined on different lignocellulosic biomass showing high delignification efficiency (Kumar and Wyman 2009; Shi et al. 2008). Biological pretreatment by white-rot fungi has been combined with organosolv pretreatment in an ethanol production process by simultaneous saccharification and fermentation (SSF) from beech wood chips (Itoh et al. 2003).

The biological pretreatment appears to be a promising technique and has very evident advantages, including no chemical requirement, low energy input, mild environmental conditions, and environmentally friendly working manner (Kurakake et al. 2007; Salvachúa et al. 2011). However, its disadvantages are as apparent as its advantages since biological pretreatment is very slow and requires careful control of growth conditions and large amount of space to perform treatment. However, the main drawback to develop biological methods is the low hydrolysis rate obtained in most biological materials compared to other technologies (Sun and Cheng 2002).

20.3.2 Saccharification

Hydrolysis is the process to break down the pretreated cellulosic molecules into cellobiose, which is then further converted to simple sugar, such as glucose molecules and short chains. Hydrolysis can be carried out biologically through enzymatic reaction or chemically using acid.

20.3.2.1 Saccharification by Enzymatic Processes

One of the basic methods of hydrolysis is enzymatic hydrolysis. Enzymatic hydrolysis occurs when enzymes are exposed to the pretreated biomass to decompose the cellulosic materials into simple sugars. Cellulose in nature is mostly decomposed by cellulolytic fungi and bacteria enzymatically. Some of the microbes that can produce cellulose enzyme are *Trichoderma reesei*, *Trichoderma viride*, and *Aspergillus niger*.

Enzymatic degradation of cellulose to fermentable sugar is generally accomplished by synergistic action of high specific cellulose. This group includes at least 15 protein families and some subfamilies (Rabinovich et al. 2002). Enzymatic degradation of cellulose to glucose is generally accomplished by synergistic action of at least three major classes of enzyme: endocellulase, exocellulase, and β-glucosidase. These enzymes are usually called together cellulose or cellulolytic enzymes (Wyman 1996). To work, enzymes must obtain access to the molecules to be hydrolyzed. Therefore, pretreatment process is needed to break the crystalline structure of the lignocellulose and remove the lignin to expose the cellulose and hemicellulose molecules.

The enzymes digest the lignin surface yielding cellulose. The endocellulase and exocellulase digest the cellulose into polysaccharide molecules. The polysaccharide molecules are then digested by the β-glucosidase yielding the final glucose product (Klass 2008). The reaction occurs around 40–50 °C and at a pH of about 5. Below, the figure demonstrates how the reaction path occurs.

However, enzymatic hydrolysis can be problematic. The hydrolysis products (glucose and cellulose chains) inhibit the ability for enzymes to convert cellulose to glucose. As more products are formed, the enzymes become more inhibited by the excess glucose present. This ultimately slows down the hydrolysis process yielding low levels of usable hydrolysis product (D'amore 1991). Another disadvantage of using enzyme is the high enzyme cost. The enzyme cost takes a part as much as 53–65 % of total chemical cost, while the chemical cost is around 30 % of the total cost.

Enzymatic hydrolysis of lignocellulose is facing a number of obstacles that diminish the enzyme performance. Recently, although enzyme price has decreased due to intensive research by giant enzyme producers, such as Novozymes and Genencor, minimization of enzyme loading is still needed in order to reduce the production cost. Thus affecting the time needed to complete the enzymatic hydrolysis process. Furthermore, high substrate concentration increases the problem of product inhibition which also results in lower performance of the enzymes. Then, lignin presence in the substrate, which shields the cellulose chains and absorbs the enzymes, is also a major obstacle for efficient hydrolysis. Moreover, the activity of enzymes could be lost due to denaturation or degradation.

20.3.2.2 Catalytic Hydrolysis of Cellulose to Glucose

Acid-Catalyzed Hydrolysis: Hydrolysis of cellulosic materials can be catalyzed by either a dilute or concentrated acid. Sulfuric acid is the most investigated acid, although other acids such as hydrochloric acid have also been applied. The acid reacts with cellulose to produce glucose and short chain molecules which is further transformed to the desired fuel grade bioethanol.

Dilute acid hydrolysis is a method that can be used either as a pretreatment preceding enzymatic hydrolysis or as the actual method of hydrolyzing lignocelluloses to sugars (Qureshi and Manderson 1995). The process is conducted under high temperature and pressure, and the reaction time is in the range of seconds or minutes, which facilitates continuous processing (Lee et al. 1999). Although the process shows low acid consumption, the combination of acid and high temperature and pressure may cause the degradation of glucose to undesirable by-products such as levulinic acid, acetic acid, formic acid, and furfural, decreasing the yield of glucose.

On the other hand, concentrated acid hydrolysis occurs in relatively mild temperatures and atmospheric pressure. The process is more efficient and produces high sugar recovery efficiency, which can be on the order of over 90 % of both hemicellulose and cellulose sugars. Typically, 1 % of sulfuric acid is used at elevated pressure (42.0 MPa) and temperature (493 K). An advantage of this process over enzymatic hydrolysis is the high hydrolysis rate, with residence times of the order of several seconds. The mild temperatures and pressures employed allow the use of relatively low-cost materials. Unfortunately, the process is time-consuming, taking up to 120 h to complete. Also, the acid catalyst after the reaction is difficult to recover generating acid wastes (Fig. 20.3).

Solid Acid-Catalyzed Hydrolysis: Homogeneous catalysts such as sulfuric acid and enzymes produce glucose from cellulose in high yields; however, these processes suffer from the complicated product recovery and high production costs. The low selectivity of product due to the further degradation of glucose in harsh conditions should also be improved. Solid acid catalysts are expected to overcome these problems as various types of the catalysts can be designed and applied in a wide range of reaction conditions. Furthermore, solid catalysts are easily recovered and reused.

Solid acids, e.g., zeolites, sulfonated zirconia and sulfonated carbons, can carry a high concentration of strong Bronsted acid sites, creating a very acidic environment in the catalyst pores or close to the catalyst surface. H-form zeolites and sulfonated mesoporous silicas were used as solid acid catalysts for the hydrolysis of soluble oligosaccharides and starch. Sulfonated activated-carbon catalysts showed a remarkably high yield of glucose, which was due to the high hydrothermal stability

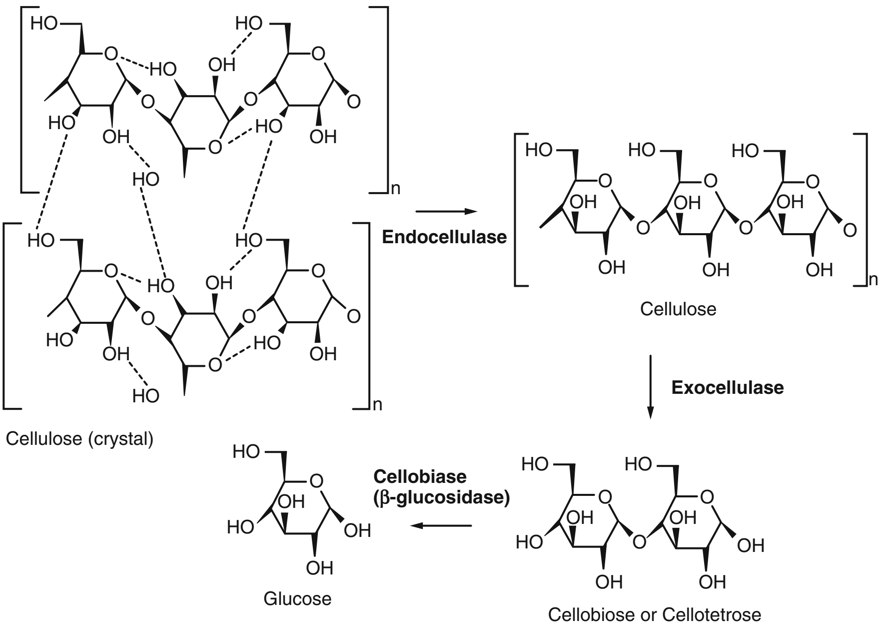


Fig. 20.3 Reaction route of cellulose to glucose

and the excellent catalytic property attributed to the strong acid sites of SO_3H functional groups and the hydrophobic planes, selectivity 90 % (Onda et al. 2008). The hydrolysis of cellulose with a highly active solid acid catalyst bearing SO_3H, COOH, and OH groups was also investigated at 323–393 K using an artificial neural network (ANN) and a response surface methodology (RSM). The study shows that hydrolysis reaction depends largely on the amount of water as the solvent. The glucose yield by the solid acid catalyst reaches a maximum with an amount of water comparable to the catalyst weight. The reaction efficiency increases with increasing reaction temperature up to 363 K and does not increase in proportion to the reaction temperature above 363 K, suggesting that degradation of the cellulose surface by the acid catalyst prevents efficient hydrolysis of cellulose (Yamaguchi et al. 2009).

Recently, many new catalysts have emerged as powerful tools for the hydrolysis of cellulose to sugars. Ferrate $CaFe_2O_4$ was used as a solid catalyst for cellulose hydrolysis giving a glucose yield of 37 and 74 % selectivity. Ionic liquid was used for pretreatment to reduce the crystallinity of cellulose. The reaction was carried out at 423 K over 24 h. Hydrolysis of cellulose using hydrotalcite $[Mg_4Al_2(OH)_{12}CO_3{\cdot}4\,H_2O]$ activated by saturated $Ca(OH)_2$ showed the conversion and glucose selectivity of 46.6 % and 85.3 %, respectively. The reaction was carried out at 423 K over 24 h with ball-milled cellulose. The solid acid catalyst could be reused four times and the catalytic activity remained. Compared with carbon-based solid acids, the activated hydrotalcite catalyst is more stable and can be separated more easily from the reaction mixture (Fang et al. 2011).

20.3.3 Fermentation

20.3.3.1 Fermentation Using Microbes

Ethanol fermentation is a biological process in which organic material is converted by microorganisms to simpler compounds, such as sugars. These fermentable compounds are then fermented by microorganisms to produce ethanol and CO_2.

Several reports and reviews have been published on production of ethanol fermentation by microorganisms, and several bacteria, yeasts, and fungi. Among those microbes that are capable of yielding ethanol as the major product, *Saccharomyces cerevisiae* and *Zymomonas mobilis* can accumulate high concentration of ethanol in fermentation media. Historically, the most commonly used microbe has been yeast. Among the yeasts, *Saccharomyces cerevisia*e, which can produce ethanol to give concentration as high as 18 % of the fermentation broth, is the preferred one for most ethanol fermentation (Lin and Tanaka 2006). This yeast can grow both on simple sugars, such as glucose, and on the disaccharide sucrose. Some other yeast species which produce ethanol are summarized in Table 20.2.

As mentioned before, that the accumulation of hydrolysis products in the medium will inhibit hydrolysis process, hydrolysis and fermentation process combination in one-step reaction could be one way to overcome the problem. Known as simultaneous saccharification and fermentation (SSF), the process allows the glucose produced from hydrolysis to be fermented immediately. This allows the concentration of the glucose in the SSF medium to remain low, so that the hydrolysis process continues without significant inhibition (Takagi 1976).

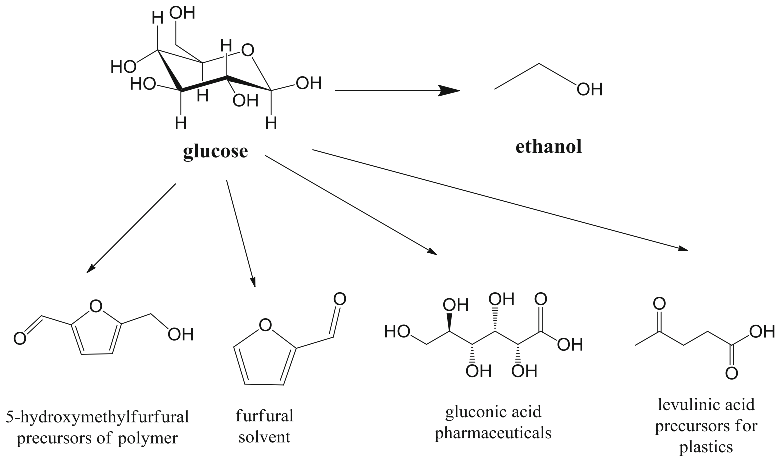
SSF possess some other advantages, such as shorter the length of time required for the lignocellulosic biomass to ethanol conversion process, fewer enzymes needed compared to that for regular enzymatic hydrolysis. Furthermore, the chances of contamination are reduced because the process occurs within the same reaction vessel. However, there are fundamental problems with SSF: hydrolysis and fermentation both require specific temperature ranges for optimal operation. *S. cerevisiae* shows the best activity at temperatures around 32 °C with a pH of between 4 and 5 (Wasungu 1982). Any extreme of temperature during fermentation, either high or low, produces lower ethanol concentrations. Yeast does not grow well in temperatures lower than 20 °C or higher than 40 °C. The hydrolysis process, however, performs best at temperatures of about 50–55 °C (Palmqvist 2000). If the temperature is lower than the optimum one, the enzymes will not digest material optimally.

The presence of the ethanol in the fermentation medium during SSF has the possibility of inhibiting the fermentation reaction. As the concentration in ethanol increases, the ethanol attacks the various microorganisms in the system. Both the enzymes and the yeast undergo plasma membrane degradation as the ethanol concentration increases. Eventually, the ethanol concentration will become high enough to cause cell death in both the enzymes and the yeast (D'amore 1991). Therefore, thermostable strains capable of producing substantial amounts of ethyl alcohol at optimum temperature saccharification and suitably resistant to ethanol are needed to

Table 20.2 Yeast species which produce ethanol as the main fermentation product

Species	Temperature (°C)	pH	Carbon source and concentration (g/L)	Nitrogen source and concentration (g/L)	Incubation (h)	Ethanol concentration (g/L)
27817-*Saccharomyces cerevisiae*	30	5.5	Glucose (50–200)	Peptone (2) and ammonium sulfate (4)	18–94	5.1–91.8
L-041-*S. cerevisiae*	30 or 35	–	Sucrose (100)	Urea (1) or ammonium sulfate (1–2)	24	25–50
181-*S. cerevisiae* (aerobic)	27	6	Glucose (10)	Peptone (5)	40–160	–
UO-1-*S. cerevisiae* (aerobic)	30	5	Sucrose (20)	Ammonium sulfate (1)	60–96	–
V5-*S. cerevisiae*	24	–	Glucose (250)	–	36	–
ATCC 24860-*S. cerevisiae*	30	4.5	Mollases (1.6–5)	Ammonium sulfate (0.72–2)	24	5–18.4
Bakers' yeast-*S. cerevisiae*	30	4.5	Sugar (50–300)	–	192	53
Bakers' yeast-*S. cerevisiae*	28	5	Sucrose (220)	Peptone (5) and ammonium dihydrogen phosphate (1.5)	96	96.71
Fiso-*S. cerevisiae*	30	5	Galactose (20–150)	Peptone, ammonium sulfate, and casamino acid (10)	60	4.8–40
A3-*S. cerevisiae*	30	5	Galactose (20–150)	Peptone, ammonium sulfate, and casamino acid (10)	60	4.8–36.8
L.52-*S. cerevisiae*	30	5	Galactose (20–150)	Peptone, ammonium sulfate, and casamino acid (10)	60	2.4–32
GCB-K5-*S. cerevisiae*	30	6	Sucrose (30)	Peptone (5)	72	27
GCA-II-*S. cerevisiae*	30	6	Sucrose (30)	Peptone (5)	72	42
KR_{18}-*S. cerevisiae*	30	6	Sucrose (30)	Peptone (5)	72	22.5
CM1237-*S. cerevisiae*	30	4.5	Glucose (160)	Ammonium sulfate (0.5)	30	70
2.399-*S. cerevisiae*	30	5.5	Glucose (31.6)	Urea (6.4)	30	13.7
24860-*S. cerevisiae*	–	–	Glucose (150)	Ammonium dihydrogen phosphate (2.25)	27	48
27774-*Kluyveromyces fragilis*	30	5.5	Glucose (20–120)	Peptone (2) and ammonium sulfate (4)	18–94	48.96
30017-*K. fragilis*	30	5.5	Glucose (20–120)	Peptone (2) and ammonium sulfate (4)	18–94	48.96
30016-*Kluyveromyces marxianus*	30	5.5	Glucose (100)	Peptone (2) and ammonium sulfate (4)	18–94	44.4
30091-*Candida utilis*	30	5.5	Glucose (100)	Peptone (2) and ammonium sulfate (4)	18–94	44.4
ATCC-32691*Pachysolentannophilus*	30	5.5	Glucose (0–25) and xylose (0–25)	Peptone (2) and ammonium sulfate (4)	100	7.8

Lin and Tanaka (2006)



Scheme 20.1 Conversion of glucose to ethanol and co-products

explore (Szczodrak and Targonski 1988). Such thermostable yeast strains make possible to conduct the fermentation at 42 °C with increased ethanol production (Sree et al 1999). One example of thermostable yeast strain is *Kluyvero mycesmarxianus CHY1612* which is possible to shift temperature for SSF (Kang et al. 2012). Furthermore, the negative effects which excessive concentrations of ethanol have on yeast activity and cellulase within the SSF system are eliminated with a vacuum cycling reactor where the concentration of ethanol was kept at a relatively low level by its removal from the flash chamber (Roychoudhury et al. 1992).

However, more efforts have to be made in the development of microorganisms for industrial ethanol production. In addition, it is important to know the rate-limiting step. In SSF, the ethanol production rate is controlled by the cellulase hydrolysis rate and not the glucose fermentation, and hence, steps to increase the rate of hydrolysis will lower the cost of ethanol production via SSF.

20.3.3.2 Catalytic Conversion of Glucose to Ethanol and Co-products

Glucose, which can be synthesized via the hydrolysis of cellulose, is a versatile precursor to valuable chemicals such as biodegradable plastics and ethanol (Scheme 20.1).

Bioethanol can be obtained from glucose by a hydrogenolysis reaction, although reports on the chemocatalytic conversion still give low yields of ethanol with primarily products such as ethylene and propylene glycols (Bozell and Petersen 2010). Metal phosphides Ni_2P, CoP, Cu_3P, Fe_2P, WP supported on carbon have been tested in the hydrogenolysis of polyalcohols and in the presence of the 2 % Ni_2P/AC catalyst in reaction conditions of 200 °C, 4.0 MPa of hydrogen, and reaction time

45 min, the yield of ethanol was only 3.2 % (Sotak et al. 2013). Biocatalysts are currently more superior in the production process of ethanol compared to that of chemocatalytic conversions. Therefore, research on the selective catalytic hydrogenolysis of glucose to ethanol is essential. On the other hand, synthesis of co-products such as furans and organic acids has been widely developed using a number of catalytic processes.

Of the first class of reactions, dehydration of glucose to 5-hydroxymethylfurfural (5-HMF) has been considered to be an important and renewable platform chemical. Reported solid acid catalysts generally included H-form zeolites, ion-exchange resins, vanadyl phosphate, and ZrO_2 (Tong et al. 2010). Around 42–54 % yield of 5-HMF can be produced from glucose and sucrose by a simple one-pot synthesis using a combination of Amberlyst-15 and Mg–Al hydrotalcite (HT) as catalyst in N,N-dimethylformamide at 100 °C (Takagaki et al. 2009). Moreover, in the Ti O_2- and Zr O_2-catalyzed conversion of glucose to 5-HMF, TPD measurement results showed that the strength of the acidity and basicity was important for the 5-HMF formation from glucose (Watanabe et al. 2005). Molecular sieves, i.e., HY zeolite, aluminum-pillared montmorillonite, MCM-20, and MCM-41, also promoted the dehydration of glucose, although formic acid or 4-oxopentanoic acid was easily formed in those processes (Lourvanij and Rorrer 1997). Meanwhile, dehydration with mineral acid as catalyst using different types of solvents has also been tested and the yield of 5-HMF could be improved in a biphasic reactor system (Szmant and Chundury 1981). Hydrolysis of the C5 sugars of hemicellulose may lead to furfural which is an important chemical solvent.

Subsequent rehydrated 5-HMF gives levulinic and formic acids as the final products. Levulinic acid has been identified as a promising green, biomass-derived platform chemical. Levulinic acid contains a ketone group and a carboxylic acid group. These two functional groups make levulinic acid a versatile building block for the synthesis of various organic chemicals (Thomas and Barile 1985). For instance, 2-methyl-tetrahydrofuran and various levulinate esters may be used as gasoline and biodiesel additives, respectively. d-Aminolevulinate is a known herbicide and the bisphenol derivative may be an interesting.

The oxidation of glucose is another representative example of the conversion of sugars using supported Pt, Pd, or Au catalyst. The primary oxidation products of glucose oxidation are gluconic acid and glucaric acid, and from gluconic acid are 2-keto-gluconic acid and glucuronic acid (Hermans et al. 2011). Gluconic acid is an important food and pharmaceutical industry intermediate that is usually produced by enzymatic or chemical oxidation of glucose (Climent et al. 2011). Recently, Tan et al. (2009)showed the selective aqueous hydrolytic oxidation of cellobiose, the dimer of cellulose, over a gold nanoparticle loaded on nitric acid-pretreated carbon nanotube catalyst (Au/CNT); achieving 68 % yield of gluconic acid at 81 % conversion. Although chemical glucose oxidation usually proceeds in a basic medium, the authors found the reaction to occur without pH control.

Bio-based products from lignocellulosic biomass such as bioethanol and valuable co-products have unique properties compared to hydrocarbon-derived products such as biodegradability and biocompatibility. Their developments are driven by the need for alternative, less expensive reagents, and the mandate to reduce the environmental impact of chemical production process. Derivative of glucose can be used as the starting materials for these bio-based products as well as for the replacement of oil-derived chemicals.

20.3.4 Separation and Purification

There are some alternative methods for recovering ethanol from aqueous solutions, in this termed as fermentation broth. These include distillation, membrane permeation, vacuum stripping, gas stripping, solvent extraction, adsorption, and various hybrid processes. The most common method applied is distillation process. However, depending on the concentration of the feed solution and other factors, some of these methods have the potential to be less energy intensive than distillation. For instance, solvent extraction of dilute feeds of 2 % ethanol has been reported to have substantially energy savings (Richard et al. 2008).

When SSF is completed, the liquid fraction of the fermentation broth contains mainly ethanol, but also a large numbers of other organic compounds, such as residual sugars, acetic acids, and amyl alcohols. The concentration of ethanol depends on the concentration solid used in the SSF. In most cases, the solid concentration is chosen to result in at least 4–5 % w/w ethanol. The broth also contains solid residue, consisting mainly of lignin, some unreacted cellulose, and yeast. The main challenges in terms of separation processes in ethanol production are downstream of the fermentation. The interesting products in the broth are ethanol, solid, and residual low molecular weight organic substances. Important separation challenges in ethanol production from fermentation broth are shown in Fig. 20.4.

In brief, separation is employed at various stage of the process. There are some alternative methods for recovering ethanol from aqueous solutions, in this termed as fermentation broth. These include distillation, membrane permeation, vacuum stripping, gas stripping, solvent extraction, adsorption, and various hybrid processes. The most common method applied is distillation process. The fermentation broth is first distilled in a stripper column, in order to separate the ethanol content from the broth and concentrate the ethanol to above 20 % v/v (Galbe et al. 2013). After the stripper, the ethanol stream is further concentrated in rectifier column. As ethanol and water form azeotrope, the distillate from the rectifier column will only be concentrated to near azeotropic concentration, 96 % v/v ethanol. To be blended with gasoline, dehydration process in order to yield water-free ethanol must be done.

Fuel ethanol or absolute alcohol is produced by dehydration of rectified product. Ethanol dehydration technologies are now very interesting to develop. Several ethanol dehydration methods, such as azeotropic distillation, extractive distillation, molecular sieve adsorption, pressure swing adsorption (PSA), pervaporation and vapor permeation (Bastidas et al. 2010), azeotropic distillation, and molecular sieve technology, are commercially available. However, PSA process is prospective to replace the common technology due to performance, cost, and environmental reason. In the PSA, two steps of adsorption and desorption are carried out in two adsorbent beds operated

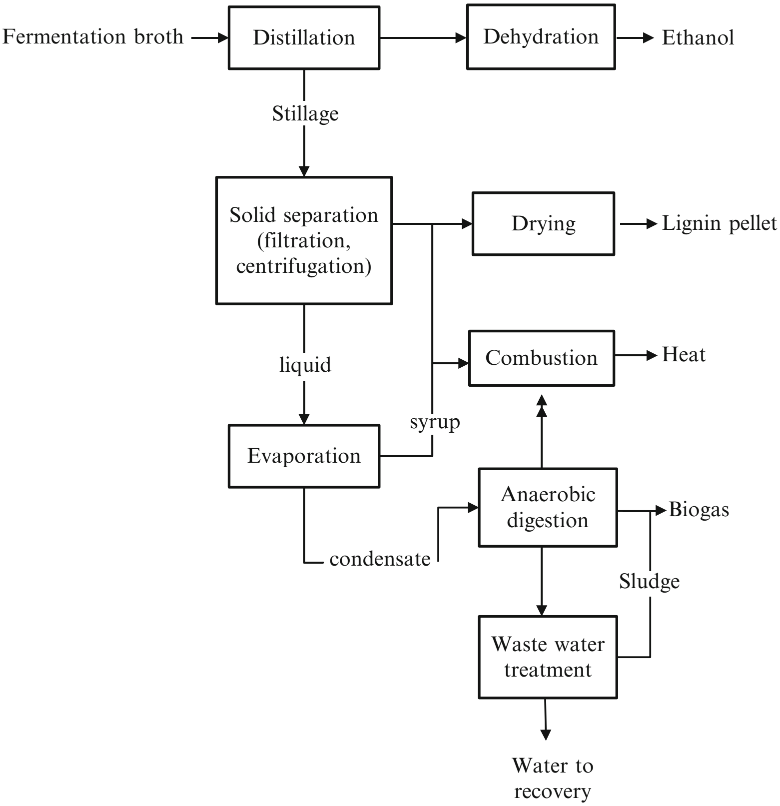


Fig. 20.4 Separation process of fermentation broth to yield ethanol and other co-products

in tandem, so that a continuous process can be operated. The adsorbent is regenerated by rapidly reducing the partial pressure of the adsorbed component by lowering the total pressure or by using a purge gas (Galbe et al. 2013).

20.4 Conclusions and Perspectives

Lignocellulosic biomass from agricultural and forest residues could prove to be an ideally inexpensive and abundantly available source of sugar fermentation into transportation fuel compared to bioethanol G1 from starch crops. Many techniques are used in the industrial ethanol production process. However, the biggest concern of the process is its effectiveness, low environmental impact, and cost-efficiency. Extensive research has been done on the development of advanced pretreatment, saccharification, fermentation, and purification technologies to prepare more digestible biomass and easy bioconversion of biomass into cellulosic ethanol. New technologies such as catalytic processes are promising due to its high selectivity toward a desired product although the balance between the overall cost and effectiveness is still being considered for industrial use. The utilization of fuel ethanol for transportation has potential to substitute gasoline and contribute to a cleaner environment. Therefore, the fuel industry will benefit from the efficient utilization of lignocellulosic biomass for bioethanol G2 production.

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K.R. Hakeem et al. (eds.), *Biomass and Bioenergy: Processing and Properties*, DOI 10.1007/978-3-319-07641-6,