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Madhumi Mitra
Abhijit Nagchaudhuri *Editors*

Practices and Perspectives in Sustainable Bioenergy

A Systems Thinking Approach

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Dedicated to my beloved mother and father
who have been my inspiration and guiding
stars that light the sky every night.
Madhumi Mitra

Preface

We are living in a world that is seeking solutions to its energy, environmental, and food challenges. The global population, increased transportation, and the production of meat are on the rise, and these are some of the active contributors to greenhouse gases. The land for biofuels can have adverse effects, as clearing of native ecosystems for the production of biofuel crops can result in the loss of biodiversity and additional greenhouse gas emissions. If land used for food crops is converted to producing biofuel crops, then there will be a compulsion for the farmers to clear wild lands and grow food crops. The indirect land-use effects will also affect the food prices. So what is the solution to this complex situation? The biofuel dialogue has become increasingly polarized. In many cases, we find politics reigning science. There is an urgent need to adopt and implement science-based environmental safeguards including changing of lifestyles for a more sustainable world. We also need to enhance collaborations among scientists, economists, engineers, social scientists, agricultural community, engaged citizens, and governments locally, nationally, and globally.

Through the book “Practices and Perspectives in Sustainable Bioenergy: A Systems Thinking Approach,” we have brought together the relevant experts in the respective fields of research and teaching in the areas of bioenergy, bioproducts, and sustainability. The contributing authors include biologists, chemists, economists, engineers, environmental scientists, and physicists. The book presents “a systems approach to bioenergy and provides a means to capture the complexity of bioenergy issues, including both direct and indirect impacts across the energy economy.” It addresses critical topics such as systems thinking; sustainability and biomass; feedstock of importance and relevance; anaerobic digestion and biogas; biopower and bioheat; and policies, economy, and rights to access to clean energy. Each chapter is an original contribution based on cutting-edge research and includes a review with highlights of the key points, critical-thinking questions, and a glossary. The open-ended questions will create the opportunity for readers to hone their content skills, explore, and think out of the box. It is our hope that as environmentally conscious global citizens, we would continue to strive towards taking steps in making our earth more habitable and sustainable.

Princess Anne, USA Madhumi Mitra, Ph.D.

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About the Editors

Dr. Madhumi Mitra received her doctoral degree (Ph.D) in Plant Biology from North Carolina State University, Raleigh, NC, USA. She is currently a professor of biological and environmental sciences in the department of natural sciences at University of Maryland Eastern Shore. Her other responsibilities include coordination of Biology and Chemistry Education programs. Her research interests and expertise include: micro and macroalgal ecology; seaweeds in human health and nutrition; biomonitoring and biosorption potential of seaweeds and seagrasses; bioenergy from algae; water quality; and reconstruction of the past environment and climate from microfossils. She is the recipient of various research and teaching awards, and has published in many peer-reviewed journals and proceedings, and presented her work at national and international conferences. She has also received many competitive grants from federal and state agencies.

Dr. Abhijit Nagchaudhuri obtained his doctoral degree (Ph.D) in Mechanical Engineering from Duke University, Durham, NC, USA. He is currently serving as a professor of engineering in the department of engineering and aviation sciences at University of Maryland Eastern Shore. His research interests and expertise include: biofuels and other forms of renewable energy; engineering mechanics; robotics and control systems; and precision agriculture and remote sensing. Dr. Nagchaudhuri has a strong record of grantsmanship and awards. He has published in various peer-reviewed journals and proceedings, and presented his research at national and international conferences.

Bioenergy Systems—A Wholistic Approach

Abhijit Nagchaudhuri and Madhumi Mitra

Abstract While reductionism has helped drive scientific and technological progress with focused attention to parts of the whole, a wholistic systems approach is imperative for effectively addressing the global trilemma of food, energy, and environment in a sustainable manner. An overview of the role of bioheat, biopower, and liquid transportation biofuel in reducing our carbon footprint and resulting global warming is provided in this chapter. The policy and logistics considerations related to land use, feedstock supply chain management, location of biorefineries, feedstock transportation and storage, and bioproducts in concert with social, environmental, and economic considerations are also advanced. Some internet resources for simulating various scenarios to appraise the consequences of possible policy decisions are also provided for interested readers.

Keywords Reductionism · Systems thinking · Climate change · Bioenergy · Feedstock · Sustainability · Bioproducts

1 Introduction

Recently, we were in Fresno to give an invited lecture to a group of faculty and students at California State University on the cross-disciplinary experiential learning and research activities that we were involved within the fields of (i) robotics and mechatronics, (ii) precision agriculture and remote sensing, and (iii) biofuels and renewable energy. While it seems the topics are quite disparate, they tie in well from the broader wholistic framework of developing engineering solutions for a sustainable future taking into account limits to unrestrained growth (Meadows et al.

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1972) and the global trilemma of food, energy, and the environment (Steinbuks and Hertel 2014). During the same trip, we took advantage of the proximity of Fresno to visit the Yosemite National Park. Quotes from famous environmental philosopher and naturalist were displayed throughout the park and one of them read “When we try to pick on anything by itself, we find it hitched to everything else in the Universe.” As human beings have more and more dissociated from nature in the ever-increasing predominance of the built urban environment, this simple truth has gotten diffused. While the reductionist approach of dissecting complex systems into individual parts and studying them independently has been the backbone of technological progress and evolution of social systems where individuality triumphs, the growing concerns with sustainability makes us wonder whether the inability sees the “big picture” and the relationship among parts of the whole is the root cause of the looming challenges of the future. John Godfrey Saxe’s version of the famous Indian legend “Blind Men and the Elephant” (Saxe 1816–1887) captures the pitfalls of the reductionist approach poignantly as portrayed literally in Fig. 1. Each of the blind men from Indostan touched different parts of the elephant and concluded that the animal which they could not see as a whole was like a rope, wall, fan, snake, tree, or a spear depending on tactile evidence based on the portion of the body of the animal they touched. The poem ends with the insightful verse:

And so these men of Indostan
Disputed loud and long,
Each in his own opinion
Exceeding stiff and strong,
Though each was partly in the right,
And all were in the wrong!

The above discussion sums up the motivation for taking a “wholistic” or the “systems” view of bioenergy and provides the platform to launch the discussion on bioenergy systems, sustainability, renewable energy, and climate change that follows.

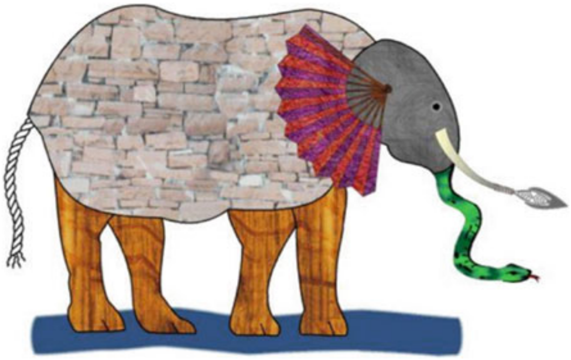


Fig. 1 Blind men and the elephant

2 Biomass, Bioenergy, and Conversion Technologies

The term "bioenergy" can be broadly interpreted as utilization of biomass to produce liquid transportation fuels (biofuels), heat, and power/electricity. Coal, oil, and natural gas are also biomass in the broader sense but they are categorized as fossil fuels. Fossilized biomass in the form of coal, oil, and natural gas in our finite earth is in limited reserves and extraction and use of them will in the long run exhaust the supplies; hence, they are also non-renewable. Moreover, burning fossil biomass or fossil fuel for transportation, heat, and electricity generation adds more carbon dioxide and other greenhouse gases (GHG) to the atmosphere resulting in environmental concerns related to "global warming" and "climate change." Burning and utilization of biomass or plant matter such as trees, grasses, agricultural crops, or other biological material that has absorbed carbon dioxide during its recent growth release the same carbon dioxide back to the environment. If the intermediate processes involved in production, harvesting, and appropriate conversion and processing are carefully structured, the net result tends to be carbon neutral or even carbon negative—a very desirable outcome for environmental sustainability. From a broader perspective, however, the social and economic considerations also play a significant role in the choices we make as we seek sustainable solutions for the global trilemma of food, energy, and environment at the common intersection of concerns related to people, planet, and profit (Fisk 2010). Improved efficiency of energy systems, wind, solar, hydroelectric, and nuclear sources along with "bioenergy" will pave the way for a future that addresses climate change issues and enables appropriate evolution of economic and social paradigms consistent with sustainability goals.

In the case of "bioenergy" unlike in the case of fossil fuel-based energy, biomass-related logistics are significant. The feedstock selection and production are constrained by space, land conditions, and management issues. Also, collection, harvesting, processing, and storage considerations all have implications related to social, economic, and environmental impact. Finally, the biomass needs to undergo various conversions such as thermochemical, physicochemical, and/or biological or biochemical processes to produce fuel and/or energy (see Fig. 2).

While extensive discussion of the conversion processes is beyond the scope of this chapter, the following overview is intended to provide some readers who may not be familiar with the terms, a brief introduction. Thermochemical conversion processes for biomass to biofuels are typically classified as combustion, gasification, or pyrolysis based on thermal conversion processes that take place under adequate, limited, or complete absence of oxygen, respectively. Fast, medium, or slow pyrolysis produces biochar, bio-oil, and syngas ($CO + H_2$) in various quantities depending on the process. Gasification, as the name suggests, produces gaseous fuel similar to syngas or producer gas, which is typically a combination of carbon monoxide, hydrogen, and methane mixed in with nitrogen and carbon dioxide. Direct combustion of woody biomass or bagasse and other crop residues with low ash content are economically viable and used for heating, as well as in boilers (co-fired) for power generation. Liquefaction and/or thermo-catalytic conversion (e.g., Fischer–Tropsch

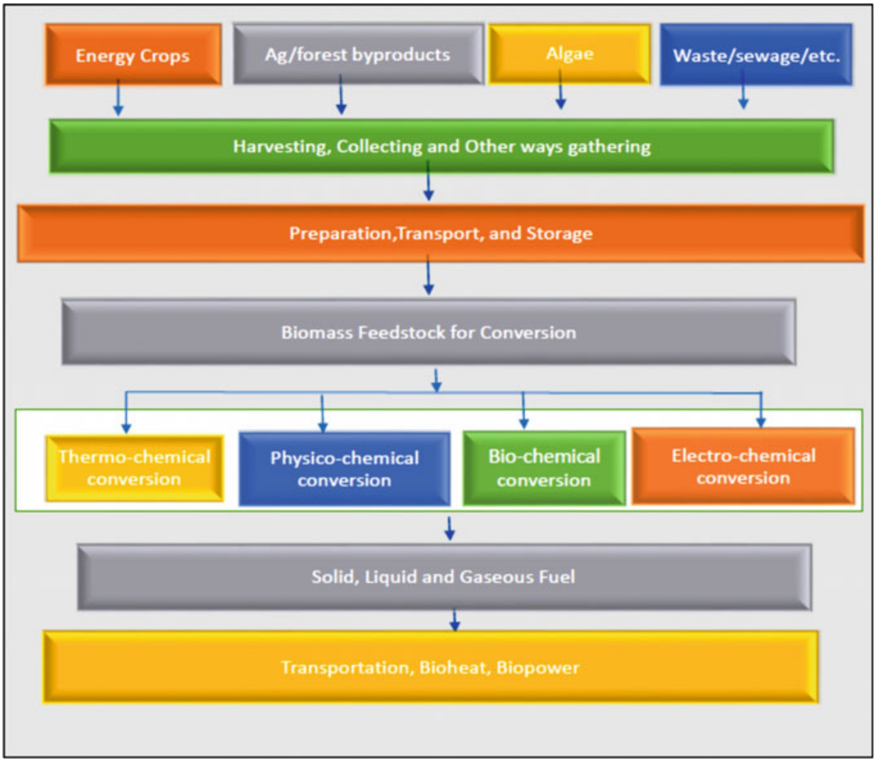


Fig. 2 Biomass feedstock—conversion processes—bioenergy

process) of synthetic gases produced by gasification or pyrolysis can be used to produce synthetic gasoline or diesel-like liquid fuel by reforming either with steam or catalytically (Pandey et al. 2015).

Rudolf Diesel (Nitske and Wilson 1965) originally designed the diesel engine to run on peanut oil but later the design got modified as cheap petroleum-based "diesel fuel" became readily available in the early 1900s. Dr. Diesel has been quoted to have said "The use of vegetable oils for engine fuel may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time." Physicochemical conversion is the combination of physical process of using an oil press to squeeze oil out from plant sources with significant lipid content and subsequent chemical process of transesterification (using methanol or acid/base catalyst) to convert the vegetable oil (or animal oil) to biodiesel that can be used as liquid transportation fuel or heating purposes.

Electrochemical conversion processes use microbial activity using biomass such as compost and mud to set up a potential difference between anode and cathode (graphite) plates to produce electricity. Extensive research is underway to develop microbial fuel cells using electrochemical conversion processes.

Biochemical conversion can be broadly classified as anaerobic digestion for biogas production and alcohol production (ethanol, butanol, etc.) by fermentation. The production of methane from anaerobic digestion of biomass follows digestive processes similar to that which takes place in the absence of oxygen in the cow's stomach but needs acid and methane-producing microbes that are naturally present in the animal. Landfills, animal farms, other accumulated organic waste are becoming recognized as significant sources of methane or biogas and are being extensively utilized for heating and cooking and in gas turbines to produce electricity. Ethanol production from sugary compounds directly available from sugarcane, corn, sweet sorghum, etc. requires only fermentation using yeast but those coming from starchy, cellulosic, or lignocellulosic sources need enzymes (such as amylases from different microbial groups) to access the sugar for fermentation. It is not surprising that in the 1920s, Henry Ford, the famous automobile industrialist, is said to have stated "The fuel of the future is going to come from fruit like that of Sumach (shrubs and trees) out by the road, or from apples, weeds, sawdust—almost anything," and he also added, "There is fuel in every bit of vegetable matter that can be fermented. There's enough alcohol in one year's yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years.

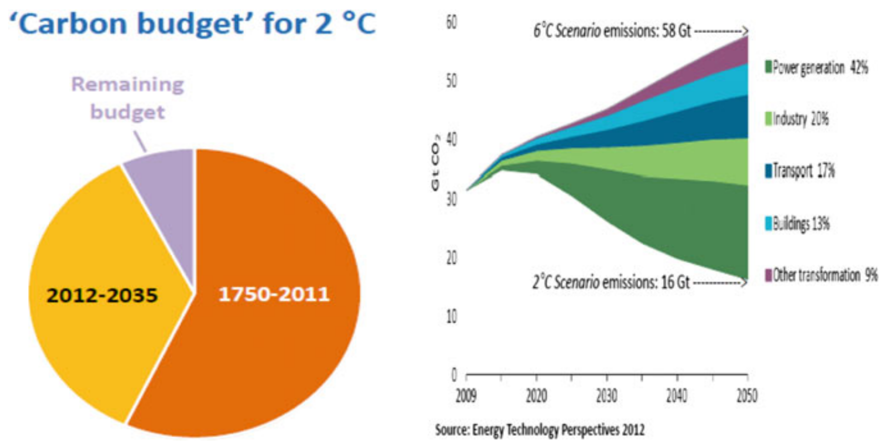
Extensive utilization of "bioenergy" replacing fossil fuel-based energy production has significant environmental benefits. However, there are several social and economic factors, which get raised in corporate boardrooms and among policymakers in different countries with regard to logistical concerns. Skepticism around climate change issues and impending environmental crises also impact policy decisions. It is, however, readily acknowledged that fossil fuel-based energy sources are in finite quantities; therefore, search for "renewable" alternatives is imperative in the long run.

Initial efforts in producing "ethanol" by fermenting sugar from food crops such as corn, sugarcane, etc. and "biodiesel" from soybean, canola, jatropha, palm oil, etc. (Coyle 2007; Demirbas 2003) have been implemented for providing alternative transportation fuels. These were mired in discussions around moral dilemma of food versus fuel (Thomson 2012); land use constraints (Pimentel 1991; Gurgel et al. 2007); lack of proper infrastructure for distribution (Lim and Ouyang 2016) and proper accounting of carbon footprint (Searchinger et al. 2009). These concerns have led to a significant effort in developing viable economic processes using non-food biomass sources to produce "biofuels." Various "grasses" that can be grown on marginal land and other lignocellulosic feedstock provide a viable alternative for producing ethanol/butanol from non-food sources. Waste vegetable oils (WVO), waste animal fat, and grease have also provided morally acceptable feedstock for producing "biodiesel." Land use concerns have also been a driver for exploring logistics of using marine and freshwater algae (Huesemann et al. 2010) as the feedstock for biofuels. "Drop-in" biofuels (Tyner 2010) that will utilize the existing infrastructure in the transportation sector are also being explored.

3 Bioenergy and Environmental Sustainability

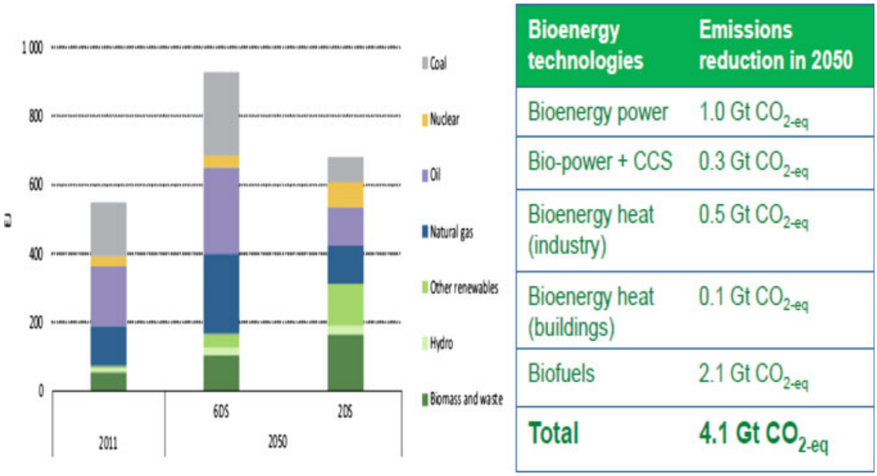
History of human civilization has been characterized by the application of energy to facilitate the needs of society. The energy trilemma of achieving environmental sustainability, energy security, and energy equity is an enormous challenge for the new millennium. A large section of the world population is yet to see the benefits of electricity, dwindling reserves of traditional energy sources and the politics surrounding it has brought energy security issues to the forefront, solving these challenges while adhering to the environmental sustainability goals will require significant effort on the part of policymakers as well as the private sector. It is anticipated that the temperature will rise by 6 °C (6DS) if we do not take the necessary steps to improve energy policies and take measures to reduce our carbon footprint and GHG emissions. 450 scenario (World Energy Outlook 2014) aimed at keeping the carbon dioxide levels below 450 ppm in 2050 and the 2 °C scenario (2DS—Energy Technology Perspective (2015)) aimed at keeping the emissions to a level that climate scientists predict will have a strong chance (80%) to limit global rise in temperature to 2 °C. Energy-related carbon dioxide (CO_2) emissions have to be reduced drastically in 2050 to achieve this target. The pie chart (Fig. 3) illustrates the small amount of carbon budget that will be left beyond 2035 even with the implementation of some of the current progressive policies. As illustrated in Fig. 3, a reduction of $58 - 16 = 44$ Gigaton (Gt) of carbon dioxide is necessary for the 2 °C Scenario (2DS) emissions between 2009 and 2050 with respect to the baseline scenario of business as usual that will result in 6° rise (6DS) in temperature by 2050.

In 2011, the world used close to 575 Exa Joules (EJ) of energy. Without serious transformation in the energy sector, world will use close to 950 EJ of energy by 2050 with 6 °C rises in temperature. With appropriate measures involving carbon capture and storage, use of renewables including bioenergy, switching to cleaner



Source: Energy Technology Perspectives 2012

Fig. 3 Carbon budget, 6° and 2° scenarios



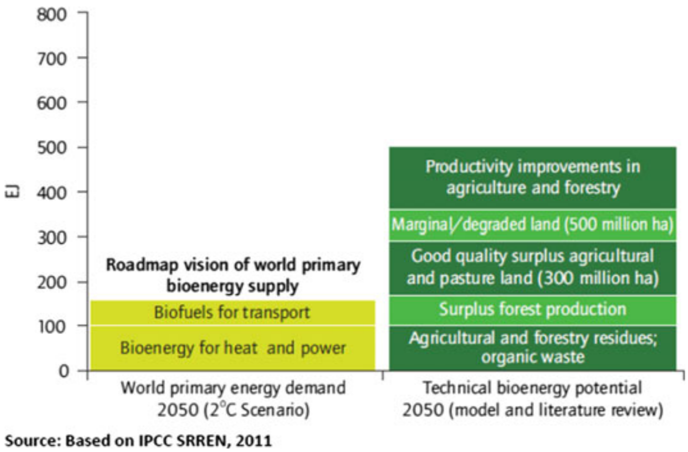
Bioenergy technologies	Emissions reduction in 2050
Bioenergy power	1.0 Gt $CO_{2\text{-eq}}$
Bio-power + CCS	0.3 Gt $CO_{2\text{-eq}}$
Bioenergy heat (industry)	0.5 Gt $CO_{2\text{-eq}}$
Bioenergy heat (buildings)	0.1 Gt $CO_{2\text{-eq}}$
Biofuels	2.1 Gt $CO_{2\text{-eq}}$
Total	**4.1 Gt $CO_{2\text{-eq}}$**

Fig. 4 Role of bioenergy in 2DS. *Source* http://www.iea.org/publications/freepublications/publication/2012_Bioenergy_Roadmap_2nd_Edition_WEB.pdf

burning fossil fuels and some utilization of nuclear energy, and improving end-use energy efficiencies, it may be possible to limit our energy use in 2050 to about 700 EJ. Moreover, it can be achieved without compromising energy security and energy equity issues significantly while dramatically reducing the GHGs emissions resulting in 80% likelihood to limit the temperature rise by 2 °C (2DS). In the 2DS, biomass and wastes can potentially contribute to one-quarter of total energy supply for the world in 2050 as shown in Fig. 4 with a 4.1 Gt CO_2 equivalent of emissions reduction which is almost 10% of the overall target of emission reduction of 44 Gt of CO_2 equivalent.

The roadmap vision for bioenergy supply in 2050 is shown in the adjacent Fig. 5. Biomass-based energy will be largely in the categories of biofuels for transport and bioenergy for heat and power. While it is envisioned, a lot of smaller light-duty vehicles will use electric power; heavier trucks, ships, and airplanes will continue to depend on liquid transportation fuel in the foreseeable future.

International Energy Association has recently published World Energy Outlook 2019 (IEA, 2019). It takes a more pragmatic and less prescriptive view with regard to increase in energy use with time, carbon emissions, and consequences. Current Policy Scenario (CPS), Stated Policy Scenario (SPS) and the desirable Sustainable Development Scenarios are discussed that limit the global rise in temperature in the 21st century to 2 degrees or less.



Source: Based on IPCC SRREN, 2011

Fig. 5 Bioenergy sources for 2DS in 2050

4 Bioproducts

The intent of this chapter is not to have an extensive discussion on bioproducts, but to bring into focus the importance of developing bioproducts as we transition to an energy production system with reduced dependence on fossil fuels.

A reduction in the use of coal with suitable alternatives does not have a significant impact with regard to coal utilization by-products (CUBs). CUBs have found limited use in mining, cement plants, and agriculture. Many technical, regulatory, and institutional barriers limit increased use of CUBs (Heidrich et al. 2013; Moretti 1996) in the commercial market. However, when it comes to liquid transportation fuels, petroleum by-products such as lubricants, heating oil, and raw materials for chemical synthesis industries for plastics, polymers, and solvents have a significant presence in the day-to-day use today. Hence, as the use of petroleum-based gasoline and diesel is gradually reduced and replaced by liquid biofuels, the need for equivalent bioproducts will grow. This will be a driver for the bioeconomy of the future. Efforts are underway to develop biomaterials such as bioplastics from plant oils and sugar, biofoam and biorubber from plant oil and latex, biocomposites and forestry biofibers (already used in automobile door panels, dashboard panels, and other parts). Efforts are also underway to develop commercial biochemicals such as resins, paints, lubricants, and solvents, biopharmaceuticals and bionutraceuticals, and biocosmetics such as soaps, body cream, and lotions (Thimmanagari et al. 2010). Bioproducts development is likely to produce increased economic opportunities for rural communities and provide environmental as well as health benefits.

5 Interactive Tools on the Internet

This section is motivated by a presumption that some of the readers of this chapter would be interested in getting a hands-on feel for some of the interactive tools available on the internet that relates to issues of energy, climate change, and sustainability. The tools mentioned are selected from a few the author has played out scenarios to develop insight (albeit limited) into a wholistic framework for beginning to comprehend the energy, environment, and population issues. The tools selected are:

1. Insight Maker Tool with particular emphasis on the World 3 model based on the findings and inferences in the book "Limits to Growth." Available at the URL https://insightmaker.com/insight/1954/The-World3-Model-A-Detailed-World-Forecaster.
2. The interactive exploratory tool based on Energy Technology Perspectives for the energy and climate change issues confronting the world. Available at the URL https://www.iea.org/reports/co2-emissions-from-fuel-combustion-2019-2.
3. Buildings, industry, transportation, electricity scenarios—an interactive scenario-based tool for exploring how alterations in energy demand and supply in the USA by various sectors can impact carbon dioxide emissions. Available at the URL http://bites.nrel.gov.

Interested readers will find playing out scenarios in these tools insightful and perhaps it will provide them motivation to get involved to influence policy decisions of our leaders with a better appreciation of the enormity of the challenges of the future.

6 Conclusion

While bioenergy and bioproducts are likely to grow in prominence as awareness of immense challenges involving energy and climate change issues grow. However, attempts to integrate bioenergy into prevailing infrastructures, and corporate and government decision-making framework will have to surmount major hurdles because it is likely to disrupt existing energy systems as well as local and regional economies. It will also impact land use systems and transport infrastructure. Biomass and bioenergy system will not only reform the way land is used and appraised; well informed decisions will also have to be taken with regard to locating production facilities and their supply chain including the number and spatial distribution of resource owners and the transportation requirements for the raw material and the finished product. In fact, the fossil fuel-driven economy largely freed our land and our transport infrastructure since we could find them in a few subsurface mines or deposits located far away from population centers. They are mostly distributed in bulk using railways, pipelines, and tankers. Progressive policies have to balance "People, planet, profit"

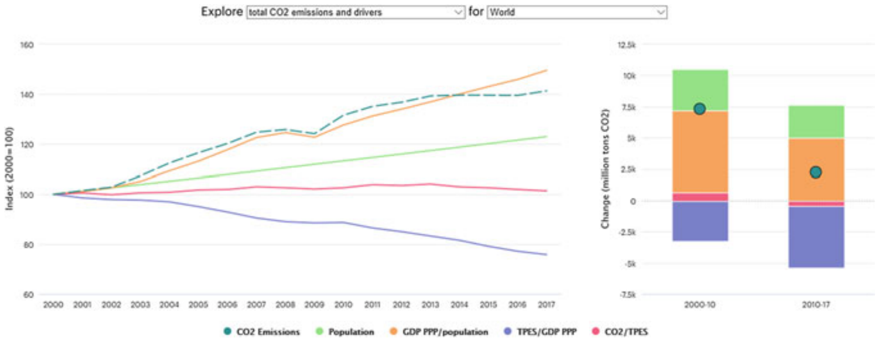


Fig. 6 : Drivers for CO2 emissions (https://www.iea.org/reports/co2-emissions-from-fuel-combustion-2019-2)

considerations and temper the world politics as world leaders aspire to transcend national boundaries to formulate and enforce policies that will effectively address the global trilemma of food, energy, and the environment to usher in a sustainable future (Fig. 6).

Glossary

Bagasse Fibrous material from sugarcane, sorghum, etc. that remains after the juices are squeezed out. Used for biofuel and bioproducts like pulp and building material.

Fischer–Tropsch process The Fischer–Tropsch (F-T) process converts a mixture of hydrogen and carbon monoxide often referred to as syngas (synthetic gas) derived from coal, methane, or biomass to liquid fuels (liquefaction).

Greenhouse Gases (GHG) Gases in the earth's atmosphere such as carbon dioxide, methane, nitrous oxide, water vapor as well as Ozone and Chlorofluorocarbon (CFCs) which trap heat and contribute to global warming and climate.

Jatropha Jatropha curcas is a perennial shrub or small tree that grows well in the tropical and subtropical regions. The plant is purported to grow in marginal lands and produces fruits with large seeds containing a non-edible oil that can be processed to make biodiesel.

Methanol Methanol, methyl alcohol, or wood alcohol, which has a chemical formula CH_3OH (frequently abbreviated as MeOH).

Microbial Fuel Cell Microbial fuel cells (MFCs) are devices that use bacteria or microbe as the catalysts to oxidize organic and inorganic matter and generate electricity. It is one of the newer approaches for renewable energy recovery.

Precision Agriculture Modern farming practice that optimizes inputs based on field variability and crop needs to increase yields and/or farmer profit utilizing geospatial information technology-based equipment and tools.

Remote Sensing Remote sensing is detecting, monitoring, and measuring an object without having any direct contact with it.

Sustainability Sustainability is the ability to endure and often used in current literature to underscore human progress on earth that addresses the needs of the present without compromising the ability of the future generations to sustain.

Transesterification Transforming one form of ester into another. It is also the chemical reaction used to make biodiesel from different oils.

Review Questions

1. What are the benefits and pitfalls of reductionist approach and the systems approach? "Jazz" and "Symphony" have been used as metaphors for the approaches to address the energy sustainability and climate change issues (World Energy Scenarios: Composing energy futures to 2050 World Energy Council Copyright © 2013 World Energy Council) while addressing innovations and policy needs. Discuss how the reductionist and systems approach are related to "Jazz" and "Symphony" approaches.
2. How is the 450 ppm scenario in 2050 related to 2° scenario (2DS) and 6° scenario (6DS)?
3. Why is it important to develop other bioproducts as we replace fossil fuels with biofuels?
4. "Bioenergy can contribute as much as one-quarter of the global energy needs in 2050." Discuss how the bioeconomy of the future will benefit the rural economy?
5. How are energy security and food security related to one another?
6. What do we mean by sustainability? Discuss how people, planet, profit, and policy decisions will play a role in forging a sustainable future?
7. The authors of "Limits to growth" have revisited the issues they raised in the original version in 1972, after 30 years in a new book "Limits to growth—the thirty-year update." Read and discuss the books in a team setting and document any conclusions that your group arrives at.
8. What do the terms "carbon footprint," "carbon neutral," and "carbon negative" mean? If you are in charge to usher in a low carbon economy, what are a few policy decisions you are likely to take?
9. Play out scenarios in the internet-based tools mentioned in the chapter (i) World 3—Insight Maker, (ii) Energy Technology Perspective—Explore and (iii) BITES and outline your experience and inferences.
10. Discuss the biomass conversion technologies. What are the challenges of scaling up these technologies to meet the future bioenergy needs?
11. Discuss the current state of technology with regard to algal biofuels and "drop-in" biofuels. Why are they growing in importance with time?

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Bioenergy, Consumer Decision-Making and Shaping the River Flow

Monisha Das and Andrew D. Schiff

Abstract All of us are consumers of energy. Even utility companies consume some form of energy to produce power and energy. Businesses are consumers of energy as are homes and individuals. In this chapter, we take the perspective of demand for energy. We explore theories of consumption, demand and consumer behavior that provide insights on how consumers make decisions regarding new forms of energy such as renewable energy. We look for explanations that may help consumers reduce or relinquish their fossil fuels-based energy consumption habits and why this has not occurred at this time. While examining the consumption side of the economic equation, we acknowledge that there are major issues in moving from a resource-based energy paradigm to a knowledge-based energy paradigm. The data on consumption is heartening as there are lead consumers such as institutions and major corporations that are adopting renewable forms of energy. Some countries have explicit goals to adopt renewable sources of energy. All these examples demonstrate that we are reaching critical mass regarding problematic awareness of the issues related to fossil fuel consumption. The next steps are cognitive awareness, affective sentience, consumer preference formation and evolution, belief shifting, adoption and advocacy. If history is plausible, this is the most likely path or model of adoption and diffusion of renewable forms of energy.

Keywords Energy consumption · Renewable energy · Consumer preference formation

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1 Introduction

Visitors to Assateague's park system are vaguely aware that this 37-mile-long stretch of barrier islands is a frontline that will be claimed by the sea as it rises in this century. Maryland and Virginia's Assateague parks have dealt with erosion, storms, hurricanes and even drought due to the inexorable March of climate change. The warming of the oceans is predicted to claim vast areas of the USA. It is anticipated that great cities along the Eastern Seaboard such as Atlantic City, the South such as Miami, Puerto Rico and 3000 other similarly located cities face risks from rising seas (National Climate Assessment Report 2015). Many scientists studying the oceans forecast that they have been rising for a long time, but the rise is accelerating.

Policies at the global and country levels have started addressing these issues seriously. Notable efforts are being made by the White House, the Vatican, WTO or the World Trade Organization, UNFCCC or United Nations Framework Convention on Climate Change, the World Bank, FAO or Food and Agriculture Organization, the OECD or Organization for Economic Cooperation and Development, USAID or US Agency for International Development and IEA or International Energy Agency. From reporting on the issues to developing metrics and responses, these institutions are on the frontline. Colleges and universities are adding climate change majors and sustainability studies (Fig. 1).

The top-down approach has an uneven record. Fossil fuel producing countries have strong pressures to protect their energy-producing economies and corporations. Protecting country and industry competitiveness pits industrializing countries against developed countries that are producing 'climate friendly' environmental goods and services such as wind turbines and solar farms. Political interests at the local and regional level have stymied national efforts to implement carbon trading. To counter

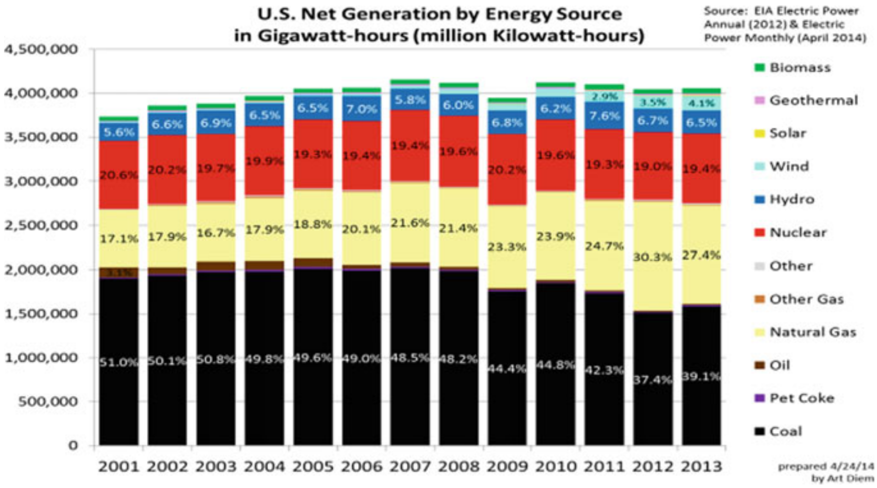


Fig. 1 Net generation of power by energy source

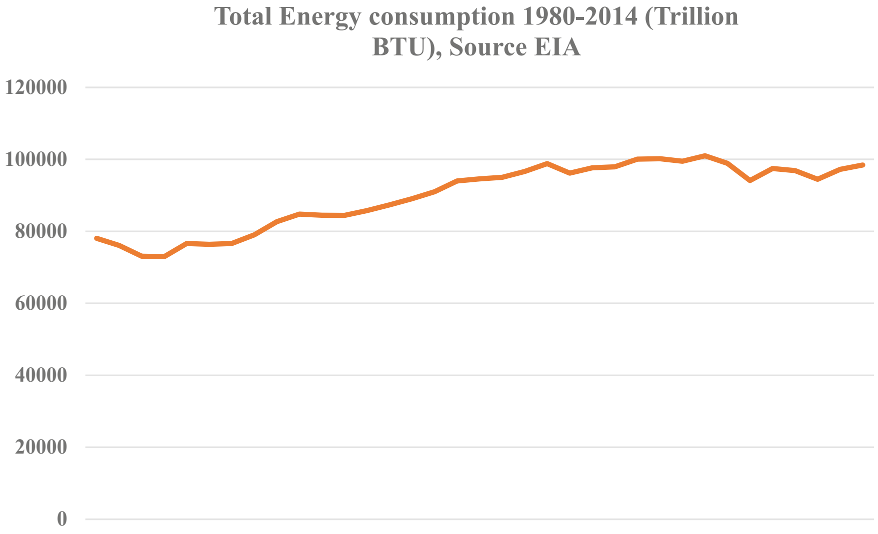


Fig. 2 Total energy consumption USA 1980–2014

them, grassroots organizations such as the Sierra Club, Greenpeace and 350.org have brought awareness to consumers.

Perhaps there is merit in taking a bottom-up approach from the consumption side of the equation to complement the top-down approach from the production side. Major corporations such as Intel, Microsoft, Apple, State Street Bank and Georgetown University are now using 100% renewable energy for electricity mainly from solar, wind and some biomass resources (EPA 2015). Cities such as Reykjavik have 100% green electricity from geothermal and hydrogen power, and Burlington, Vermont, Greensburg, Kansas, and Aspen, Colorado, are running on 100% renewable energy power. These efforts acknowledge that change driven by consumption is a powerful driver of solutions. In 2014, biomass sources accounted for approximately 9% of the energy consumption in the USA (Fig. 2).

2 Issues Regarding Energy Consumption

A major issue in the debate on climate change has been whether it is anthropogenic or man-made. Another is whether there is an ideal fuel source that can mitigate climate change. Questions as to whether biofuel and biodiesel are better than other renewable sources are subjects of multiple studies. The IPCC or Intergovernmental Panel on Climate Change is a source of expert scientific opinion. In 2014, it stated that it is mostly certain that climate change and the rate at which it is changing is a product of human activity. The key measure is the generation of greenhouse gases or carbon dioxide. Most of the greenhouse gases have led to global warming. Most of the warming is considered a result of consumption by burning a variety of fossil fuels (firewood, gas, petroleum, coal and fertilizers). NASA on its Web site lists statements from 18 major scientific associations that greenhouse gas emissions are mainly due to human activities of production and consumption (climate.nasa.gov/scientific-consensus). Alternative points of view are offered by other associations to support the status quo. They claim that climate change is not man-made but natural.

Fossil fuel consumption in the USA is linked to its national security. Reliance on imports of fossil fuels from countries that are linked to terrorism and its financing has led to a focus on new extractive technologies to produce more domestically on land and offshore. Fracking, train accidents, tanker incidents and tremors in several states as well as methane gas production are ongoing issues related to fossil fuel production, distribution and consumption. None of these new extractive technologies such as fracking address greenhouse gas generation and global warming.

Prices of fossil fuels have been volatile making household and business decision-making complex. Markets for domestic renewable fuels have also experienced price volatility due to changes in seasonal weather patterns. However, FAO has found that in spite of agro-fuel demand, food prices have remained stable (Fig. 3).

As government mandates and demand for renewable fuels have grown, land use has become a topic of contention. Globally, forests have been cut down to grow more corn and soy for ethanol and biodiesel. In Brazil, there have been inroads into rain forest areas that have affected the future survival of rare species. In Bolivia, the headwaters of the Amazon such as the river Beni have started flooding due to cutting down of vegetation for fuel crops. The Quechua tribe that inhabits the rain forest around Rurrenabaque, Bolivia, is concerned that they may have to relocate as the climate changes.

In order to meet increased demand for energy, dams are being constructed to generate hydroelectric energy. This energy will be used to run renewable energy processing plants as well as fossil fuel refineries. Not all dams will be beneficial, and

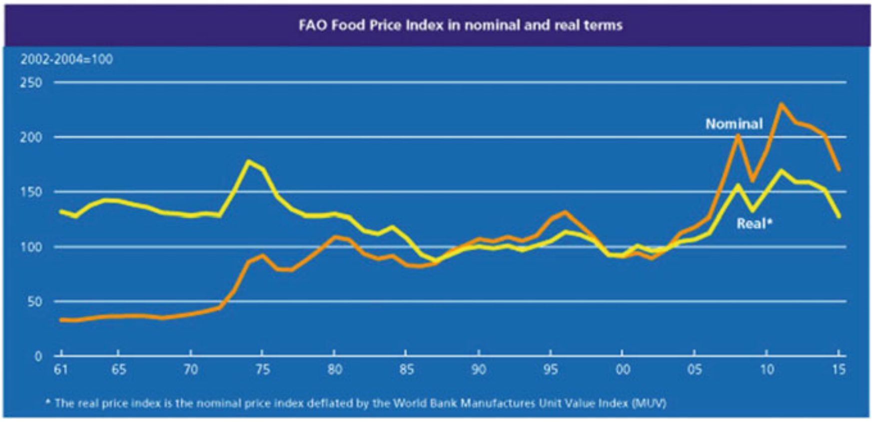


Fig. 3 FAO food price index (1961–2015)

many lands now in use will be covered by man-made lake waters. This problem is likely to get worse as human populations increase.

There are issues of investment in setting up renewable energy fuel stations for consumers. Ethanol and biodiesel are available, but there is need for much more investment in such infrastructure. In the face of uncertainties and regulatory confusion, investments have not kept up the pace needed to grow a market.

Energy is also linked to food security and may have to decouple from fossil fuel-dependent supply chains. For example, fish are regularly examined for energy pollution and certified unfit for human consumption in several countries. Such issues also underlie the intractable poverty of around 800 million people who FAO says cannot be reached by food distribution systems although the food production system has an overabundance of food for all. Much food is lost or wasted due to the lack of food distribution system capabilities. Energy security and energy access are two sides of a coin. (FAO.org)

These are some of the major issues with respect to the consumption of renewable fuels.

3 Perceived Characteristics of Biofuel by Consumers

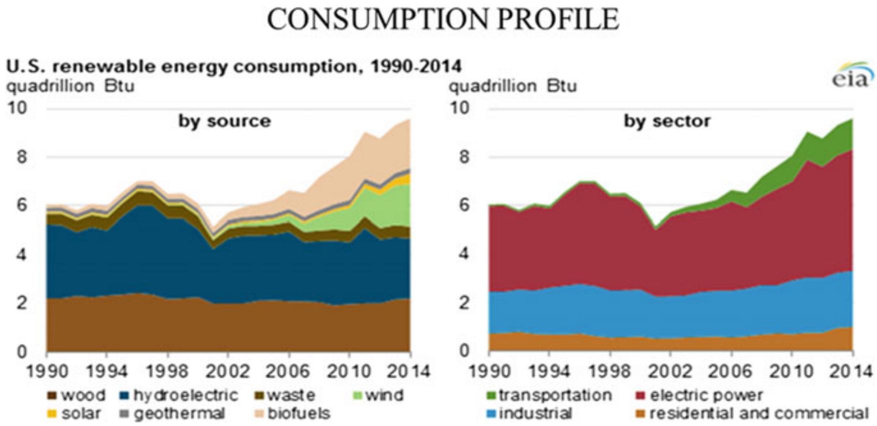
From the consumption perspective, biofuel or ethanol is the most likely substitute for fossil fuels used in transportation. Solar and wind resources are used mainly for power generation and home energy use.

Consumers desire clean burning fuel with low or no environmental impact on air, water or land. The source of such a fuel should be renewable and easily available (Rogers EM, ’95) so that prices are competitive. Multiple suppliers of these fuels should exist. Hence there should be a stable supply infrastructure in place to assure consumers of a steady supply of such fuel. Biofuels such as ethanol have to overcome infrastructure constraints to be accepted by most consumers. It would also be desirable that there be multiple grades of quality, multiple products, services and a biofuel economy in place that would provide potential jobs.

Biofuels would have to be miscible and blend easily so as to work with current homes, cars and other common uses. An established supply chain would have minimal barriers to entry and have small- and large-scale manufacturing establishments similar to the fossil fuel-based economy. Consumers would be able to compare biofuel usage to fossil fuel usage and expect similar performance if not better.

On an economy-wide scale, one would not want biofuel sources to be linked to national security concerns. Imported fossil fuels have been a source of such concern. Energy efficiency standards would have to meet or exceed current fossil fuel standards. The supply chain would enable recycling and not exacerbate calamities from spills and natural disasters. Above all, biofuel would have to be affordable given levels of income and expenditures.

Figure below shows the current consumption of biofuels.


CONSUMPTION PROFILE

4 Theories of Consumption and Demand

In order to understand the nature of consumption, one can explore theoretical models for analytical rigor and objectivity. Even before the Industrial Revolution took off, academics were writing about consumption models. Over 200 years of theoretical literature on consumption and demand has been documented. In Adam Smith's world, self-interest drove both demand and supply. On the other hand, Malthus feared that growing populations would outgrow the resource base of food, water and other natural resources that sustained them. In a Malthusian world, a consumer would be required to readjust, realign, recycle, reduce and rationalize consumption. Current writing on energy matters seems to have come full circle.

Karl Marx constructed a labor theory of value. More control through concentration of power in the hands of producers would bring about lower wages and shortfalls in consumption. J. S. Mill, Jevons and Marshall of the Cambridge School tried to reconcile classical theory with utility theory to formulate neoclassical theory. Consumption was driven by utility maximization which can be seen as a form of efficiency. Mill was concerned with educational barriers that limited opportunities in production and consumption and called for social remedies. Malthus and Mill anticipated ecological economics which is concerned with the quality of consumption and institutional economics which is concerned with the regulation of economic conflicts. Jevons claimed that consumers would be influenced by the subjective assessment of marginal utility. In Marshall's world, a consumer would consume as long as there was some benefit or consumer surplus. There would be diminishing marginal utility of consuming influenced by the income and substitution effects. Changes in price and budget constraints would influence consumer choice. These theories focused on responses to price changes in relatively free markets. There is theoretical discussion of consumer surplus but no explicit recognition of negative externalities. Pigou started conceptualizing externalities from production and consumption. Based on Pigovian theories, taxes and subsidies would impact what was produced and therefore influence what was consumed. Pigou anticipated market and institutional failures.

Kelvin Lancaster, John Kenneth Galbraith, Ernest Dichter and Thorstein Veblen came up with different variables that influenced consumer choice. Veblen critiqued conspicuous and over-consumption. He conceptualized the consumption decision as influenced by social factors and not economic or psychological variables. Irving Fisher used utility maximization assumptions in his theory of interest developed in the 1920s. Fisher's Quantity Theory of money explained how aggregate demand or economy-wide demand would respond to interest rates.

Most theories such as Keynesian theory focus on households' choosing products and services based on their income. Keynes's General Theory (1936) included a consumption function in which as incomes rose, expenditures did not rise as much over time. He saw low-interest rates and easy credit enabling consumption and raising employment. Keynes urged the public sector to increase consumption through deficit spending in times of recession.

Milton Friedman's 'permanent-income' hypothesis led to more modern forms of consumption theory. Permanent income comes from assets consumers buy and build with savings. Friedman put a floor on consumption by hypothesizing that rational consumers smoothen consumption, debt and spending over their lifespan rather than on the marginal propensity to consume. On the other hand, Simon Kuznets' theory was concerned with the 'relative-income' hypothesis. Decisions to consume would be based on current and past levels of household income. The expenditures would be in line with expenditures of other similar households. He found a u-shaped relationship between income and growth in underdeveloped and developed economies.

Franco Modigliani came up with a life cycle of consumption theory which started focusing on individual consumers making choices based on age and other demographic factors rather than household level factors as was the basis of prior theories. Consumers prefer a stable path over a lifetime to plan consumption.

Several modern consumption theories are based on the rational expectations hypothesis which demonstrates that consumption is strongly influenced by an information set on which consumer expectations are based. Fama's random walk hypothesis is concerned with the financial decisions of individuals and firms. Market prices signal efficiency and guide rational consumer and investor choices. Paul Samuelson proved mathematically that individuals and organizations maximize their consumption based on rational self-interest. Arrow contributed social choice theory which aggregates individual consumer preferences using a utility function. A major contribution was using the Pareto principle in which Pareto improvement is reached when a change makes an individual better off without worsening another individual. Amartya Sen used social utility theory to demonstrate that partial comparisons of utility may lead to efficiency, but the end result may not be socially equitable consumption or Pareto optimal. This work is being carried forward by Piketty (2014).

A theory based on the 'golden rule' as per John Von Neumann, Edmund Phelps and Solow imply that quality of life and consumption can be maintained at a maximal level based on prior investment decisions in new technologies. Applying this rule to renewable energy, investments supporting new technologies in food and energy, especially renewable energy such as biofuel and biodiesel, become crucial.

Joseph Stiglitz developed information economics. He hypothesized that individuals and organizations spend resources to acquire information. Stiglitz, Akerlof and Spence were awarded the 2001 Nobel Prize for their work on asymmetric information and risk distribution. Stiglitz has argued that global warming is perilous and a threat to the economy. He calculated that extreme weather incidents in the USA have caused over $1 trillion in costs. Climate change has coincided with a global economic downturn since 2008. Stiglitz contends 'retrofitting the global economy for climate change would help to restore aggregate demand and growth.' Paul Romer's utility path is based on investing in ideas grounded in codified knowledge. New technologies create new wealth, employment and growth in consumption leading to increasing returns rather than diminishing returns. Knowledge is cumulative and limitless in his schema. Creative destruction of old knowledge is intrinsic to growth and produces positive spillovers or externalities that lead to increasing returns.

Microeconomic and macroeconomic models of consumer choice model how consumers maximize utility subject to budget constraints. Prices, wealth endowment and variety of goods shift consumption. Almost every economic theory relating to consumption can be applied to describe some aspects of renewable energy consumption. None offer a fundamental or clear cut explanation as to why renewables are not the preferred choice of households and organizations.

5 Consumers Are Information Processors

With the cognitive theory of information processing (Bettman 1979), focus shifted to the consumer as a decision-maker with limited processing power. Simon's bounded rationality constraint is as much of an influence on choice behavior as the budget constraint. Given a choice set or consideration set of alternatives, consumers will set about the task of evaluating attributes with limited budgets and limited information processing capabilities. The consideration set of alternatives may vary from consumer to consumer. Not all alternatives make it to a consideration set. All alternatives have some attributes that have known value. Other attributes may have unknown value. For a consumer, a gallon of biofuel is a known quantity, but its reliability in different engines may be difficult to value. The buyer decision process is studied as stages. Both consumers and organizations go through the decision-making stages of problem definition, search behavior, bounded consideration set of alternatives, evaluation of alternatives, choice, post-purchase evaluation and post-purchase behavior.

The evaluation stages are strongly influenced by types of available information. Information content and how it is structured or framed will have an influence on the outcome. Prior experiences and prior information in short- and long-term memory will be compared with new information and new experiences and a consumption decision or choice will emerge. Furthermore, the urgency or importance of the attributes can change. A subjective threshold of acceptable standards may cut down the size of the consideration set making a choice easier. It is much like choosing an applicant out of a set of candidates. The rules or heuristics used in evaluating choices may change or be used in various combinations.

The following are descriptions of some heuristics.

a. The weighted additive rule states that given all attributes, scores based on multiplying the weight times the attribute value are summed to arrive at an overall evaluation. This is a normative and comprehensive approach. In reality, consumers would simplify the task. Given all attributes of fuels, a rating system based on importance of the attribute to the decision-maker would be multiplied by the relative performance value of the attributes to arrive at a score.
b. The satisfying heuristic states that a cutoff level or base level is arrived at subjectively or objectively and available alternatives may be rejected if they fail to meet the cutoff level. The decision-maker is satisfying not maximizing choice. A base price may make certain fuels acceptable if within budget or unacceptable if above.
c. The lexicographic heuristic helps the decision-maker narrow down the most important attribute. The alternative which would rank highest such as least carbon footprint would narrow down the choice set. If two fuels make the cut due to a tie, a second attribute such as availability or price may be considered.
d. The elimination by aspect heuristic starts with a set of attributes and choices. In every round, one attribute ranking is used to eliminate alternatives until a single choice emerges. The attribute sets of fuels are as important as the fuels themselves.
e. The majority of confirming dimensions heuristic works like bracketing. Pairwise comparisons are made until a final winning alternative is selected.
f. The frequency of good and bad features heuristic works like a balance sheet of liabilities and assets. The balance sheet can be visualized as a T of assets and liabilities on both sides. The alternative fuel with the best trade-offs or balance sheet will be selected.
g. The equal weight heuristic is a special case of the weighted additive rule. This is a simple summing of values of attributes assuming no difference in importance.
h. Combined heuristic rules may be used in complex situations such as elimination by aspects and the weighted additive rule.
i. Habitual heuristic states that no new evaluation will occur. Consumers have made their final choices based on prior experience and use.

What a policy maker gains by considering the consumer as an information processing decision-maker is a more realistic assessment of how consumers approach the complex task of shifting choices from fossil fuels to biofuels and biodiesels. What policy makers will not obtain is how the evaluations are formed in the first place. Can the reasoning be explained by culture-specific, location-specific or norm-specific factors? For some answers, we consider another theory.

6 Consumers Plan Their Consumption Behavior

The prescriptive theory of planned consumption (Ajzen 1991) constructs a psychological framework in which beliefs play a major role in choice behavior. Intent, perception, attitude and belief formation influence choice. Planned consumption prioritizes ethical concerns over value maximization. This explains green consumerism. Consumers expend cognitive resources to arrive at choice decisions. Socially conscious consumers will evaluate choices based on the consequences of their choices on the environment and society. Eco-friendly products would be selected over other products that do not fit the criterion.

Much learning takes place so that higher-order motives drive choice. Three sets of beliefs are learned. They are behavioral, control and normative beliefs. Behavioral beliefs are based on self-evaluation of a behavior that will produce a certain outcome. Control beliefs are based on the self-efficacy or conviction that a certain behavior or choice will lead to a certain lifestyle outcome. Normative beliefs are based on a self-assessment of the value of social approval or disapproval of a choice. So the policy maker's task will be to give consumers the facts, evidence and cost-benefit evaluations of alternative renewables so that consumers can make informed decisions. Consumers would be in control and make decisions that befit their lifestyles, environmental consequences and societal requirements. Consumers will through reasoning plan their consumption choices. Expending cognitive resources to make choices will result in increasing returns to individual, environmental and societal welfare. These are higher-order outcomes. Consumers become better managers of their consumption portfolios through planned behaviors. Consumers would balance economic and ethical utility and remain actively engaged in their consumption behavior. Hence the quality of information and acceptable choices must grow to allow for better maximization. Information and knowledge are critical to the formation of the intent or antecedents of the planned behavior. Not all consumers are high information processors and therein lies a problem. Consumers have biases regarding what information they are willing to process.

7 Consumers Have Cognitive Biases

In the behavioral theory of consumption, Kahneman and Tversky (1974, 1979, 1999) have shown that many decisions are made where it is difficult to make a commitment. For example, given current technologies and information, biofuel may be the best fuel. What if the consequences of large-scale adoption lead to less food and higher prices for less prepared consumers? What if the technologies change? What if another champion emerges? To simplify decision situations or even forego decision-making consumers may use simpler rules or heuristics. Mental shortcuts ease the pressure of the cognitive task and a probable solution is found.

Humans have acquired universal cognitive wiring that frames the way we view choices. The scope of the climate change problem is so vast, so intangible, beyond single life spans that it is difficult to comprehend. The problem is conceptualized as change or cutting back on lifestyle possibilities. Consumers seem unwilling to take perceived losses now or even share it. Media is a large provider of information and the topic of climate change slips in and out of consumer awareness based on media narratives. Instead of evaluating product attributes, consumers prefer to postpone such decisions which cause anxiety and fear. Emotional override occurs and scientific rational knowledge takes a backseat. Peers can be given higher ratings than experts which seems paradoxical. Affect heuristics loom as large as cognitive heuristics.

Based on the work of Kahneman and Tversky, three cognitive heuristics or biases are at play in consumer decision-making.

- Availability heuristic: We base decisions and predictions on vivid, unusual, emotional, easy to recall or recent events. We rely heavily on short-term memory. As decision-makers, we are better at dealing with short-term problems and short-term solutions. We are poor at forecasting or evaluating long-term decisions. This reliance on availability leads to biases.
- Anchoring heuristic: We start from an initial value and frame the problem and solution around it. We seek information that will confirm our thinking even if it is inferior. This leads to framing errors such as a frame game. Basing decisions on one specific piece of information, reference point, generally first or core belief, intuitive point and not making adjustments lead to decision errors.
- Representativeness heuristic: basing decisions on the chance of an occurrence by our familiarity or lack of it. We match the choice with a small sample set or anecdote which may be in our long-term memory. We ignore new information especially if it is presented quantitatively or probabilistically as a large sample set. We ignore new base rates. We suffice with an illusion of truth. We prefer pleasant feelings to tough information. We prefer reduced vigilance.

All these cognitive biases create problems for policy makers. What energy to use and where to obtain it is a major consumption problem. Decisions regarding the benefits, costs and risks are complex. Public opinion and its formation is a major challenge given the underlying heuristics. Before we can reconfigure the energy sector, we have to reconfigure public opinion. Difficult choices lie ahead. New technologies, new industries and new policies will guide the decision choices. Much will be driven by what is acceptable to consumers. Through ballot measures and legislation, advances and setbacks have been made. Trial and error seems to be the way forward.

8 Renewable Energy Delivery Structure

How policies on renewable energy are delivered to form public opinion needs to be addressed given the above considerations. Before policies can be formulated, the public has to complete an evaluation of the issues. Policy channels that enable learning, diffusion of ideas, opinion transfer mechanisms and signaling information quality are all important. The goal to achieve aggregate consensus will occur through both evidence and anecdote. These will influence expectations, standards, favorability and outcomes. Signals through fiscal funding, project support, grants, championing, licensing and other incentives will move the needle in the appropriate direction.

Besides policy delivery structures, industry delivery structures have to be in place. Fossil fuel industry structures have been in place for two centuries and have become efficient and home to millions of jobs around the world. There are institutional, private and public participants in the fossil fuel industry value network. There is a precedent here than biofuel industry participants can emulate or improve upon.

The same network can be adapted synergistically by new industry players. Some sense of continuity will win more support and enthusiasm for change. Public opinion channels, policy delivery channels and industry value delivery channels need to be synchronized for a move to biofuel to occur efficiently. How renewable energy is recycled will add new dimensions to value delivery. Private investment channels will be critical in managing the risks of the changes (Fig. 4).

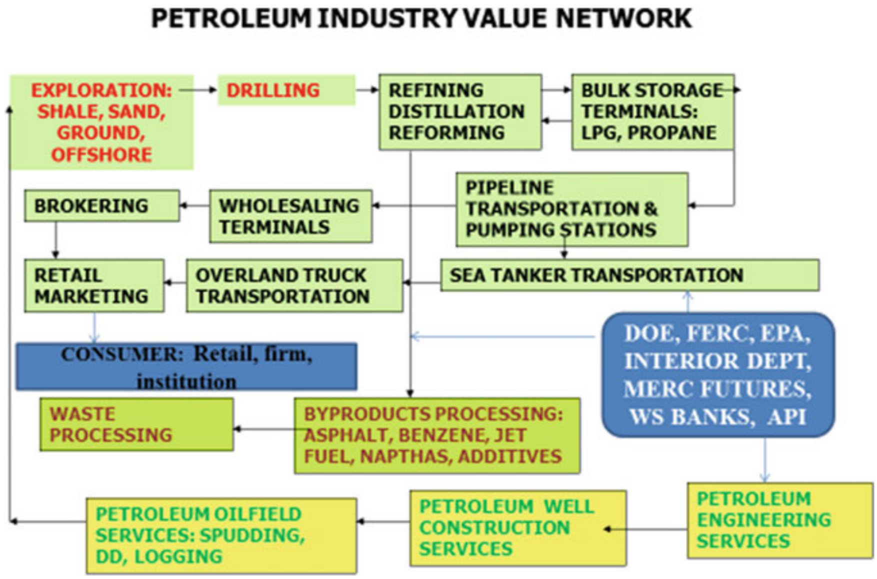


Fig. 4 Industry value network of fossil fuels

9 Discussion

To form a market, three fundamental factors evolve. Consumer needs evolve. Consumers' willingness to buy evolves. Finally, consumers' means to pay for the products and services evolve. When there is a failure in any one of these characteristics, there can be market failure. The river of demand can stop flowing. Hence shaping the river flow is an important consideration.

Our energy needs are not just choices about products and services. They are choices about how our society will bear the costs of producing and distributing affordable, reliable energy. There are some current costs that will grow to unsustainable levels if no changes are made such as healthcare costs. At this time, they are being borne by society. There are social costs that have to be weighed against economic costs.

The public has not chosen biofuel as the ideal fuel. That case has to become clearer to all participants not just consumers. The public does not really concern itself with the source of energy be it natural gas, shale oil, hydropower, nuclear, solar, wind or biomass. That there are so many sources is promising. Multiple sources can raise energy output and improve all lives everywhere.

The greening of energy is happening. However, we are far from 100% green energy. We are still highly dependent on fossil fuels. Even fossil fuel production, distribution and use have become more efficient in raising the bar for all forms of energy and power generation. All energy forms are moving toward cleaner energy with a smaller carbon footprint. Whether the changes are timely or not greening is the guiding light.

Neither climate change nor global warming are kitchen table issues for American consumers or consumers around the world. How to engage the public to get there and drive preferences has not happened. Therefore, market formation around renewable energy has not happened. If there is a lifecycle of a crisis from problem identification to resolution, we are still searching for solutions and are far from resolution. It may take another two, twenty or two hundred years to get the river to flow. This is the greatest journey of our times.

10 Conclusion

There is no way to avoid the problem of clean and sustainable energy use. There will be no quick fixes that can solve it. Wishful thinking cannot solve it. The way forward implies answering again and again the hard questions until the answers are clear and indisputable. Those key questions are as follows:

What do consumers really want?
Do we have certain and sustainable ways to produce and deliver future energy?
Who do we trust the most to lead us on this journey?
Do we know with reasonable certainty what the threats truly are?

Can we measure these threats and opportunities accurately?
What trade-offs will consumers have to make going forward?
Finally: If this is truly the priority of our times, how should we convince the public?

Glossary

Aggregate Demand is the total amount of expenditure in nominal terms on goods and services.
Biomass is organic waste from agricultural, livestock and lumber industry products, dead trees or foliage. Biomass can be used as fuel and to make transportation fuels like ethanol and biodiesel.
Consumer surplus is the added satisfaction gained by a consumer over and above the price the consumer was prepared to pay.
Cost-benefit analysis is the use of economic analysis of tangible and intangible gains and losses from a policy or program on targeted samples or populations.
Derived demand is demand for the underlying product or service as is demand for a form of energy so that heating, transporting, processing or consuming can be achieved.
Economies of scale exist where a production or distribution facility exhibits decreasing average long-run costs because of increases in size or scale.
Marginal utility is the increase in satisfaction an individual derives from use or consumption of one additional unit of a good or service.
Neoclassical theory is based on Alfred Marshall's writings. There was a shift to the study of diminishing marginal utility from optimal allocation of scarce resources based on a division of labor of the classical economists.
Propensity to consume explains the amount of resources or income expended to achieve a certain amount of consumption.
Utility maximization is the point at which the consumer maximizes satisfaction from spending under a given income amount.

Questions

1. Is climate change man-made? If so, what evidence would you consider to explain your point of view?
2. What attributes should a perfect fuel have? Based on your understanding, what is a perfect fuel?
3. Is there a market for a renewable fuel such as ethanol? Assess it from a consumer perspective.
4. Is there a market for a renewable fuel such as biodiesel? Assess it from a consumer perspective.

5. What according to you are current problems consumers face in adopting biofuel?
6. What costs and benefits are consumers who adopt biofuel likely to face?
7. What cognitive barriers influence consumer adoption of biofuel?
8. What beliefs affect the consumer decision to choose renewable fuels such as biofuel?

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The Global Scenario of Biofuel Production and Development

Mingxin Guo

Abstract Bioenergy has been ranking number one among all forms of renewable energy consumed by human beings. Over the past two decades, tremendous investment has been made in biofuel development and production. This chapter reviews the global research, refinery, and utilization of biomass-based liquid biofuels as transportation petro-fuel substitutes. There are four major types of liquid biofuels: bioethanol, biodiesel, pyrolysis bio-oil, and drop-in transportation fuels. Bioethanol has been commercially produced from lignocellulosic materials since 2013, supplementing the annual 25.7 billion gallons from food crops. Biodiesel from oilseeds and animal fats reached the 8.3 billion gallons/yr production capacity, with further increases depending on new feedstock development. Pyrolysis bio-oil and most drop-in transportation fuel candidates are still in the development stage, facing cost-effective conversion and upgrading challenges. Commercial production of two drop-in biofuels, hydrotreated vegetable oil (HVO), and Fischer–Tropsch liquids has just started or is starting. Overall, the global development and consumption of bioenergy and biofuels are steadily advancing, particularly in the cellulosic bioethanol and HVO sectors. By 2050, biofuels will likely account for 27% of the world's liquid transportation fuel supply.

Keywords Bioenergy · Biofuel · Bioethanol · Biodiesel · Drop-in fuel · Fischer–Tropsch liquids · Hydrotreated vegetable oil · Lignocellulosic biomass · Pyrolysis bio-oil

1 Introduction

In physics, energy is defined as "the capacity of a physical system to perform work," and work is "to move a physical object against a force over a distance." Energy exists in various forms that can be classified into two broad categories: kinetic

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energy (electric energy, thermal energy, radiant energy, and motion energy) and potential energy (chemical energy, nuclear energy, mechanical energy, and gravitational energy) (Aubrecht 2005). The energy stored in biomass is termed "**bioenergy**," a chemical energy in the potential energy category. The First Law of Thermodynamics states that energy can be converted from one form into another, or transferred from one object to another, but it cannot be created or destroyed (Hasse 1971). When biomass is combusted, bioenergy is transformed into thermal energy (heat) and radiant energy (light) and released into the environment.

Bioenergy originates from solar energy. Plants, algae, and cyanobacteria utilize solar energy (predominantly 400–700 nm radiation) to synthesize organic matter from CO_2 through photosynthesis. To produce 1 g of biomass carbon, approximately 833 kJ of solar energy are absorbed but less than 5% of it (~39 kJ) is transformed to chemical energy and stored in the synthesized carbohydrates (Klass 1998). Globally soil-grown plants produce around 120×10^{15} g of dry biomass (equivalent to $\sim 56 \times 10^{15}$ g organic carbon) each year (Broadmeadow and Matthews 2003, Beer et al. 2010), storing 2.2×10^{18} kJ of bioenergy. The annual bioenergy generation through terrestrial plant photosynthesis nearly quadruples the present global energy need ($\sim 5.6 \times 10^{17}$ kJ; Enerdata 2015). However, not all land is accessible and can be used to produce bioenergy for human purposes. Cropland, remote areas, wildlife habitats, and domestic facilities occupy a significant portion of the world's total land surface. The practical bioenergy potential of the Earth's terrestrial ecosystem is predicted at 1.9×10^{17} kJ yr^{-1} (Haberl et al. 2013), deliverable to meet one-third (~34%) of the global energy consumption at the present level (Enerdata 2015).

When biomass and its processed products are combusted, the inherent bioenergy is released in heat and light. If used for energy purposes (except for food consumption), the biomass materials are termed "**biofuels**." Broadly, biofuels can be of solid, liquid, and gaseous forms, all combustible and carbon-rich. Starting from the discovery of fire at the dawn of human history, biofuels have been utilized to provide energy in numerous civic activities. Wood was the primary fuel worldwide before the twentieth century. Wide exploitation and use of coal, petroleum, and natural gas for energy did not start until the early nineteenth century (Hulse 1999). It was in 1881 that the USA began to consume more fossil energy than bioenergy. Today 87% of the US energy demand comes from fossil fuels (EIA 2013a). Worldwide, fossil energy shares nearly 80% of the global energy consumption (IEA 2013a). The intensive mining and consumption of fossil fuels, however, have generated disastrous environmental impacts. The uneven distribution and dwindling supply of fossil fuels further pose threats to modern energy independence and security (IEA 2013b). In the past two decades, tremendous endeavors have been made to develop and utilize renewable energy including bioenergy, hydropower, solar energy, wind electricity, and geothermal heat.

The world transportation relies on liquid fuels. Petroleum is refined to produce gasoline, diesel, aviation fuel, bunker fuel, and other liquid fuels to power vehicles, aircrafts, and ships. The global daily consumption of petroleum mounted to 93.2 million barrels (1 barrel = 42 gallons) in 2014 (EIA 2015a). Every day 930 million gallons of gasoline are being used worldwide by more than 600 million traveling passenger cars. The US daily consumption of gasoline was 384.7 million gallons in 2015 (EIA 2016a). To produce liquid fuels, biomass is the sole **renewable** feedstock. More important, biomass is extensively available from well-established production systems, engendering the practicality of manufacturing renewable liquid biofuels. Tremendous research has been carried out to develop efficient techniques for converting biomass into liquid fuels such as bioethanol, biodiesel, pyrolysis bio-oil, and drop-in transportation fuels. Bioethanol and biodiesel have been increasingly produced in many countries since 1980 to supplement the petro-gasoline and diesel supply. For example, 6% of the global crop grains went to biofuel production in 2014 (REA 2015); in the same year, 37% of the US corn grain was used to generate 14.3 billion gallons of bioethanol (IAState 2015). The European Union (EU) has established the goal to meet 10% of its liquid transportation fuel demand with biofuels by 2020 (USDA 2015). As such, biofuels mostly refer to biomass-based liquid fuel products, though there are solid biofuels (e.g., firewood) and gaseous biofuels (e.g., biomethane). This chapter adopts the narrow meaning of "biofuel." It reviews the development and production of various liquid biofuels from different biomass materials in the global scenario, helping envisage the future of biofuels. Perspectives of other solid and gaseous biofuels can be found in Guo et al. (2015).

2 Development and Production of Bioethanol

Most four-wheeled passenger automobiles are powered by a four-stroke, spark-ignition internal combustion engine that runs on gasoline, a liquid (density ~0.745 g cm^{-3} at 15 °C) of C_4–C_{12} hydrocarbon mixture (higher heating value 46.5 kJ g^{-1}) refined from petroleum by fractional distillation (1 barrel of crude oil yields 19 gallons of gasoline). Today, gasoline engine vehicles and gasoline supply infrastructure are all over the world and become a critical component of the modern economy.

The supply of gasoline depends solely on the availability of petroleum, the so-called crude oil formed from the remains of ancient marine organisms under specific geologic conditions (e.g., high temperature and high pressure) over millions of years (NGS 2013). Petroleum exists only in underground pockets of certain geographic locations, and therefore, reliance on crude oil for gasoline poses threats to the energy independence and security of many nations. The energy crisis in the 1970s during which the USA, Western Europe, Japan, and other industrial countries suffered from extraordinarily high crude oil price and severe gasoline shortage, for example, was caused by the petroleum export embargo from Organization of the Petroleum Exporting Countries (OPEC) and the Islamic Revolution-induced social chaos in Iran (a major crude oil exporting country) (Lifset 2014). Moreover, petroleum is non-renewable; its limited reserve can only maintain the supply of crude oil at the current trading flow into the future 50 years (IEA 2013b). In addition, extraction of crude oil and consumption of gasoline have engendered enormous environmental impacts such as water pollution, wildlife habitat destruction, and climate change.

Renewable fuels alternative to gasoline have been intensively researched, especially in the recent fifteen years.

Biomass-derived ethanol or **bioethanol** is such a candidate. Ethanol, a 2-C alcohol with the chemical formula CH_3CH_2OH, is a clear, volatile, and combustible liquid at room temperature. Bioethanol is typically generated by alcoholic fermentation of plant sugars (e.g., the hexoses glucose, fructose, mannose, and galactose and the pentoses xylose, arabinose, and ribose) and used as a fuel. If used as a beverage, the liquid is called "alcohol." Alcoholic fermentation is activated by zymase-producing yeast and can be described by the following reactions:

$$C_6H_{12}O_6 \text{ (glucose, fructose, mannose, etc.)} \overset{\text{yeast}}{\rightarrow} 2C_2H_5OH \text{ (ethanol)} + 2CO_2 \quad (1)$$

$$3C_5H_{10}O_5 \text{ (xylose, arabinose, ribose, etc.)} \overset{\text{yeast}}{\rightarrow} 5C_2H_5OH \text{ (ethanol)} + 5CO_2 \quad (2)$$

Plant tissues are composed predominantly of cellulose, hemicellulose, and lignin (Table 1). Of these three backbone construction compounds, cellulose and hemicellulose are polysaccharides and can be hydrolyzed into simple sugar molecules. These two constituents account for up to 70% of dry plant matter (Table 1). Cereal grains (e.g., corn, wheat, and rice) and tuberous roots (e.g., yam, potato, and cassava) are rich in starch (a polysaccharide). Sugar beets, sugarcane, and sweet sorghum are abundant in sugar (sucrose, a disaccharide). Cellulose, hemicellulose, starch, sucrose, and simple sugars (monosaccharides or sugar monomers such as glucose, fructose, mannose, galactose, xylose, and arabinose) are carbohydrates, consisting solely of C, H, and O following the formula $(CH_2O)_n$, where $n \geq 3$. Through hydrolytic decomposition as shown in Eqs. 3, 4, and 5, polysaccharides and disaccharides can be transformed into simple sugars ready for alcoholic fermentation (Eqs. 1 and 2).

$$(C_6H_{10}O_5)_n \text{ (cellulose, starch)} + nH_2O \rightarrow nC_6H_{12}O_6 \text{ (glucose)} \quad (3)$$

Table 1 General biomass composition (% of dry weight) of lignocellulosic plant materials (Lee et al. 2007; Sannigrahi et al. 2010; Limayem and Ricke 2012; Serapiglia et al. 2013)

Raw material	Cellulose	Hemicellulose	Lignin	Ash
Crop residues	30–50	15–40	10–20	3–9
Hardwood	40–50	25–35	20–25	0.80
Softwood	40–45	25–30	25–35	0.50
Herbaceous plants	25–45	15–35	10–20	3–12
Newspaper	40–55	25–40	18–30	0–2
Switchgrass	30–45	25–30	15–20	4–9
Shrub willow	39–45	31–35	20–23	0.5–2.2
Hybrid poplar	42–49	17–23	21–30	0.6–2.0

$$C_{12}H_{20}O_{10}\text{ (sucrose)} + 2H_2O \rightarrow C_6H_{12}O_6\text{ (glucose)} + C_6H_{12}O_6\text{ (fructose)} \quad (4)$$

$$C_m(H_2O)_n\text{ (hemicellulose)} + H_2O \rightarrow C_6H_{12}O_6\text{ (hexoses)} + C_5H_{10}O_5\text{ (pentoses)} \quad (5)$$

Considering the dominant presence of cellulose and hemicellulose in plant tissues (Table 1), all vegetative materials are potential feedstocks for simple sugars (Eqs. 3, 4, and 5) and bioethanol (Eqs. 1 and 2). In plants, however, cellulose, hemicellulose, and lignin are interwoven with one another to form a recalcitrant structure of cell walls (Fig. 1). It is rather difficult to separate cellulose and hemicellulose from lignin in twisted fibrils and decompose the polysaccharides into sugar monomers. All the currently designed procedures for the purpose are inadequate in rate and efficiency, requiring stringent conditions and specialized enzymes. Even worse, the resulting

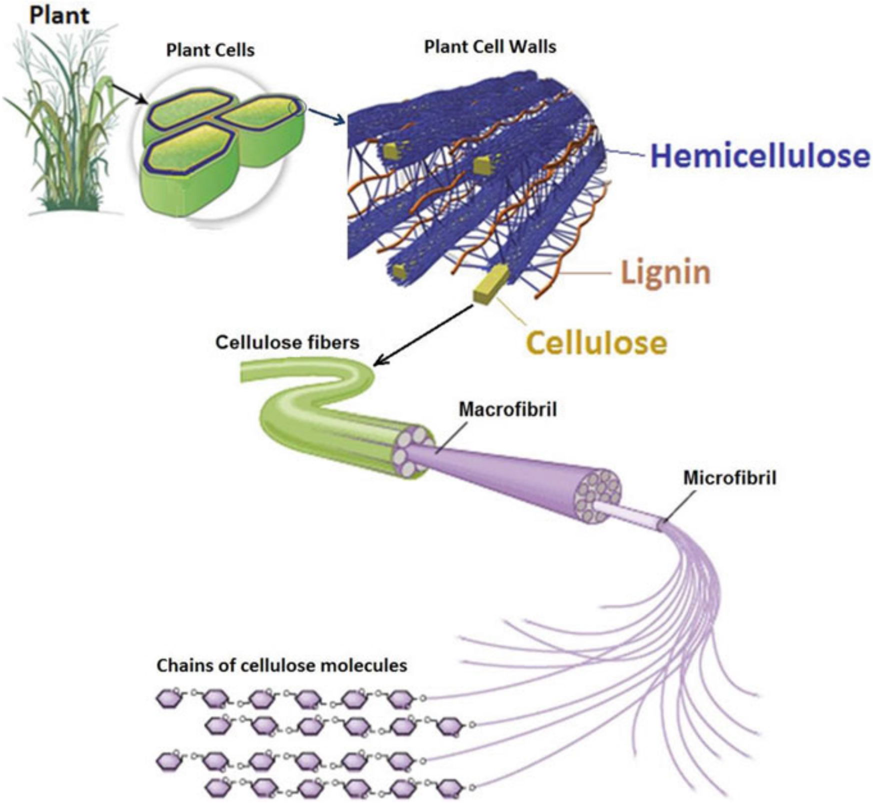


Fig. 1 Interwoven structure of lignocellulosic plant materials

sugars are generally unstable in rigorous environments, degrading to other compounds prior to alcoholic fermentation. Further research is needed to develop practical “pretreatment” methods for efficiently extracting sugars from lignocellulosic materials.

2.1 Food Crop-Derived Bioethanol

Figure 2 illustrates the common procedure for generating bioethanol from starch- and sugar-based feedstocks. The procedure covers three major phases: (1) conversion of starch in food crops to simple sugars or extraction of sugar from sugarcane/beets, (2) fermentation of sugars to ethanol, and 3) refinery of ethanol from the fermentation beer. In a dry-milling corn ethanol plant, for example, pre-cleaned dry corn grains (moisture ≤14%) are milled to <4 mm flour (the milling step) and added with water to form cornmeal slurry. The slurry is conditioned in a cooker at 40–60 °C for 12 h and then cooked (with heat from steam) at 110–120 °C for 2 h to prepare a corn mash (the cooking step). Prior to cooking, corn germ can be recovered by flotation and skimming for oil extraction (Singh and Eckhoff 1999). The mash, with pH 6.0–6.5, is then cooled by settling to 80–90 °C, added with the enzyme α-amylase, and liquefied for at least 30 min (the liquefaction step). The liquefied corn mash is further cooled to 30 °C, added with another enzyme glucoamylase, and settled for 30 min to allow conversion of starch to glucose (the saccharification step). The corn mash is transferred to a fermenter, where yeast is added to start ethanol generation at 32 °C for 48 h (the fermentation step). In fact, continuing saccharification concurs with

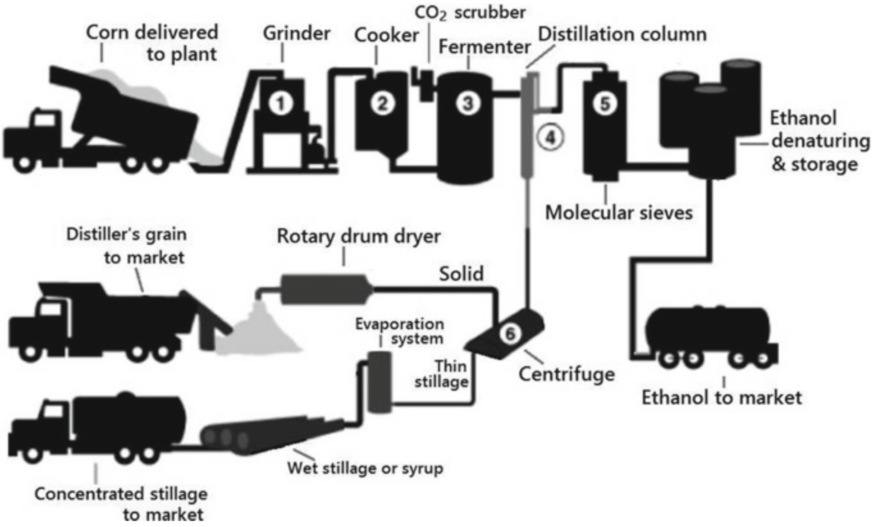


Fig. 2 Technical flow chart of bioethanol production from corn in the USA

fermentation in the fermenter. The fermented "beer" containing 8–12% ethanol by weight is then distilled to recover ethanol (the distillation step). The ethanol is passed through molecular sieves to remove water (the drying step), and gasoline is added at 2–5 vol% to denature its beverage function (the denaturing step) (Purdue Extension 2006). The stillage can be separated by centrifugation into the solid portion (dried distiller's grain, DDG) and the liquid portion (thin stillage) and used as animal feed. Corn oil can be recovered from the thin stillage if it is not extracted before the "cooking" process. The entire corn ethanol process takes 55–60 h, with the average productivity of 2.7 gallons of ethanol per bushel (25.4 kg) grain. Different from dry-milling, the wet-milling corn ethanol technique starts with soaking corn kernels in dilute SO_2 solution for 48 h (steeping). The softened grains are then milled, removed of germ, bran fiber, and gluten protein, and the resulting starch slurry is further processed for ethanol (AMG 2013).

Currently, food crops are the predominant feedstock for commercial production of bioethanol. These food crops are high in starch or sugar content, exemplified as corn, wheat, barley, sugarcane, sugar beet, sweet sorghum, potato, yam, and cassava. In 2015, the world annual bioethanol production reached 25.7 billion gallons, of which merely 11.8 million gallons were from nonfood crops. The top five bioethanol production countries were the USA, Brazil, China, Canada, and France, contributing 57.7%, 27.6%, 3.2%, 1.8%, and 1.2% to the world 2015 bioethanol output, respectively (AFDC 2016a). The feedstocks used in these countries for bioethanol were corn, sugarcane, corn/wheat/cassava, corn/wheat/barley, and sugar beet/wheat/corn, respectively. In the past five years, the USA invested its 37–42% of annually harvested corn grains (~125 million tons) in bioethanol production, targeting on 10% replacement of the nation's demanded gasoline (IAState 2015). Overall, the global commercial bioethanol production has been expanding rapidly, in particular since the beginning of the twenty-first century (Fig. 3). In 1980, the annual bioethanol production was 1.15 billion gallons. The number increased to 4.02 billion gallons in 1990 and to 4.52 billion gallons in 2000. In 2005, the annually produced bioethanol amounted to 8.23 billion gallons. The volume was abruptly raised to 23.31 billion gallons in 2010. It was further increased to 25.68 billion gallons in 2015 (Fig. 3). The USA has been the world's largest bioethanol producer since 2000. Especially in the past six years, the USA produced more than 13.2 billion gallons of bioethanol each year, accounting for >55% of the global production (Fig. 3). When food crops are used as the feedstock, bioethanol competes with human food and animal feed for natural resources and, therefore, influences the global food security. As such, the EU has set up the 7% cap for investing its food crops in biofuels (EurActiv 2015). Indeed, the present food crops-based bioethanol production has nearly reached its practical potential.

Bioethanol has been used in gasoline blends. In the USA, E10 (blends consisting of 10 vol% ethanol and 90 vol% gasoline) is being supplied through all gas stations across the nation, E15 (blends containing 10.5–15 vol% ethanol) is fueling the 2001 and newer light duty cars, while E85 (blends containing 51–83 vol% ethanol) only applies to flexible fuel vehicles (FFVs) (AFDC 2016b). In the EU, supply of 5 vol% ethanol gasoline blends (E5) is mandatory; the ethanol blending rate will be elevated

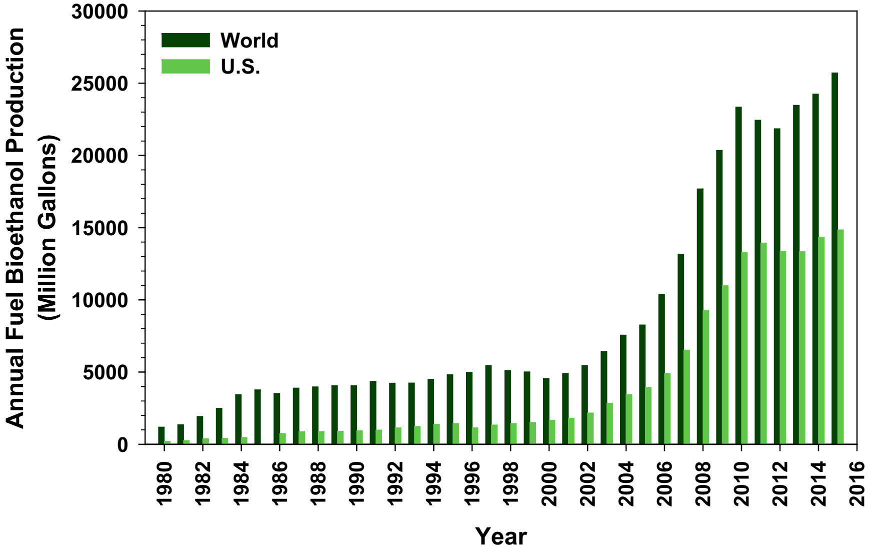


Fig. 3 The world and US fuel bioethanol production from 1980 to 2015. *Data sources* Licht (2012); RFA (2016); EIA (2014)

to 10 vol% in the soon future (EBTP 2015a). In Brazil, E25 (blends containing 25 vol% ethanol) is the fuel norm at gasoline stations (EBTP 2015a).

2.2 *Nonfood Crop-Derived Bioethanol*

Starch- and sugar-based bioethanol is categorized as one of the "**first-generation biofuels**," which source from food crops and, therefore, compete with human food and animal feed. Production of bioethanol from nonfood materials such as plant debris and algae has been enthusiastically explored, attempting to manufacture the "**second-generation biofuels**." Indeed, relative to food crops, lignocellulosic biomass is much more available, with wild grasses, forest thinnings, crop residues, yard trimmings, and food processing waste nearly everywhere. The US annual generation of vegetative residues is estimated at 1.02 billion tons, including 500 million tons of crop residues, 240 million tons of forestry debris, 210 million tons of municipal organic waste, and 65 million tons of animal manure (USDA 2006; McKeever 2004; EPA 2014). Globally, 3.76 billion tons of crop residues and 11.81 billion tons of forestry debris are generated each year (Lal 2005; FAO 2010). Furthermore, intensive research has been conducted to develop dedicated energy crops excelling in biomass yield, soil fertility and water requirements, climatic adaptation, and handleability. The promising candidates include switchgrass, miscanthus, shrub willow, and hybrid poplar (Bomgardner 2013). Typical annual biomass yields of these plants are demonstrated

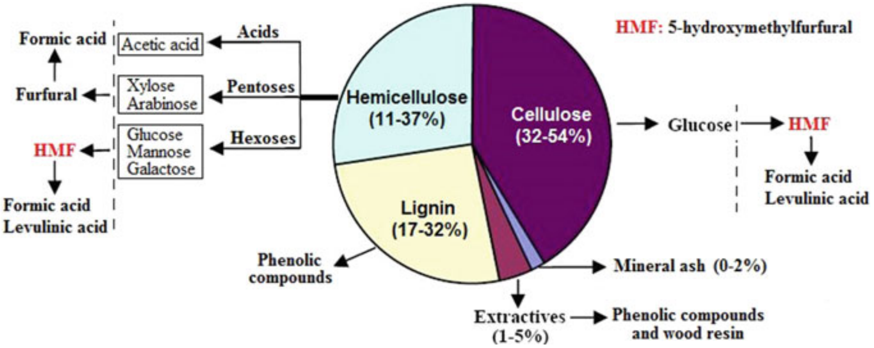


Fig. 4 Hydrolysis products of lignocellulosic materials and their further degradation compounds (chemicals behind the dashed line). *Source* Taherzadeh and Karimi (2007)

at 10–15, 13–25, 10–12, and 9–11 dry tons ha^{-1}, respectively (Fuentes and Taliaferro 2002; Pyter et al. 2007; Sannigrahi et al. 2010; Volk et al. 2011).

Based on their (hemi)cellulose contents (Table 1), lignocellulosic materials possess the ethanol potential of 97–113 gallons ton^{-1} (AFDC 2013a). The practical ethanol yields, however, are substantially lower. The major challenge is to effectively extract simple sugars from lignocellulosic materials and conserve the sugars from rapid degradation prior to fermentation (Fig. 4). Over the past two decades, breakthrough progress has been achieved in developing feasible cellulosic ethanol production systems. However, further technological and economic optimization of the system in feedstock supply, sugar extraction, and alcoholic fermentation remains necessary. Especially the technical efficiency and the involved cost for extracting sugars from lignocellulosic materials have not met the requirements of commercial-scale cellulosic ethanol production. To date, two extraction methods have been intensively tested for recovering sugars from lignocellulosic materials: acid treatment and enzyme treatment (Badger 2002). Acid treatment (acid-catalyzed hydrolysis) is to soak plant materials in an acid solution (e.g., sulfuric acid) to promote (hemi)cellulose hydrolysis for releasing sugars. If dilute acids (e.g., 1–10% H_2SO_4) are used, the treatment is typically carried out under high temperature (e.g., 237 °C) and high pressure (e.g., 13 atm) conditions. In such stringent environment, sugars can be rapidly transformed to furfural and other chemicals (Fig. 4), leading to the overall low sugar recovery (i.e., ~50% of the theoretical level assuming complete hydrolysis of feedstock (hemi)cellulose. The process, however, is prompt (i.e., <15 s) and can be conducted in a continuous feedstock flow. Trials with sawdust showed an ethanol productivity of 38 gallons/ton feedstock following the dilute acid treatment method (Badger 2002). Considering that pentoses (5-carbon sugars) are more susceptible than hexoses (6-carbon sugars) to a high temperature and high pressure environment, the acid treatment can be separated into two stages to improve the sugar recovery: in the initial stage, cellulosic materials are subject to mild conditions (e.g., 100 °C) for 2–6 h to allow hemicellulose to hydrolyze and release pentoses; the residual feedstock is then water rinsed, press-drained, and conveyed to the second stage hydrolysis in a rigorous environment (e.g., 230 °C) to recover hexoses (Lenihan et al. 2010). By the two-stage treatment method, the sawdust ethanol productivity was elevated to 55 gallons/ton feedstock (Badger 2002). Alternatively, concentrated acids (e.g., 30–40% H_2SO_4) could be used in the second stage to facilitate cellulose hydrolysis. In this case, the residual feedstock is typically soaked in the concentrated acid for 2–4 h at 100 °C. The resulting sugar/acid solution is then neutralized by lime and fermented for ethanol. The strong acid treatment takes longer time, but the sugar recovery can be increased up to 80%. Following this treatment method, corn stover demonstrated an ethanol productivity of 65 gallons/ton feedstock (Badger 2002). Enzyme treatment (or enzymatic hydrolysis) is to use active enzymes in place of inorganic acids to facilitate the hydrolytic decomposition of lignocellulosic feedstock. To prepare favorable substrate for enzymes to work efficiently, appropriate pre-processing of the feedstock becomes essential. Lignocellulosic materials are commonly pretreated by hydrothermal softening, ammonia fiber explosion, and dilute acid hydrolysis to help "unbraid" plant microfibrils (Kumar et al. 2009; Talebnia et al. 2010; Conde-Mejia et al. 2012). Other pretreatment methods have also been explored, such as steam explosion, lime extraction, co-solvent fractionation, dilute sulfite pulping, and ionic liquid deconstruction (Conde-Mejia et al. 2012; Nguyen et al. 2016; Xu et al. 2016). All these pre-processing methods are effective to disintegrate the rigid lignocellulosic structure (Fig. 1) through providing a temperature-, pressure-, and pH-controlled environment, but the preferable ones are those using a high solid/water ratio, yielding highly digestible (hemi)cellulose, causing minimal sugar degradation, consuming low chemicals and electricity, requiring low infrastructure cost, and having low operational risks and downstream waste (Novozymes 2016). Once cellulose and hemicellulose are liberated from the interwoven fiber structure (Fig. 1), the polysaccharides can be readily transformed into simple sugars (hexoses and pentoses, Fig. 4) by cellulolytic enzymes such as glycoside hydrolases. Substantial research endeavors have also been invested in selecting highly efficient, low-cost cellulases and carbohydrate esterases. The identified enzyme candidates, however, remain marginally satisfactory for commercial applications. Today the relatively high enzyme preparation cost is still a major factor throttling industrial-scale cellulosic ethanol production (Gies 2014). To improve the cellulose-ethanol conversion, more efficient yeast strains used in alcoholic fermentation have continuously been explored (Bratis 2013). Integration of best feedstock pre-processing, enzymatic hydrolysis, and alcoholic fermentation technologies allowed pilot cellulosic ethanol plants to achieve the cellulose saccharification rate up to 80% and the ethanol yield up to 90 gallons/ton cellulosic biomass (Novozymes 2016).

Alternative to the biochemical fermentation pathway, the thermochemical pathway has also been investigated to produce ethanol from lignocellulosic materials, in which the feedstock is transformed by gasification in a 700–900 °C, O_2-controlled chamber to syngas (a mixture of CO and H_2) and then synthesized into ethanol using particular catalysts ($3CO + 3H_2 \rightarrow CH_3CH_2OH + CO_2$) (NREL 2007; Gonzalez et al. 2012). Synthesis of ethanol from syngas may also be realized by anaerobic fermentation in a specially designed fermenter with acetogenic bacteria capable of utilizing CO and H_2 as the carbon and energy substrates (Liu et al. 2014).

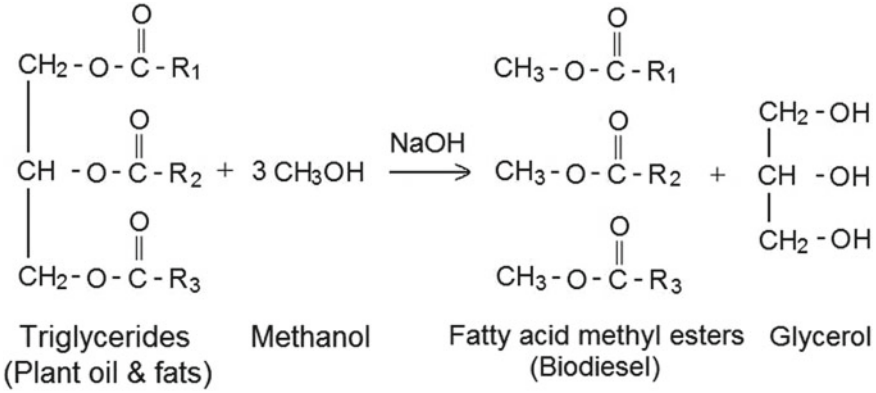
Practically, 75 gallons of ethanol would be generated per dry ton of lignocellulosic biomass (containing ~65 mass% carbohydrates), assuming an 80% (hemi)cellulose-sugar conversion rate (Johnson 2016). The 2015 commercial cellulosic ethanol production cost ranged from $2.63 to $3.16 per gallon (IEA 2015). Preparation of the required cellulase using lignocellulosic materials instead of glucose would reduce the cost to $2.36 per gallon (Johnson 2016). However, at above $2.15/gallon cellulosic ethanol is not cost competitive (NREL 2016). Even at the competitive cost level, cellulosic ethanol production could not be economically viable if the crude oil market price was below $80/barrel (IEA 2015). In fact, commercial production of cellulosic ethanol just started in October 2013 by the Crescentino Biorefinery (Crescentino, Italy), in which rice/wheat straw and giant reed were processed by dilute acid hydrothermal softening, enzymatic hydrolysis, and alcoholic fermentation to generate bioethanol. To date, there are nine operational commercial-scale cellulosic ethanol plants worldwide, with a total production capacity of 156.2 million gallons per year (MMGY): **Crescentino Biorefinery** at 20 million gallons per year (MMGY), **Enerkem Alberta Biofuels** (Edmonton, Canada) with thermochemical production of methanol and ethanol from municipal organic waste at 10 MMGY, **GranBio** (Alagoas, Brazil) with biochemical production of ethanol from sugarcane bagasse at 21.6 MMGY, **Raizen** (Piracicaba, Brazil) with biochemical production of ethanol from sugarcane bagasse and straw at 10.6 MMGY, **Abengoa Bioenergy** (Hugoton, KS, USA) with biochemical production of ethanol from corn stalk/grass/switchgrass at 25 MMGY, **DuPont Cellulosic Ethanol** (Nevada, IA, USA) with biochemical production of ethanol from corn stover at 30 MMGY, **Fiberight of Blairstown** (Blairstown, IA, USA) with biochemical production of ethanol from municipal vegetative waste at 6 MMGY, **INEOS-Indian River Bioenergy Center** (Vero Beach, FL, USA) with thermochemical production (gasification and anaerobic fermentation) of ethanol from municipal solid waste at 8 MMGY, and **Poet-DSM Advanced Biofuels** (Emmetsburg, IA, USA) with biochemical production of ethanol from corn stover/cobs at 25 MMGY (EPM 2016). Due to the high production cost, cellulosic ethanol has shared <0.05% of the overall bioethanol market since its emergence. In 2013, 2014, and 2015, for example, the US actual cellulosic ethanol volumes were 0.22, 0.73, and 2.2 MMGY, respectively, though the nation's cellulosic ethanol capacity (including demonstration, pilot, and commercial-scale plants) was above 100 MMGY (EPM 2016). Worldwide, the number of commercial cellulosic ethanol plants and the total production capacity has been slowly yet steadily increasing, indicating the thriving future of this nonfood renewable liquid fuel (Novozymes 2015).

The biomass of carbohydrate-rich algae such as the strains *Euglena gracilis*, *Prymnesium parvum*, *Sargassum horneri*, and *Gracilaria edulis* also serves as the potential feedstock for "second-generation bioethanol." Productive cultivation of target algae, however, is not cost-competitive. Currently, algal ethanol remains at the research stage (Oilgae 2016; Opposingviews 2016).

3 Development and Production of Biodiesel

Different from gasoline engine-powered passenger cars, heavy vehicles such as trucks and tractors are typically driven by mightier diesel engines. The ignition mechanism of diesel engines is different, and therefore, only diesel fuel can be used to run the engines. Slightly denser than gasoline, diesel is another refinery product of petroleum. One barrel of crude oil yields approximately 10 gallons of diesel by fractional distillation at 200–350 °C. In chemical nature, diesel is a C_8–C_{25} liquid hydrocarbon mixture that possesses a density of 0.835 g cm^{-3} (15 °C) and a higher heating value of 45.8 kJ g^{-1} (EIA 2013b; AFDC 2013b). The global annual diesel consumption is around 385 billion gallons, of which nearly 10% occurs in the USA (EIA 2013c; American Fuels 2014). Biomass-based liquid fuels have been developed to supplement the petro-diesel supply.

Biodiesel, a renewable biofuel produced from natural lipids via basic chemical transformation, is a substitute for petro-diesel. In the presence of an alkaline catalyst, the predominant component triglycerides of vegetable oil, animal fats, algal lipids, and waste grease react rapidly with methanol to form fatty acid methyl esters (FAME)—biodiesel. The reaction is termed transesterification and can be described as:



(6)

where R_1, R_2, and R_3 are aliphatic C_{11}–C_{24} hydrocarbon chains. Potassium hydroxide (KOH) can be used in place of NaOH as the catalyst if the resulting glycerol (glycerin) is disposed of by composting. The yield of biodiesel is dependent on the quality of the feedstock oil and fat (i.e., moisture, impurity, and free fatty acid contents), the reaction conditions (time, temperature, mixing, and airtightness), and the oil/methanol ratio. Under optimal conditions, up to 98% of the feedstock lipids can be transformed into biodiesel (Guo and Xiao 2012). The properties of biodiesel, however, vary with the lipid feedstock. In general, biodiesel is a mixture of numerous mono-alkyl fatty acid esters. It is a yellow-tinted, transparent liquid at room temperature, with density ranging from 0.873 to 0.884 g cm^{-3} and kinematic viscosity ranging from

3.8 to 4.8 mm s^{-2}. Compared with petro-diesel, biodiesel possesses a slightly lower energy density (38–45 kJ g^{-1}, ~90% of that of petro-diesel), a higher cloud point (−4 to 14 °C vs. −9.5 °C for No. 2 diesel), and a lower stability against oxidation (Hoekman et al. 2012). As a fuel, biodiesel low in cloud point but high in oxidation stability is more desirable. If feedstock oil contains high contents of long, saturated hydrocarbon chains, the derived biodiesel typically shows a higher cloud point and higher oxidation stability. Biodiesel generated from the oils rich in short, multi-unsaturated aliphatic carbon chains demonstrates a lower cloud point and lower stability (Hoekman et al. 2012). Evidently, the quality of biodiesel can be improved by manipulating the feedstock constitution.

Vegetable oil and animal fats have long been used in the human history as a fuel for lighting. It was until the 1900s that vegetable oils were tested for powering diesel engines (Knothe 2001). Due to its relatively high viscosity, however, raw vegetable oil failed to flow at desirable rates in the engine fueling system. An array of methods such as pre-heating, thermal cracking, and diesel mixing was attempted to reduce the viscosity of vegetable oil. The transesterification approach (Eq. 6) was discovered by George Chavanne, a Belgian scientist, who noticed that vegetable oils became much less viscous after reacting with methanol or ethanol. He patented the "Procedure for the transformation of vegetable oils for their uses as fuels" in 1937 (Knothe 2001). Forty years later, the Brazilian scientist Expedito Parente developed the first industrial biodiesel production process. In 1989, Austria established the first commercial biodiesel plant to produce diesel substitute from canola oil. Coming to the twenty-first century, the global production and demand for biodiesel have been progressively increasing, owing to the soaring crude oil price and the dwindling petroleum reserve.

Biodiesel feedstocks extend to plant oils, animal fats, and yellow grease (used cooking oil): theoretically all biomaterials that are rich in lipids. Many crops and trees have been intentionally cultivated for harvesting oilseeds to produce biodiesel, including canola, rapeseed, soybean, sunflower, camelina, castor bean, jatropha, tung, and palm (Table 2). The machinery and techniques for growing and harvesting soybean, peanut, sunflower and the oil food crops canola, rapeseed and camelina are existing, and therefore, biodiesel has been produced predominantly from these food crops. Food crop-based biodiesel belongs to the "first-generation biofuels." The biodiesel from nonfood crops such as jatropha, castor bean, tung, and algae is viewed as advanced biofuels or "second-generation (2G) biofuels." It is worthy to mention that significant research has been conducted to develop algal biodiesel. The algal strains with high body lipid accumulation have been screened, including *Chaetoceros calcitrans*, *Dunaliella teriolecta*, *Phaeodactylum tricornutum*, *Neochloris oleabundans,* and *Scenedesmus obliquus*. Commercial-scale algal cultivation and oil extraction, however, are not cost competitive at the current technological stage (Biofuels Digest 2014a; CleanTechnica 2015; DOE 2016a).

Figure 5 illustrates the general procedure for producing biodiesel from vegetable oil. The feedstock oil needs to be low in water and free fatty acids (FFA), with moisture <0.2% and the FFA value (amount of KOH required to neutralize one unit mass of oil) <5 mg/g. A measured volume of vegetable oil is transferred into the reactor.

Table 2 Average seed oil contents and typical seed yields of selected feedstock crops for biodiesel (AGMRC 2013)

Crop	Oil content (% dry mass)	Seed yield (kg ha^{-1})
Soybean	20.0	3363
Canola	43.8	2782
Rapeseed	40.0	2430
Camelina	35.0	1687
Sunflower	44.0	1697[a]
Peanut	48.5	4250[a]
Castor bean	50.5	2243
Jatropha seed	35.0	2500
Oil palm	35.0[b]	10,800[b]

[a] Include shell weight
[b] Fresh fruit

Methoxide (methanol + sodium hydroxide) is prepared by thoroughly dissolving NaOH at ~5 g L^{-1} oil in methanol (20% volume of the oil). The vegetable oil is heated to 50–60 °C, followed by addition of the prepared methoxide under stirring. The reactor is immediately closed and maintained at 50–60 °C to allow transesterification (Eq. 6) to carry out for 2 h under continuous agitation. The reacted mixture is then settled for 2–12 h at room temperature to separate crude biodiesel in the top layer from crude glycerin in the bottom layer. The crude glycerin containing excess methanol, the alkaline catalyst, and small amounts of soap and mono/di/triglycerides can be funnel-drained out of the reactor and refined to recover the methanol and purify the glycerin. The crude biodiesel containing excess methanol and trace quantities of soap and mono/di/triglycerides is typically purified by membrane refining or water washing to remove the impurities (Atadashi et al. 2011; Guo and Xiao 2012). Yellow grease usually contains high contents of FFA. If this material is used for biodiesel production, it needs to be pretreated by filtration and settling to remove solid particulates and water. Methanol and concentrated sulfuric acid are subsequently added to initiate "acid-catalyzed esterification" to transform FFA and part of the triglycerides into biodiesel. After removing the generated glycerin and the acid catalyst, the remaining mixtures are subject to transesterification reactions for further biodiesel production (Fig. 5).

The quality of biodiesel is regulated in the USA by the American Society for Testing and Materials (ASTM) standard D6751 and in Europe by EN14214, with specifications in flash point, cloud point, kinematic viscosity, cetane number, acid number, glycerin content, methanol content, water content, sulfur content, oxidation stability, and other parameters (eXtension 2012). Relative to petro-diesel, biodiesel demonstrates a cleaner emission profile and higher use safety. Biodiesel is normally distributed to end users in blends with petro-diesel. In the USA, the most common blend is labeled as B20, containing 6–20 vol% biodiesel. Low-level blends containing $\leq$5 vol% biodiesel do not carry distinct labels, while use of biodiesel as the sole fuel (B100) requires special handling and even equipment modifications and therefore, is

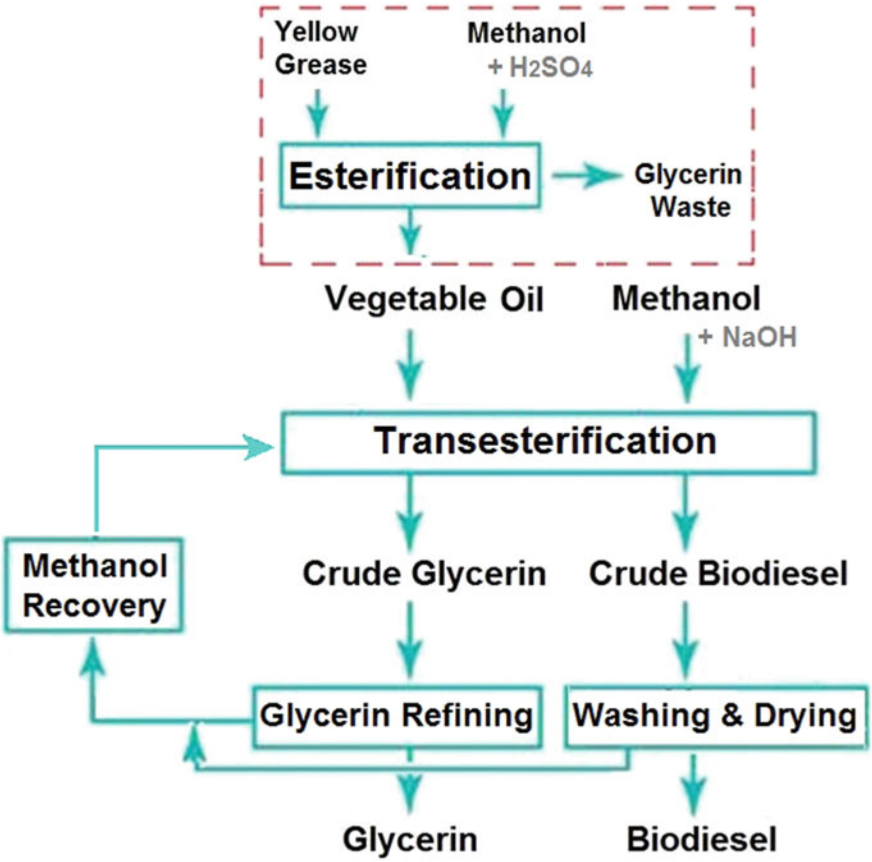


Fig. 5 Technical flow chart of biodiesel production from vegetable oil. If yellow grease (used cooking oil) is the feedstock, acid-catalyzed esterification (in the dashed square) is additionally needed at the beginning to remove excess free fatty acids

not encouraged (AFDC 2016c). In Argentina, use of B10 (10 vol% biodiesel blends) is mandatory. The EU and Brazil have adopted the B7 (containing 7 vol% biodiesel) and B5 (containing 5 vol% biodiesel) diesel blend forms, respectively (Biofuels Digest 2014b).

The global production and consumption of biodiesel have been progressively increasing. In 1991, merely 2.9 million gallons of biodiesel were produced; the annual production increased to 265 million gallons in 2001 and further to 5651 million gallons in 2011 (Fig. 6). In 2015, a total of 8331 million gallons of biodiesel were produced and consumed, of which 39.8% was produced in the EU (primarily in Germany, France, Spain, Italy, and Poland) from rapeseed oil, animal fats, and yellow grease, 15.2% in the USA solely from soybean oil, 12.7% in Brazil mainly from soybean, castor bean, and sunflower oils, 7.4% in Argentina from soybean oil and used vegetable oil, 3.6% in China predominantly from yellow grease, and the rest

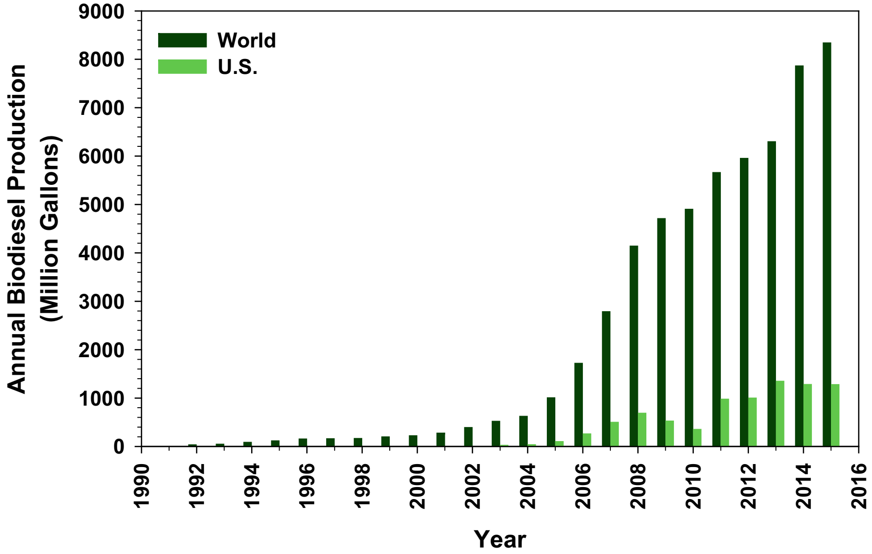


Fig. 6 The world and US biodiesel production from 1991 to 2015. *Data sources* Licht (2012); EIA (2014, 2016b)

in other countries from mixed feedstocks. With improvements in nonfood feedstock production such as cultivation of oily algae and oilseed trees, the global production and consumption of biodiesel will maintain a gradual increasing trend into the near future.

4 Development and Production of Pyrolysis Bio-Oil

A thermochemical pathway for generating liquid fuel from biomass is pyrolysis. The technology is to transform plant materials in a high temperature (300–900 °C), O_2-absent environment to charcoal (the black solid residue), bio-oil (the brown vapor condensate), and syngas (the uncondensable vapor, mainly CO and H_2) (Fig. 7; Vamvuka 2011). Pyrolysis has been practiced to produce wood charcoal since the beginning of human civilization. Depending on the heating rate of biomass in the reactor, pyrolysis can be implemented in two patterns: slow pyrolysis and fast pyrolysis. In slow pyrolysis, plant materials are placed in a batch reactor or a continuous flow bed and heated to 300–500 °C for a number of minutes or even days. Air is prevented from entering the reactor during the heating. Slow pyrolysis has a low yield of bio-oil, typically 30% of the feedstock dry mass (Guo et al. 2012). In fast pyrolysis, the feedstock is ground to <2 mm particles and delivered into a high-temperature (e.g., >900 °C) reactor, in which the fine biomass particles are heated to approximately 500 °C in 2 s, yielding bio-oil at 50–70% of the feedstock dry mass from

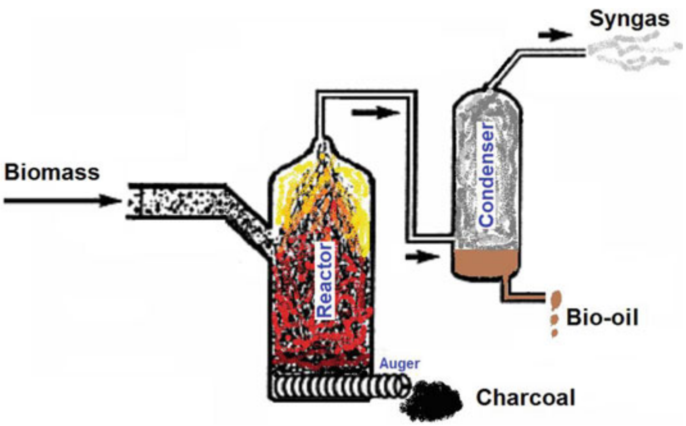


Fig. 7 Pyrolysis of plant biomass to generate char, bio-oil, and syngas

rapid vapor condensation (e.g., <2 s) (DOE 2016b). In fact, other thermal treatment techniques (e.g., incomplete combustion and gasification) also result in bio-oil, but it is fast pyrolysis that maximizes the bio-oil yield among the three products.

Theoretically, all solid biomass residues can serve as the feedstock for pyrolysis bio-oil. To avoid reactor clogging and to reduce pollutant emissions, however, wood is the preferred source material owing to its low mineral ash, nitrogen, and sulfur contents (Vamvuka 2011). Under optimized fast pyrolysis conditions, 60–75% of the ash-free feedstock mass (and the inherent energy) can be recovered in bio-oil (Chatham-Kent 2013; Carpenter et al. 2014).

Crude pyrolysis bio-oil is a blackish-brown fluid consisting of water, colloidal char particulates, and various organic compounds (Table 3). It is acidic (pH 2–3), corrosive (abundant in low molecular weight organic acids), instable (layer separation after settling), and inflammable. More than 300 organic compounds have been identified in bio-oil, including acids, alcohols, aldehydes, esters, ketones, phenols, alkenes, sugars, furans, and aromatics. The organic mixture, in general, contains 54–58 wt% C, 5–7 wt% H, 35–40 wt% O, and 0–0.2 wt% N (Ringer et al. 2006; Vamvuka 2011). Prior to being utilized as a petro-distillate alternative, pyrolysis bio-oil needs to be upgraded to reduce its moisture content, acid content, and viscosity and improve its energy density, ignitability, and storage stability (Czernik and Bridgwater 2004; Xu et al. 2008). A variety of upgrading methods have been developed, including hydrogen treatment, catalytic cracking, molecular distillation, supercritical fluidization, esterification, emulsification, steam reforming, Fischer–Tropsch process, and red mud processing (Zhang et al. 2013; Ruddy et al. 2014; Xiao 2014; Open Source Ecology 2016). Successful applications of upgraded bio-oil in place of heavy petro-distillates (e.g., diesel and No. 2 heating oil) to power diesel engines, furnaces, and electric generators have been reported (Lehto et al. 2013; WSU Extension 2014). Nevertheless, the available upgrading techniques are

Table 3 Properties of wood-derived pyrolysis bio-oil as compared with petroleum distillate fuels (Czernik and Bridgwater 2004)

Properties	Pyrolysis bio-oil	Petroleum distillate fuel
Water content (wt%)	15–30	0.1
pH	2–3	–
Density (kg m^{-3})	1.2	0.94
Elemental composition (wt%)		
C	54–58	85
H	5.5–7.0	11
O	35–40	1.0
N	0–0.2	0.3
Ash	0–0.2	0.1
High heating value (MJ kg^{-1})	16–19	40
Viscosity (50 °C) (cSt)	33–83	190
Solid particulates (wt%)	0.2–1	1
Distillation residue (wt%)	Up to 50	1

not cost-competitive at the industrial scale. Economically feasible upgrading protocols for transforming crude pyrolysis bio-oil into petroleum distillate fuel substitute are desperately warranted (Valle et al. 2014; Ciddor et al. 2015).

Currently, the European Committee for Standardization is developing quality specifications for pyrolysis bio-oil as a fuel substitute for heavy fuel oil, light fuel oil, and stationary combustion engine fuel (EBTP 2015b). Nevertheless, the production and application of bio-oil remain at the fledging stage. No industrial-scale manufacturing of bio-oil has existed. Worldwide, a few pilot plants are operating to produce bio-oil from wood at the 10–130-ton d^{-1} feedstock processing capacity. These plants are exemplified as Ensyn Technologies, Inc. (Canada and USA), DynaMotive Energy Systems (Canada and USA), Agri-Thermo (Canada), Fortum Co. (Finland), and BTG-BTL Empyro (The Netherlands) (Chatham-Kent 2013). The chief barrier to commercialization of bio-oil production is lack of cost-effective technologies for upgrading crude pyrolysis bio-oil into petro-distillate alternatives (Lehto 2012).

5 Development and Production of Drop-in Biofuels

Unlike petro-distillate hydrocarbon fuels that contain little oxygen in their componential molecules, the most popular biofuels bioethanol and biodiesel are relatively high in oxygen content. As a result, bioethanol and biodiesel possess moderate dissolution capability and are corrosive to elastomer and metallic apparatus (Kass et al. 2011). The existing fuel supply infrastructure is not fully compatible with these biofuels. It is not safe to use the current fueling system without modifications to distribute bioethanol and biodiesel. Even in gasoline and diesel blends at above 20 vol%, bioethanol and biodiesel can dissolve rubber gaskets and rust certain metal parts, causing damages to engines, storage tanks, and fuel dispensers (Kass et al. 2011; DOE 2016c).

It is desirable to produce "drop-in" biofuels that possess chemical composition, fuel characteristics, and energy density comparable to those of petro-distillate fuels and, thus, fully compatible with the existing distribution equipment. Drop-in biofuels can be directly distributed to end users through the available fuel supply system and used in fuel engines without any infrastructure modifications or petro-fuel blending. The promising drop-in biofuel candidates have been identified as hydrotreated vegetable oil, Fischer–Tropsch biofuels, butanol, liquefied biomass, sugar hydrocarbons, syngas complexes, and others (AFDC 2012; EIA 2015b). These drop-in biofuels vary in biomass feedstocks and refining techniques.

Hydrotreated vegetable oil (HVO), so-called green diesel or renewable diesel or Hydroprocessed esters and fatty acids (HEFA), is a diesel substitute produced from vegetable oils and animal fats by catalytic hydrogen processing (Fig. 8). The involved chemical reactions can be simplified as:

$$\begin{array}{l} CH_2\text{-}OCOR_1 \\ | \\ CH\text{-}OCOR_2 \\ | \\ CH_2\text{-}OCOR_3 \end{array} + H_2 \underset{\Delta}{\overset{\text{Catalyst}}{\rightleftarrows}} \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + \begin{array}{c} H_3C-R_1 \\ H-R_2 \\ H_3C-R_3 \end{array} + H_2O + CO_2$$

(7)

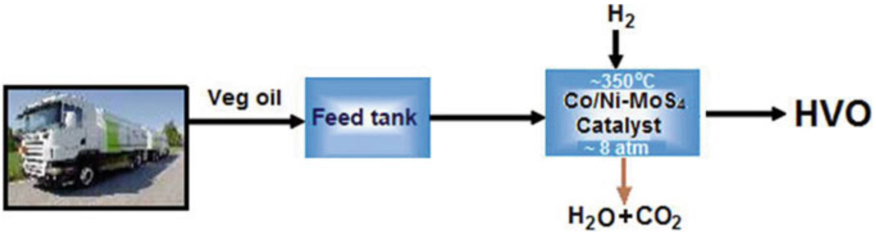


Fig. 8 Catalytic hydroprocessing of vegetable oil for a drop-in biofuel

where R_1, R_2, and R_3 are aliphatic hydrocarbon groups in the fatty acid moiety of oil molecules (triglycerides). The product HVO is a liquid mixture of straight chain aliphatic hydrocarbons free of oxygen, nitrogen, and sulfur. It possesses an energy density roughly identical to that of petro-diesel. In comparison with the latter, HVO is lower in lubricity, poorer in cold flow properties, and higher in cetane number (Lapuerta et al. 2011). Nevertheless, HVO has a much lower emission profile, higher storage stability, and lower cloud point (EBTP 2015c) than biodiesel.

Vegetable oils, animal fats, and yellow grease can be used as the source material to produce HVO. Commercial production of HVO started in 2010. There are a number of HVO biorefinery plants operational in Singapore, USA, The Netherlands, Italy, and Finland. The global capacity has been steadily growing, from 350 million gallons/yr in 2011 to nearly 1200 million gallons/yr in 2014 (EIA 2015b). Currently, HVO is being used as an aviation fuel in 50 vol% blends with petro-jet fuel. Depending on the market price of petroleum, production of HVO is technically feasible and may be economically feasible (Hilbers et al. 2015).

Fischer–Tropsch biofuels are liquid transportation fuels manufactured from biomaterials through the “biomass to liquid via Fischer–Tropsch synthesis” (BTL-FT) process, in which biomass is first converted to syngas via gasification, the syngas is then synthesized into a liquid mixture of gasoline (>70 wt%), diesel (15–20 wt%), middle and heavy distillate oils in the presence of cobalt-based catalysts at 180–200 °C and 5–15 atm, and the synthesized liquid fuels are eventually recovered by fractional distillation (Ail and Dasappa 2016). The BTL-FT process can be described as:

$$\text{Biomass} \overset{\text{gasification}}{\rightarrow} H_2 + CO(\text{syngas}) \tag{8}$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{9}$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{10}$$

The composition of the synthesized liquid can be manipulated by controlling the H_2/CO ratio of the syngas. At a ratio of 2.0:1–2.3:1, the gasoline yield is maximized (Ail and Dasappa 2016). The gasoline generation can be further improved by using shape-selective zeolite catalysts instead of cobalt-based catalysts, as outlined in the syngas to gasoline plus (STG+) technique (Primus 2015):

$$2H_2 + CO \rightarrow CH_3OH\ (\text{methanol}) \tag{11}$$

$$2CH_3OH \rightarrow H_3COCH_3\ (\text{dimethyl ether}) + H_2O \tag{12}$$

$$nH_3COCH_3 \rightarrow C_6 - C_{10}\ \text{hydrocarbons (gasoline)} + nH_2O \tag{13}$$

Commercial production of liquid transportation fuels via FT process or STG + synthesis from coal-derived syngas (coal gasification) and natural gas-derived syngas (steam methane reforming) has been realized (e.g., the Sasol Synthetic Fuels, Ltd established in 1982 in Secunda with 85,000 barrels per day capacity and the Qatar Shell Service Company established in 2009 in Qatar with 14,000 barrels per day capacity). To date, however, there are no commercial scale BTL-FT plants operating to synthesize liquid transportation fuels from biomass, largely due to the high production cost. In 1996, CHOREN Industries installed a demonstration BTL-FT plant in Freiberg, Germany, with 1000 barrel per day capacity (Ail and Dasappa 2016).

Another drop-in biofuel candidate is biobutanol. Biomass-derived sugars can be converted to butanol (a drop-in fuel) through acetone-butanol-ethanol (ABE) fermentation by the anaerobic, spore-forming bacterium strains of *Clostridia* (Schiel-Bengelsdorf et al. 2013). The molar ratio of acetone, butanol, and ethanol in the fermented slurry is typically 3:6:1. The sugar to ABE conversion rate, however, is merely 8%. Furthermore, separation of butanol from the ABE mixture can be costly (Sreekumar et al. 2015). Biomass-derived sugars can also be synthesized into petroleum-like drop-in biofuels through a series of catalytic chemical transformations (catalysis) including dehydrogenation, deoxygenation, hydrogenolysis, and cyclization (Biddy and Jones 2013). Pyrolysis of plant and algal biomass in an H_2-abundant environment (hydropyrolysis) yields a black liquid (85% of feedstock mass) in addition to minor char and syngas; the liquid (hydropyrolysis oil) can be refined to recover quality transportation fuels (Duan et al. 2013). Biomass can also be processed by hydrothermal liquefaction, through which biomass/water slurry (5–35% dry solids) is treated under high temperature (e.g., 300–350 °C) and high pressure (e.g., 100–200 atm) conditions to form an organic liquid (biocrude). Biocrude is a complex mixture of organic acids, alcohols, ketones, phenols, naphthol, benzofurans, and others and can be upgraded in existing refineries to gasoline, diesel, and related distillate fuels (Biddy et al. 2013; Elliott et al. 2015). These drop-in biofuel technologies, however, are still at the research and development stage.

6 Summary and Conclusions

The global renewable energy utilization has been notably expanding over the past two decades. Bioenergy is the largest renewable energy sector, accounting for more than 65% of the global renewable energy consumption and contributing 10% to the world's primary energy supply (REN21 2015). Within twenty years, the world's bioenergy consumption increased by 34.8% to 69.1×10^{15} kJ in 2013. It is estimated that by 2050, the world's annual bioenergy consumption will reach 190×10^{15} kJ, and biofuels will provide up to 27% of the world transportation fuel (WEC 2013; IEA 2016).

Biomass is the sole renewable source for manufacturing liquid transportation fuels. Worldwide, tremendous efforts have been made to develop liquid biofuels as substitutes for petro-gasoline and petro-diesel. The liquid biofuels include bioethanol, biodiesel, pyrolysis bio-oil, and drop-in biofuels. The global annual bioethanol production increased from 8.2 billion gallons in 2005 to 25.7 billion gallons in 2015. At the same time, the world's annual biodiesel production increased from 1.0 billion gallons to 8.3 billion gallons. Nevertheless, these gigantic volumes of biofuels were sourced exclusively from food crops, imposing great pressure on human food and animal feed supply. Refining biofuels from nonfood biomaterials has been intensively explored. Breakthrough progress has been achieved in extracting simple sugars from lignocellulosic biomass for bioethanol production. With effective feedstock pretreatment techniques, efficient cellulosic enzymes, and improved fermentation yeast strains, commercial production of bioethanol from lignocellulosic materials has become technically feasible and economically viable. Starting from 2013, the global production of lignocellulosic ethanol has been gradually expanding. Development of new, nonfood source materials for biodiesel has been focusing on algal oil, but algal cultivation and oil extraction need further improvement to reduce the production cost. The fast pyrolysis technology has also been researched to convert solid biomass into liquid fuel. Refining the resulting pyrolysis bio-oil for liquid transportation fuels, however, has not been cost-competitive. In recent years, significant investments have been committed to developing drop-in biofuels that are compatible with the existing fuel supply infrastructure. A successful candidate is HVO, with the current global production capacity of 1.2 billion gallons/yr. Production of drop-in biofuels via BLT-FT synthesis is promising, yet the technology remains at pilot production stages. Other drop-in biofuel technologies are being investigated, such as hydropyrolysis, hydrothermal biomass liquefaction, ABE fermentation, and sugar catalysis.

Given the present renewable energy and climate change policies, it is evident that global production and consumption of liquid biofuels will continue to increase. Biofuel has been playing a major role in the emerging "green economy."

Review Questions

1. Globally, what is the bioenergy potential for meeting human fuel demands?
2. Give examples of lignocellulosic materials.
3. What is the technological bottleneck for producing bioethanol from lignocellulosic materials via alcohol fermentation?
4. Describe the advantages and challenges of second-generation biofuels.
5. What is transesterification?
6. Compare biodiesel with petrol diesel for differences in physical, chemical, and energy properties.
7. What is pyrolysis? What products can be obtained from fast pyrolysis of wood?
8. Pyrolysis bio-oil is comparable in fuel quality to commercial heating oil from petroleum. Is it true?
9. Name three candidates of drop-in transportation biofuels and briefly explain how they can be produced from plant biomass.

10. In the USA, what are currently the predominant feedstocks for bioethanol and biodiesel? Will these feedstocks be taken place of by other plant materials in the future?

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Bio-oil
Cellulose
Drop-in
Feedstock
Fermentation
Hemicellulose
Lignocellulosic
Pyrolysis
Syngas
Transesterification

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Production Potential and Logistics of Biomass Feedstocks for Biofuels

Weiping Song, Rachel Apointe and Mingxin Guo

Abstract Intensive biofuel production and utilization require an adequate and sustainable supply of biomass feedstocks. Globally, net terrestrial primary production is estimated at 56×10^{15} g C yr^{-1}, storing 2.2×10^{21} J bioenergy in the annually synthesized biomass. Approximately 8.7% of this primary production can be sustainably used for energy purposes to meet 34% of the current human energy demand. Sustainable bioenergy feedstocks extend to feasible portion of food grains, crop residues, dedicated energy crops, forest debris, animal manures, and domestic organic waste. To transfer biomass feedstocks from the production field to biorefinery plants, an array of unit operations are involved, including harvesting, drying, transportation, densification, storage, and pre-processing. Machineries and equipments have been developed to implement the feedstock logistics. The overall biomass handling cost accounts for 35–50% of the total biomass production budget. Biomass logistics are a critical component in a biofuel production system and an essential part of the bioenergy supply chain. Technological advancement is warranted to improve the efficiency of biomass feedstock logistics.

Keywords Biomass · Biofuel · Feedstock · Harvest · Transportation · Storage · Pre-processing

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1 Introduction

All human activities require energy. The energy is obtained predominantly from food and fuel. Through combustion, the chemical energy stored in fuels is released in heat (thermal energy) and light (radiant energy). The light can be utilized for lighting (e.g., oil lamps), while the heat is used for heating, cooking, powering engines, and running electricity generators.

The energy that drives the Earth system processes (e.g., wind, ocean currents, hydrological cycle, rock weathering, and ecological dynamics) originates from the Sun. Plants absorb solar radiation and grow biomass via photosynthesis, providing food and fuel for human consumption. Before the nineteenth-century wood was the primary fuel for energy to fulfill various domestic purposes (Smil 2010). Wood was burned for heat and light to cook food, illumine night, warm shelters, smelt ores, and treat clay artifacts. Commercial mining and wide use of fossil fuels (coal, petroleum, and natural gas) for energy did not start until the 1800s, when steam engines, gas lights, electric motors, and internal combustion engines were invented during the Industrial Revolution. It was not until 1900 that human consumption of fossil energy exceeded wood energy (Smil 2010). Today, however, fossil fuels are the principal energy sources to power engineering machines, transportation vessels, and electricity generators. The world annual energy consumption reached 5.6×10^{20} J in 2014 (Enerdata 2015), of which >80% was provided by fossil fuels (IEA 2013a). Nevertheless, fossil fuels are nonrenewable and their reserves are limited. At the current consumption rates, the supply of petroleum, natural gas, and coal will only be able to last for another 45, 60, and 120 years, respectively (IEA 2013b). The global energy demand will rise to 6.6×10^{20} J in 2020 and 8.6×10^{20} J in 2040 (EIA 2013), while the fossil fuel supply is dwindling, the world is compelled to develop renewable energy alternatives. Moreover, tremendous amounts of greenhouse gases have been released from fossil fuel consumption into the atmosphere, elevating the atmospheric CO_2 concentration from the pre-industrial level of 280 ppm to the present nearly 400 ppm and causing disastrous climate change effects (IPCC 2013). The incentives for energy independence, security, and climate change mitigation are stimulating international communities to invest in the development and utilization of renewable energies, including solar, wind, hydro, geothermal, and biomass energy. Of these renewable energies, biomass energy (**bioenergy**) draws major and particular development endeavors, primarily due to the extensive availability of biomass, already-existence of biomass production technologies and infrastructures, and biomass being the sole feedstock for renewable liquid transportation fuels. Research has been intensively conducted to develop best technologies for effectively processing biomass materials into solid (e.g., pellets, char), liquid (e.g., bioethanol, biodiesel, pyrolysis bio-oil, and drop-in biofuels), and gaseous (e.g., syngas, biogas) fuels (Guo et al. 2015). Commercial generation of electricity, transportation fuels, and biogas using biomass feedstocks has been practiced in many nations. Production of biomass for fuels, however, competes with food for land, water, and other resources. It is questioned whether sufficient biomass can be produced for biofuels that meet the human energy demand. Also, harvesting, transporting, storing, and pre-processing biomass for biofuel refinery involve a number of biomass preparation steps. Systems thinking becomes essential in establishing the biofuel supply chain starting at biomass production and preparation. This chapter elucidates the global biomass production potential for biofuels and the general logistics of biomass feedstocks.

2 Production Potential of Biomass for Biofuels

Biomass is biological material derived from living, or recently living organisms. Biomass contains energy that is originally transformed from solar radiation by plants, algae, and cyanobacteria through photosynthesis. Biomass can be directly combusted for heat and light. Biofuels refer to the biomass and its refined products to be combusted for energy. The utilization of bioenergy in biofuels for different human purposes started from the initial discovery of fire. Even today, nearly 40% (2.6 billion) of the world population relies on firewood to meet its energy requirement (FAO 2013).

The Sun is the primary energy source of the Earth system. It is the solar energy that drives the dynamic processes in the atmosphere, hydrosphere, lithosphere, and biosphere. The average solar energy flux at the top of the Earth's atmosphere is 340 W m^{-2} (Lindsey 2009). On an annual basis 5.5×10^{24} J of solar energy are irradiated to the Earth (surface area 510.1×10^{12} m^2). After reflection and absorption by the atmosphere and the Earth's albedo, 48% of this incoming energy is absorbed by the Earth (Skinner and Murck 2011). At the Earth surface, plants, algae, and cyanobacteria absorb a narrow range of solar radiation (mainly 400–700 nm, accounting for 43% of the overall solar irradiance) and conduct photosynthesis to convert solar energy into chemical energy and store it in the synthesized biomass. The reaction is described as:

$$6CO_2 + 6H_2O + \text{light} \rightarrow (CH_2O)_6 + 6O_2 \quad (1)$$

To convert 1 mol of CO_2 to carbohydrates through photosynthesis, approximately 10,000 kJ of light energy are absorbed but only 470 kJ stored in plant biomass (FAO 1997). The balance is dissipated as heat and long-wavelength radiation. The photosynthetic efficiency—the fraction of light energy converted into chemical energy during photosynthesis—is generally low and influenced by a number of factors, including light intensity, temperature, CO_2 concentration, plant species, and plant growth stage. For a single leaf, the efficiency is typically 5% (maximum 8–9%) of total incident solar irradiance (Bolton and Hall 1991). The photosynthetic efficiency of most plants peaks at 25% of maximum full sunlight; above this light intensity, the efficiency decreases in proportion to the excess radiation absorbed (Ort et al. 2011). At 30 °C and 380 ppm atmospheric CO_2, the maximum photosynthetic efficiency is 4.6% for C3 plants and 6.0% for C4 plants (Zhu et al. 2008). The highest photosynthetic efficiencies observed in the field according to plant growth rates are 3.5% for C3 species and 4.3% for C4 species over a short term. Over a full growing season the figures drop to 2.4% and 3.4%, respectively (Monteith 1977; Piedade et al. 1991; Beale and Long 1995). Intensively cultivated agricultural crops show a photosynthetic efficiency ranging from 1 to 4% and averaging at 3% (Moore et al. 1995). Approximately 39 kJ of energy are fixed per gram biomass carbon via photosynthesis (Klass 1998). Globally, photosynthesis converts ~200 × 10^{15} g C-equivalent CO_2 into biomass each year (FAO 1997). Overall, around 0.3% of the solar energy absorbed by the Earth is stored in biomass through photosynthesis, equivalent to ~7.9 × 10^{21} J/year.

The global gross primary production is estimated at 200 × 10^{15} g C yr^{-1} (FAO 1997). Respiration of the primary producers, however, consumes nearly half of the photosynthesized organic compounds and the inherent energy. The net primary production of the whole Earth is 104.9 × 10^{15} g C yr^{-1}, of which 53.8% is by the terrestrial ecosystem and 46.2% by ocean autotrophic organisms (Field et al. 1998). The annual **terrestrial** primary production amounts 123 (range 107–139) × 10^{15} g C in gross and 56 (range 48–69) × 10^{15} g C in net (Beer et al. 2010). Considering that herbaceous plants typically contain 45% of carbon by dry weight and woody plants 50% of carbon (Chapin et al. 2011), the terrestrial primary production adds approximately 120 × 10^{15} g of dry vegetative biomass each year (Broadmeadow and Matthews 2003). Though different organic compounds vary in energy content, whole plant tissues demonstrate a relatively constant value at 20 kJ g^{-1} of ash-free dry mass (Chapin et al. 2011). The energy density of dry wood ranges from 18 to 22 kJ g^{-1} (Ashton and Cassidy 2007). As such, through photosynthesis 2.2 × 10^{21} J of bioenergy is stored in the annually produced terrestrial plant materials.

The current world energy demand is ~5.6 × 10^{20} J (Enerdata 2015). Largely, the bioenergy captured each year by land plant biomass production is 3–4 times greater than human energy demands. However, most of the annually added plant biomass is present in remote areas and wildlife habitats. It is not economically viable or ecologically sustainable to harvest and transport the biomass for biofuels. Practically, bioenergy feedstocks refer to crop residues, animal manures, timber and forestry refuses, municipal organic waste, dedicated biomass crops, intentionally cultivated algae, and appropriate portion of starch/sugar/oil-rich food crops. It is projected that future bioenergy feedstock production would use 2.0 billion hectares of accessible land (Dale et al. 2014). Cultivation of dedicated biomass crops on marginal land (e.g., under-utilized land, abandoned land, and land with degraded agricultural soils) and growing algae in artificial bioreactors have been proposed. Worldwide there are approximately 500 million hectares of marginal land available (Tilman et al. 2006). Sustainable biomass feedstock production, however, should not compromise food security, wildlife habitat, or soil conservation. Land clearance or conversion of agricultural land from food to grow bioenergy crops should be avoided. The removal rates of crop and forestry residues should be reasonable to prevent soil erosion or soil fertility deterioration (Woolf et al. 2010). Within these restrictions, Woolf et al. (2010) estimated the global bioenergy feedstock potential was 2.81 × 10^{15} g C yr^{-1} (Table 1), equivalent to 5.0% of the global annual terrestrial net primary production. The energy stored in this amount of biomass is 1.1 × 10^{20} J, matching 20% of the current global energy demand. Estimates by others on the global bioenergy potential

Table 1 Sustainable biomass feedstock availability

Biomass	Global production ($\times 10^{15}$ g yr^{-1})	Scenario	Maximum sustainable potential ($\times 10^{15}$ g C yr^{-1})
Crop residues	Rice: 0.89	Rice husks and 90% of paddy rice straw not used for animal feed	0.28
	Other cereals: 2.60	20% of total straw and stover (45% extraction rate minus animal feed)	0.18
	Sugar cane: 0.31	Sugar cane: Waste bagasse plus 75% of field trash	0.13
Manures	1.74	25% of cattle manure plus 90% of pig and poultry manure	0.19
Biomass crops	1.25	100% of potential production of abandoned, degraded cropland that is not in other use	0.60
Forestry residues	1.90	Firewood plus 44% of difference between reported feelings and extraction	0.64
Agroforestry	1.28	170 Mha of tropical grass pasture converted to silvopasture	0.62
Municipal organic waste	0.52	75% of global yard trimmings and food waste, including 80% of waste sawn wood	0.17
Total			2.81

Data source World Bank (2013), Woolf et al. (2010)

using different methodologies and scenario considerations show a wide range from 0.30 to 13 × 10^{20} J (Haberl et al. 2011; WEC 2013). Dornburg et al. (2010) narrowed the range to 2–5 × 10^{20} J by conducting a sensitivity analysis and incorporating the limiting factors such as water availability, biodiversity, and food demand. The most promising energy crops switchgrass, miscanthus, shrub willow, and hybrid poplar have a typical biomass yield of 12, 20, 11, and 10 dry tons ha^{-1}, respectively (Fuentes and Taliaferro 2002; Pyter et al. 2007; Volk et al. 2011; Sannigrahi et al. 2010). Considering the land availability and the practical biomass yields, the Global Energy Assessment concluded that the global bioenergy potential was 1.6–2.7 × 10^{20} J yr^{-1} (IIASA 2012).

At present, the global biofuel utilization reaches approximately 0.55×10^{20} J yr^{-1} (Haberl et al. 2013). Worldwide, bioenergy provides nearly 14% of the energy demand and counts for 75% of the total renewable energy (IEA 2013c). In 2015, the world bioethanol production was 25.7 billion gallons and biodiesel production was 8.3 billion gallons (RFA 2016; EIA 2016). These biofuels, however, were predominantly from food crops, including corn, sugar cane, wheat, soybean, and canola. If the current food crop portion is included, the global bioenergy potential should reach 30% of the current energy demand. Further considering the selection of new energy crop cultivars with higher biomass yields and the intentional cultivation of algae, the global potential of biomass production for biofuels is reasonably at 4.9 $\times 10^{15}$ g C yr^{-1}, delivering bioenergy 1.9×10^{20} J yr^{-1} and meeting 34% of the current global energy demand (Haberl et al. 2013).

3 Biomass Feedstock Logistics

3.1 Bioenergy Pathways

To utilize bioenergy, biomass materials can be directly burned or processed into various biofuel products through physical, chemical, biological, and thermal transformations. Similar to fossil fuels, there are solid, liquid, and gaseous biofuels. The biomass materials and conversion technologies vary with different biofuels. All biomass materials, however, require land, water, nutrients, and favorite climate to produce. Furthermore, all biomass materials have to be collected from the field and transported to a processing plant. The steps and efforts (e.g., harvesting, drying, pre-processing, densification, loading, transportation, and storage) involved in moving biomass materials from the production field to a biorefinery plant are termed “biomass logistics” (Fig. 1). At each step, there are distinct engineering and infrastructure constraints that affect costs. Feedstock production and handling costs account for 35–50% of the overall cellulosic ethanol production cost (Hess et al. 2007). Regardless of the logistic costs, the payment at the farm gate for one dry metric ton of cellulosic biomass ranges from $11 to $44 (Hess et al. 2007). It is critical to develop a biomass feedstock supply chain that functions efficiently and cost-effectively.

Dried plant biomass can be directly burned as firewood to release energy. Wood can be chopped into chips or ground and pelletized into pellets. Pelletization of herbaceous biomass is also feasible. Through a chemical reaction “transesterification”, vegetable oil and animal fats can be transformed into biodiesel. Starch, sugar, and cellulosic materials are used to produce bioethanol and biobutanol through microbial fermentation. Organic waste, such as animal manure and food waste, is typically used to generate biomethane through anaerobic digestion, a microbial decomposition pathway of organic residues in the absence of air. Pyrolysis and gasification are two thermochemical methods for producing biofuels. Pyrolysis by heating wood chunks without air generates charcoal and bio-oil. Gasification of wood, crop residues, and

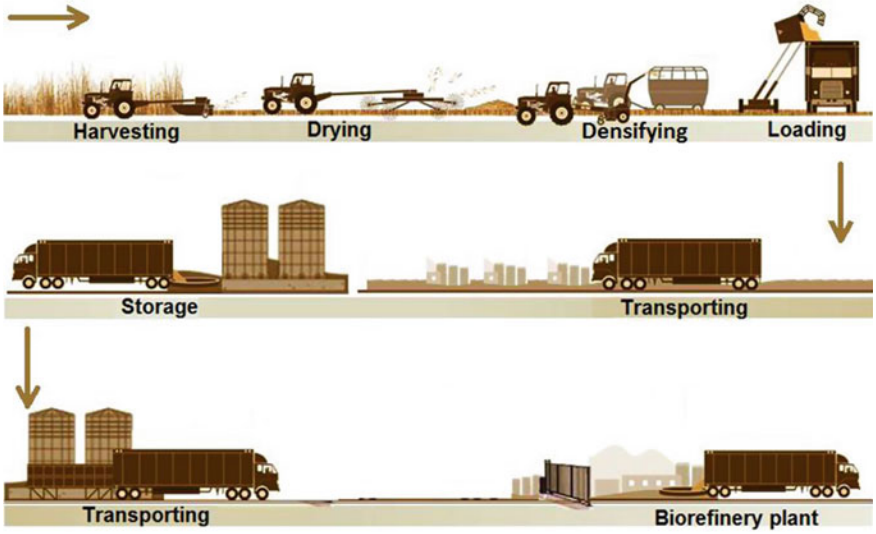

Fig. 1 Logistics of biomass feedstock for biofuels

other lignocellulosic biomaterials at high temperature with controlled O_2 availability produces syngas (a mixture of CO and H_2) and bio-oil (Fig. 2).

3.2 *Biomass Harvest and Collection*

Crop grains such as corn, soybean, canola, and wheat are usually harvested by a combine (harvester) from the field. The combine automatically reaps, threshes, and winnows the grains from the stover/straw and then collects the grains in a hopper tank or blows the grains into a side-running truck. The grains have to be adequately dry prior to harvesting. Normally, the crops are left in the field until the grain moisture content drops to below 25% for shelling corn, 15% for soybean, 17% for wheat, and 10% for canola (Prairie Grains 2006; ISU Extension 2008; Wiatrak and Frederick 2014). The harvesting costs range from \$85 to \$110 ha^{-1} (UIUC 2008). Crop residues can be collected by shredding, raking, and round baling following grain harvest.

Bioenergy grasses such as switchgrass are typically cut down and form windrows in the field for drying by a hay swather (a disk cutterbar mower). Annually, a single harvest after plant flowering or after the first frost is recommended (OCES 2010). The cutting and crushing costs are estimated at \$44 ha^{-1} (2013 value; Khanna et al. 2008). The taller grasses such as miscanthus, giant reed, sugar cane, and sweet sorghum are harvested with a forage reaper or a cane harvester (an exact chopper equipped with a big baler). The best time for annually harvesting miscanthus and giant reed is the end of the growing season when the plants become dormant (Pyter et al. 2008). Sugar

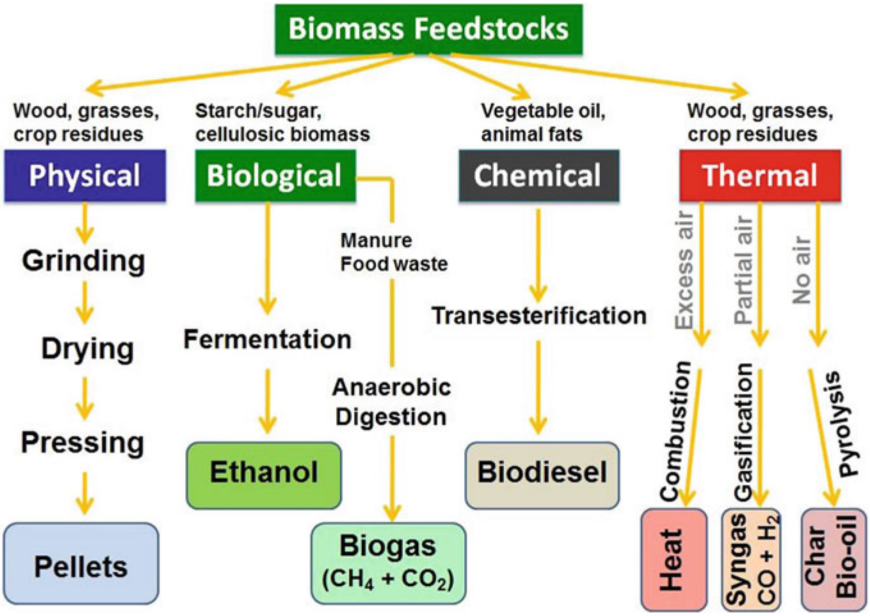

Fig. 2 Common bioenergy pathways from different biomass feedstocks

cane and sweet sorghum are harvested between June and December after 12 months of plant growth at a cost of \$196 ha^{-1} (Salassi and Deliberto 2013).

The woody bioenergy crop shrub willow is harvested every three years after the first coppice. This occurs in November after the leaves fall. The equipment can be a New Holland forage harvester with a willow-cutting head, which cuts willow stems at 10–15 cm above the ground, chops the stems into chips, and blow the chips into an alongside wagon (Abrahamson et al. 2010). Hybrid polar is typically harvested at 6–10 year rotation using standard forest harvesting equipment (e.g., feller bunchers, skidders, forwarders, and chippers). The trees are bunched and chipped (Townsend et al. 2014). If harvested at 2–3 year short rotation, a New Holland forage harvester can be used (Townsend et al. 2014). The harvesting cost is approximately \$250 ha^{-1} (Volk et al. 2012).

Animal manures are collected regularly from animal houses using available tools. Poultry litter is cleaned out of chicken houses once a year. If new bedding is expensive and birds have to be reared on built-up litter, the litter is generally conditioned by annual decaking using a decaking machine, between-flock tilling using a shallow-tine roto-tiller, or between-flock windrowing using a six-blade windrower (Macklin et al. 2008). In case of decaking, litter cakes (fresh manure mixed with bedding materials and spilled feed) are removed and replaced by new bedding (up to 43% of the original volume) (Sistani et al. 2003). Swine manure is typically collected in gutters underneath a slotted shelter floor. The gutters are periodically flushed or drained to an outside lagoon or storage pond. Manure in lots outside the shelter is scraped weekly and stacked in compost piles (EPA 2015). Cattle manure is handled as a solid, semi-solid, or liquid. Solid manure in open lots or in barns collected in gutters behind cows is usually scraped every week and stockpiled in a solid manure storage facility prior to land application. The manure pack in loafing sheds is removed once or twice a year. Manure slurry from open lots or from free stall alleyway and liquid manure from loafing shed are periodically flushed, scraped, or pumped into a storage tank (sump) or an earthen lagoon (EPA 2015).

3.3 Drying Biomass

Fresh biomass generally contains 60–70% of moisture. It has to be dried for transportation and storage convenience. The moisture requirements for crop grains in the marketplace are below 15% for corn, 14% for soybean, 13% for wheat, and 8% for canola. The cost for reducing corn from the moisture 25% to 14% using a propane-powered grain dryer is \$17.3 ton^{-1} (OSU Extension 2011).

At cutting in October, switchgrass typically contains 50% of water (wet basis). The moisture content is required to reduce to below 18% prior to baling. Switchgrass is commonly conditioned upon cutting by passing through two rollers to crush the plant stems, dried in the field in windrows for 3–7 days with occasional raking the swaths, and baled (Sokhansanj et al. 2009). The cost is roughly \$11 ha^{-1} for raking/swathing (Khanna et al. 2008). Miscanthus and giant reed have to be dried to below 20% moisture content prior to storage. If harvested in the spring (e.g., March–April), the plant materials can be baled directly. The plants harvested in November are commonly chopped and mechanically ventilated for drying at a cost of \$15 ton^{-1}. Chopped materials reduced their moisture from 60 to 17.5% under 21,500 m^3 air h^{-1} ventilation for 91 h (Kristensen 2003). Sugar canes and sweet sorghum canes are immediately transported to sugar mills and crushed to extract juice after field harvesting. No drying is necessary.

Greenwood contains moisture up to 65%. It should be seasoned in a well-ventilated place for at least 6 months to bring its moisture content to below 20% prior to use. Fresh wood chips are commonly dried using a mechanical drying conveyor, in which heated or ambient air is forced through stockpiles of wood chips. The latent heat of water evaporation is 2470 MJ ton^{-1} of water, but dryers require 1.4–2.0 times more energy to drive away the same amount of water from wood chips due to low energy efficiency. The drying cost is ~\$2.0 ton^{-1} of dry matter per % moisture reduction (or \$200 to remove 1 ton of water; Price 2011).

Animal manures do not require drying if used in anaerobic digestion for biogas. If used as feedstocks in pyrolysis and gasification, drying is necessary. Solid manures can be naturally dried in a thin layer. Mechanical drying by passing through a heater to raise the temperature to 80–110 °C is also practiced. Manure slurries can be conditioned with polymers, dewatered using belt filter presses, and dried to below 20% moisture by heating. According to the energy consumption, \$100 is needed

Fig. 3 Baling switchgrass (left) and bundling forest slashes (right)

to remove 1 ton of water from moist manure (Price 2011). If labor and equipment wearing are considered, the drying cost may reach \$200 ton^{-1} of water removed.

3.4 Pre-processing and Densification of Biomass

Plant materials collected from the field are bulky (e.g., density < 60 kg m^{-3}). Densification is generally needed to facilitate transportation. Baling air-dry switchgrass, crop residues, and other herbaceous plant materials into round (1.2–1.8 m in diameter and 1.2–1.8 m in length) or rectangular (0.9–1.2 m in height and width and 1.8–2.4 m in length) bales using a hay baler increases the density to 650 kg m^{-3} (Fig. 3). The cost is approximately \$140 ha^{-1} (Khanna et al. 2008). Densification of forest debris is usually carried out by compressing thinnings and slashes into bundles (3 m by 60–80 cm, density ~380 kg m^{-3}) using a biomass bundler (Solomon and Luzadis 2009). The bundling cost is \$46.5 dry ton^{-1} (Harrill 2010). Slash bundles can be stockpiled in the field or under a shed for natural drying.

Pelletization is another method for biomass densification, applicable to wood, bioenergy grasses, crop residues, and animal manures. Pellets are made by grinding dry plant materials into fine particles through a hammer mill and subsequently compressing the particles through 6–8 mm holes in the die of a pelletizer. The pellets are 2–3 cm in length, possessing a low moisture content in the range of 5–10% and a high packing density at around 650 kg m^{-3}. Pellets show advantages in biomass storage, bunker transfer, and long-distance transport. However, the pelletization cost is high, up to \$50–130 ton^{-1} (Pirraglia et al. 2010; Qian and McDow 2013).

3.5 Biomass Transportation

Crop grains are mostly transported from the production site to a storage facility by trucks. From a storage silo, grains are shipped in bulk containers or cargo bags by trucks, barges, and railroad to end uses and export markets. Depending on the distance, the transportation costs by truck, rail, and ocean average at \$11, \$15, \$30 ton^{-1}, respectively (USDA 2012).

Switchgrass and crop residues are usually transported in bales by hauling trucks. The transportation cost is approximately \$0.20 (ton mile)$^{-1}$ (Purdue Extension 2008). A mechanical loader is required to upload the bales onto trucks. This operation costs additionally \$65 ha^{-1} (Khanna et al. 2008). Biomass chips and pellets are typically transported by trucks/self-unloading trailers, barges, and railroad. The related costs are \$0.20, \$0.10, \$0.05 (ton mile)$^{-1}$, respectively (Short 2009).

Transportation of solid manure is generally realized by hauling trucks, while manure slurry by 3000–9000 gallon tank spreaders. Including lagoon agitation and pumping, liquid manure transportation costs reach \$12 (kgal mile)$^{-1}$ (Hadrich et al. 2010).

3.6 Biomass Storage

Normal operation of a biorefinery requires a substantial amount of biomass feedstocks to be safely stored on a year-around basis. One option is to transport biomass to a central location and subsequently dispatch it to conversion facilities. While in a depot, the biomaterials can be ground into powders for minimal pre-processing or further treated and pelletized.

Crop grains are normally stored in grain silos. Grain elevators are used to load grains into silos. A delivery auger is installed at the bottom of silos to unload grains. Grains in silos are continuously aerated to maintain an optimal temperature and humidity environment for quality storage. The overall storage cost is estimated at \$7 ton^{-1} for 6 months (Hofstrand and Edwards 2009). During the silo storage, however, grains usually decrease their weight by 1.3% due to moisture reduction (shrinkage) (Hofstrand and Wisner 2009).

Biomass bales can be stockpiled outdoor on graveled surfaces and covered by plastic film. Indoor storage in enclosed buildings is generally more expensive (e.g., \$17 ton^{-1} for 12 months; Duffy 2008), yet the extra costs can be partially offset by reductions in storage losses and feedstock quality degradation. Trials in Texas showed that 5–13% of the original weight of switchgrass round bales was lost during 6–12 months outdoor storage; the loss was 0–2% for indoor storage (Sanderson et al. 1997).

Wood chips should be stored under a shelter (e.g., a shed) or outdoor with a water-proof cover. Uncovered open storage is discouraged. Wood chips may lose significantly in dry matter weight and energy value during storage (White et al. 1983). Covered storage of pre-dried wood chips is economical for bioenergy recovery (Purdue Extension 2011). To minimize wood chip deterioration during storage, torrefaction of the material may be employed. Torrefaction is to heat wood at 240–300 °C in the absence of air for partial pyrolysis. The treatment can reduce wood chips by 20% in dry mass and consequently 10% in heating value, but results in a dry, hydrophobic, sterile, and stabilized product.

3.7 Biomass Pre-processing

Before dispatched from a depot or processed at a biorefinery, biomass needs to be pre-treated for feedstock quality and effective biofuel conversion. The pre-processing operations may extend to one or several of the following: cleaning, grinding, heating, steam cooking, and conditioning (Fig. 4). For example, corn and canola seeds need to be cleaned to remove dirt, dust, weed seeds, leaf debris, and any other foreign materials. The cleaning is typically achieved using a grain cleaner by screening, vibration, aspiration, or purging. Grinding into fine particles is a minimal pre-processing requirement for all biomaterials before biofuel refining.

Lignocellulosic materials, especially straw, stover, and other herbaceous biomass, tend to form loose, dusty pellets. To increase pellet durability and reduce percent fines, chemical binders are generally added upon pelletization, undesirable for biofuel refinery. Through physiochemical pre-processing to partially break down cellulose, hemicellulose, and lignin into smaller amorphous molecules, however, the compression and compaction characteristics of lignocellulosic materials can be improved. Pre-treatments such as steam explosion and acid or alkaline hydrolysis significantly

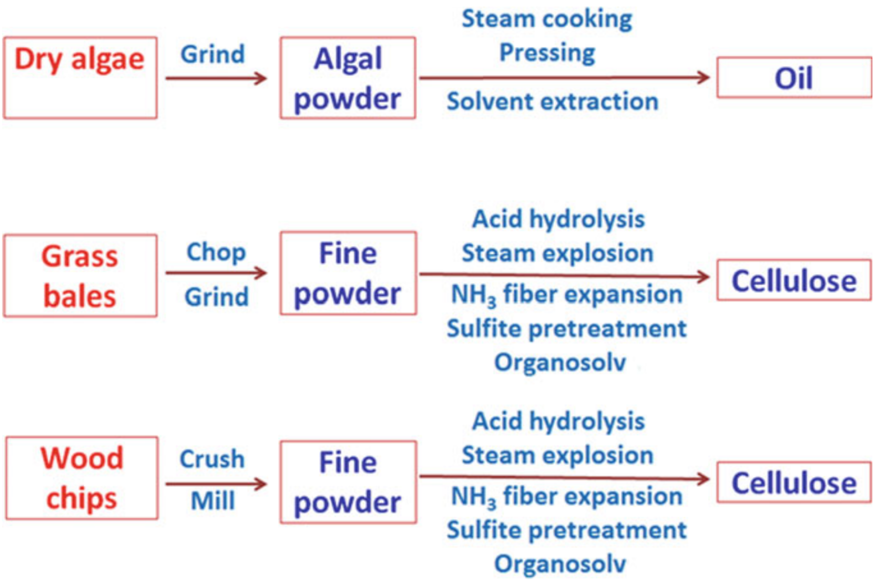

Fig. 4 Common pre-processing operations of algal, grassy, and woody biomass for biodiesel and bioenthanol production

increase the cohesiveness of lignocellulosic materials and their readiness for simple sugars (Chen et al. 2004). Steam explosion is to heat biomaterials with hot steam at 180–230 °C and high pressure for 2–10 min and then flash the cooker to atmospheric pressure. Water inside the substrate rapidly vaporizes, expands, and disintegrates the biomass (Zimbardi et al. 1999). Acids, alkalis, and oxidizing agents can pre-treat lignocellulosic materials for facilitating lignin removal and (hemi)cellulose digestibility. Dilute H_2SO_4, ammonium hydroxide, sodium sulfite, ozone, and other chemical agents are widely tested to disrupt lignin and loosen cellulose structure (Tabil et al. 2011). To separate lignin from cellulose without structural disruption, the technique organosolv fractionation is being developed in which biomass is treated with ethanol at 160–200 °C and 5–30 bars for 20–120 min prior to enzymatic hydrolysis (Huijgen et al. 2010). These essential pre-pretreatments, however, incur additional costs to biofuel production.

4 Summary and Conclusions

Bioenergy originates from solar radiation. Through photosynthesis, plants absorb solar energy and store it in biomass. Globally, net terrestrial primary production is estimated at 56×10^{15} g C yr^{-1}, adding 2.2×10^{21} J of bioenergy to the Earth system. Due to limitations from land availability, wildlife protection, and soil conservation, approximately 8.7% of the primary production can be practically used as biofuels in a sustainable manner, meeting 34% of the current human energy demand. Bioenergy feedstocks include feasible portion of food grains, crop residues, dedicated energy crops, forest debris, animal manures, and domestic organic waste. The biomass feedstocks can be converted into solid, liquid, and gaseous biofuels through physical, chemical, biological, and thermal pathways. A number of unit operations are involved in moving biomass feedstocks from the production field to a biorefinery plant, including harvesting, drying, transportation, densification, storage, and preprocessing. In addition to field production, handling biomass materials also requires a variety of machineries and infrastructures. The costs involved in biomass logistics range from 35 to 50% of the overall biomass production budget. It is critical to consider biomass logistics in designing bioenergy refining systems. Technological advancement is urgently needed to improve the efficiency of biomass feedstock logistics.

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Review Questions

1. Briefly describe the energy budget of the Earth system.
2. Define photosynthesis efficiency. What is the photosynthesis efficiency of intensively cultivated crops?
3. Globally, how much solar energy is captured by plants, algae, and cyanobacteria through photosynthesis each year?
4. What is the net annual primary production of terrestrial plants?
5. What is the global sustainable bioenergy production potential? Is this figure significant in the current global energy demand?
6. What biomass materials are identified as bioenergy feedstocks?
7. What are biomass logistics? Name the typical operations of biomass logistics.
8. Explain the general logistics of switchgrass production for bioethanol.
9. What equipment is commonly used for collecting and densifying woody biomass in the field?
10. What techniques have been tested to pre-process lignocellulosic materials for bioethanol generation?

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Bottlenecks in Biomethane Production from Agro-Industrial Wastes Through Anaerobic Digestion

Samuel Jacob, Lakshmishri Upadrasta and Rintu Banerjee

Abstract Anaerobic digestion (AD) is a commercially viable option for treating several kinds of agro- and food processing wastes. It has been demonstrated as energy-efficient and eco-friendly technology for bioenergy production. It generates not only biogas, but can also provide essential nutrient recovery (N, P and K) from digested wastes which can be applied as biofertilizer. The present knowledge on anaerobic digestion is not sufficient and the full potential of it could not be tapped due to certain bottlenecks associated with it. Process inhibition is related to the characteristics of the substrate, type of the inoculum, pH, temperature, reactor configuration and the concentration of inhibitory substances. For wide dissemination of biogas plants there is a requirement in the improvement of process efficiency through modifications in the existing design of anaerobic digester for recycling of organic matter and the development of new mitigation technologies to overcome inhibitions caused by intermediate compounds. This chapter is focussed on the options and essential modifications needed to harness the full potential of biomethane production from agro-industrial wastes through anaerobic digestion.

Keywords Biomethane · Anaerobic digestion · Agro-industrial wastes

1 Introduction

Anaerobic digestion (AD) of wastes not only facilitates the mitigation of pollution from agricultural and industrial operations but also provides biomethane which can be reused as fuel, thus limiting the usage of fossil fuels. AD has been proven to be one of the widely accepted and successful technologies for the treatment of fruit and vegetable processing, household, municipal and agricultural wastes (Parkin and Miller 1983). These wastes were found to be potential feedstock as far as the energy sector is concerned. In developing countries, waste biomass constitutes a significant

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portion of total energy consumption. To process 1 t of the main product, on an average, 1.5 tonnes (t) of crop residue are generated. Moreover, significant quantities of secondary crop residues were produced during agro-industrial processing of farm produce which include sugarcane, coconut, paddy, dairy, distillery, fruit and vegetables. In next two decades, annual production of crop residues may increase by 250 Mt or more (Shyam 2002).

Anaerobic digestion is a natural biochemical process where organic waste materials were broken down by microorganisms and converted into biogas (a mixture of methane, carbon dioxide, H_2S and traces of other gas like H2, N2). The liquid and solid digestate obtained after biogas production is an important by-product which can be used as an organic fertilizer.

In spite of the beneficial aspects of AD, process instability is often encountered which leads to the low methane yield, thus averting it from being widely applied. Thus, a wide range of barriers being faced by this technology must be removed for promoting their commercialization.

The full-fledged utilization of this technology in the agro-industrial sector is impeded due to the various factors. Some of these limitations that are seemingly inevitable include:

(i) Organic compounds present in the waste undergo only partial degradation.
(ii) Rate of the reaction is slow and requires digester of high capacity which incurs more cost.
(iii) Inhibitors that released during the process are more vulnerable.
(iv) The presence of an excess concentration of CO_2, H_2S and moisture along with methane makes it less economical.
(v) The presence of hazardous undegraded volatile and non-volatile matter (heavy metals) in the resulting sludge causes secondary pollution.

In order to strike an ecological and economical balance, formidable technological and dissemination of challenges need to be addressed (Venkataraman et al. 2010; Smith 2010). In India, the proportion of functional biogas plants was found to range from 40 to 81% (Dutta et al. 1997; Bhat et al. 2001). The non-functional biogas plants were due to failures caused by design, feedstock, inoculum and maintenance problems. Thus, having recognized the potential of using the biogas as energy source, currently technologies are being developed to alleviate the challenges and to enhance performance quality and energy use. The present chapter gives an insight into anaerobic digestion technology, the possible bottlenecks, process parameters, mitigation measures and recent developments in reactor design to overcome the impact on the problems.

2 Agro-Industrial Wastes

During the processing of agricultural produces either at farm site or industrial level led to the production of large quantum of agro-industrial wastes. Agro-based industry, particularly the food industry, generates significant amount of liquid, solid and gaseous wastes, which emerge not only from processing operations but also from their treatment and disposal. These wastes are therefore multi-phase and multi-component. They are mostly unutilized, untreated and disposed-off by incineration, dumping or by unplanned landfilling. These practices lead to the wastage of bioresources apart from greenhouse gases emissions which are the primary cause of the climate change (Bhattacharya 2002). Organic wastes, in spite of being a menace to the environment, represent a potential source for the production of value-added products such as bioenergy, biofertilizer and other bio-based products. Majority of wastes generated from agricultural sources are sugarcane bagasse; paddy; sorghum and wheat straw; husk; wastes of vegetables; food-producing wastes obtained during dairy, tea and oil production; jute fibre; coconut husk; groundnut shell; cotton stalk. These wastes are abundantly available throughout the year and renewable in nature. These wastes composed of carbohydrates, proteins, lipids and minerals which have industrial importance. The presence of the biodegradable organic compounds in agro-industrial wastes represents a suitable substrate for the microbes, which are able to grow efficiently by utilizing these wastes. Thus, the reuse of these wastes was found to be beneficial in terms of both economical and environmental aspects (Kalra and Panwar 1986).

3 Classification of Wastes

Organic wastes are classified depending upon the site of the origin. A schematic representation of the classification of wastes has been represented in Fig. 1.

This chapter is mainly focussed on agro-industrial wastes, their treatment and bottlenecks associated with it.

4 Characteristics of Wastes

The selection and design of waste treatment are based on the following criteria:

- Physical, chemical and biological characteristics of waste
- Quality that must be maintained in the environment to which the waste/wastewater is to be discharged or for the reuse
- Applicable environmental standards or discharge requirements that must be met.

Some of the important characteristics of waste generated from agro-based industries have been provided in Table 1. The effluent standard of wastewater that can

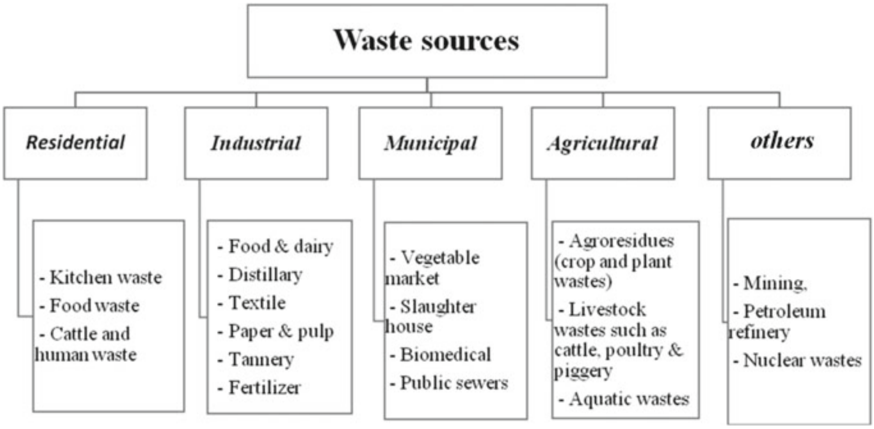


Fig. 1 Classification of wastes

Table 1 Characteristics of agro-industrial wastes

Industries	Characteristics					
	pH	TS (mg/L)	TSS (mg/L)	COD (mg/L)	BOD (mg/L)	References
Paper and pulp	6.5–8.5	1200–2000	350–500	500–750	100–250	Bhattacharyya and Banerjee (2007)
Sugar	4.6–7.1	870–3500	220–800	600–4380	300–2000	
Tannery	4–6.5	17,240–63,156	1008–4968	23,712–35,000	10,660–24,000	
Distillery	3–5.4	42,400	4200	57,164	32,300	Ansari et al. (2012)
Dairy	7.2–8.8	8000–10,000	NA	2500–3000	1300–1600	Qazi et al. (2011)
Slaughter house	8–8.5	NA	10,120–14,225	6185–6840	3000–3500	Kundu et al. (2013)

Note TS total solids; *TSS* total suspended solids; *COD* chemical oxygen demand; *BOD* biological oxygen demand; *NA* data not available

be released into different locations such as inland, public sewers and agricultural farmland has been represented in Table 2.

5 Compositional Variations of Feedstock

5.1 Variation in Cell Wall Characteristics

The agro-industrial wastes are mainly composed of carbohydrates, proteins and fats which are biodegradable organic fractions. In most of the cases, it has been seen that there is an unbalanced C:N ratio in majority of the plant-based feedstock. The

Table 2 Effluent quality of wastewater to be released into the environment

Characteristics	Inland surface water	Public sewers	Irrigation land
BOD (ppm)	30	500	500
COD (ppm)	250	250	250
pH	5.5–9.0	5.5–9.0	5.5–9.0
Total dissolved organic solids (ppm)	NA	2100	2100
Temperature (°C)	40	45	NA
Oil and grease (ppm)	10	100	30

Note NA data not available

biopolymers thus obtained contain carbohydrates as one of the major nutrients. Carbohydrates are mainly composed of mono-, di- and polysaccharides (cellulose, hemicellulose and starch). The lignocellulosic substrates such as agro-residues, which are mainly of plant biomass, consist of three polymers, viz. cellulose, hemicellulose and lignin. These cell wall components are closely associated with each other, providing protection and mechanical support to plant biomass. In the plant cell wall, cellulose forms an inner layer which is surrounded by hemicellulose and lignin. It has been reported that vegetable matter obtained from tender plants is more readily biodegradable than from older plants, and also the dry matter produces more biogas than fresh biomass (Bhattacharyya and Banerjee 2007). During anaerobic treatment of wastes, it is more important to consider not only the nature of feedstock but also the relative ease with which it can be digested/degraded by the microbes. Lignin is one of the recalcitrant compounds which resist microbial degradation and prevent the accessibility of biodegradable components. In such cases, pretreatment strategies are to be adopted for the removal of lignin present in the plant cell wall. Cell wall component variations of some important crop residues have been represented in Fig. 2.

5.2 *Variation in C:N*

During anaerobic digestion, the ratio of carbon to nitrogen of organic waste added to a reactor plays an important role in controlling the growth rate of the microorganisms and biogas production. Different groups of bacteria present in the digester selectively utilize the components of the feedstock. High C:N reduces the efficiency of the process due to limited availability of nitrogen and leads to accumulation of volatile fatty acids (VFA) whereas low C:N results in the excess formation of ammonia which is toxic to bacterial population. For efficient metabolic functioning, microorganisms need an appropriate ratio of carbon to nitrogen. During thermophilic anaerobic digestion of manure (cow and poultry) with cellulosic materials from paper, it has been seen that C:N (carbon to nitrogen) higher than 23:1 and lower than 10:1 was found to be unsuitable for optimal digestion (Kimchie 1984). Dairy and swine manure typically contain a C:N of approximately 9:1 and 6:1, respectively. Methane production

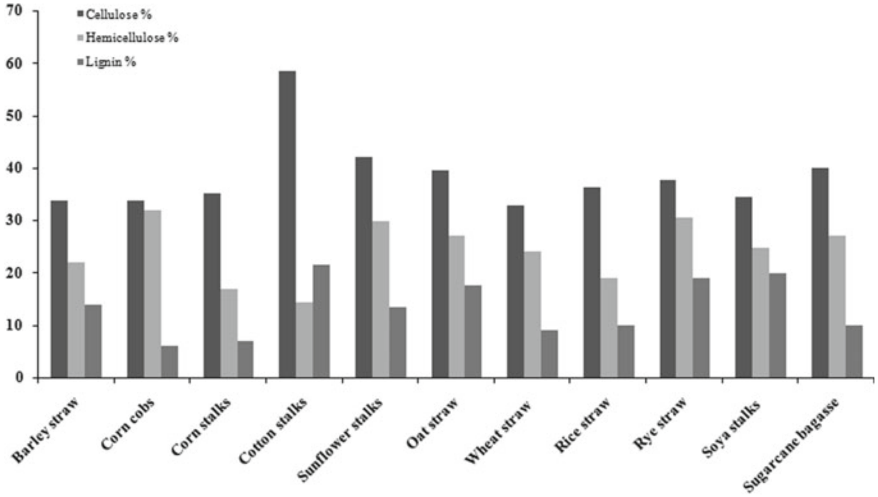


Fig. 2 Main components of some lignocellulosic wastes (Nigam 2009)

Table 3 Carbon–nitrogen ratio of different agro-wastes

Substrate	C:N
Cow manure	19
Poultry manure	6–15
Corn cobs	56–123
Corn stalks	60–73
Fish scrap	3.6
Raw garbage	15–25
Grass	12–19
Night soil	5–10
Pig manure	14
Sewage sludge	5–16
Slaughter waste	2–4
Wheat straw	80–127
Vegetable waste	19
Water hyacinth	20–30

can be significantly improved by the process of co-digestion in which substrates containing high nitrogen content which is added to the substrates containing low C:N, thereby bringing a well-balanced nutrient ratio. For instance, the low C:N of the dairy and swine manures may be increased by the addition of food processing residues such as potato waste with a C:N of 28:1 or crop residues, such as oat straw with a C:N of 48:1. Table 3 represents different agro-wastes and their corresponding C:N ratio.

5.3 Variation in Volatile Matter

Volatile matter that presents in the organic wastes is a crucial parameter that defines the organic loading into the reactor. Most of the biodegradable organic material is present in the volatile solids, and the non-biodegradable substances will constitute ash. Loading of a reactor with 7–9% of total solid will yield optimum biogas production (Bhattacharyya and Banerjee 2007). A substrate diluted or concentrated from this range could hamper the process. When compared to other organic wastes, animal manures undergo slow digestion.

6 Availability of Waste Materials

In addition to the source of the waste material, it is essential to estimate the quantity of material that would be generated from that source. Based on the availability, suitable reactor could be designed for the treatment of wastes. The amount of wastes generated depends on various factors such as raw material handling, processing steps involved and product quality. In case of animal farms, factors such as feeding habits, size and age of cattle will determine the quantity of waste generated. Crops such as paddy, maize, barley, wheat, sugarcane, soybeans and groundnuts could generate a significant quantity of residues annually. These residues constitute a major proportion of total annual production of biomass residues and represent an important energy source both for domestic and industrial purposes. Productivity of some of the major agricultural crop residues has been given in Fig. 3.

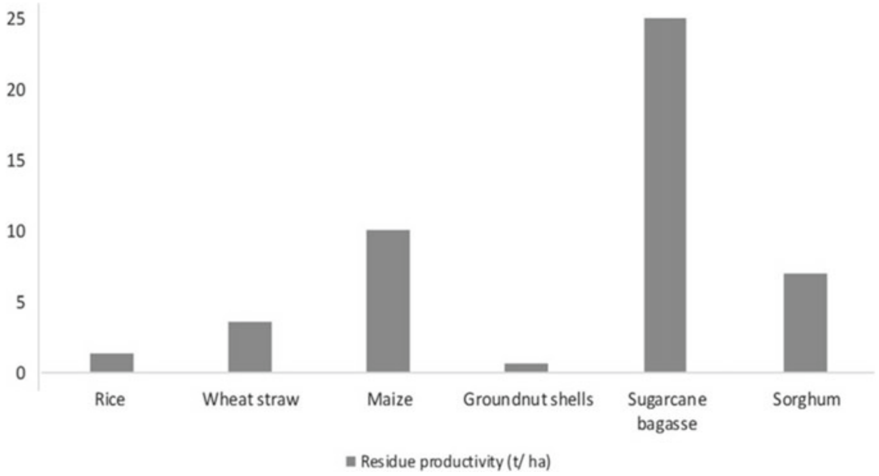


Fig. 3 Productivity of crop residues (Bhattacharyya and Banerjee 2007)

Table 4 Biomethane potential of agro-industrial wastes

Substrate	Biogas production (m^3/ton of dry mass)	Methane (%)
Cattle manure	244	65
Pig manure	325	65
Food waste	618	63
Slaughter house waste	575	63
Fish waste	1279	71
Potato wastes	453	56
Straw	265	70

Biomass has been recognized as an important energy source which constitutes ~14% of world energy consumption (IEA 1998). As per an estimate, solar derived energy (photosynthesis) yield biomass of 220 billion tonnes annually with the conversion efficiency of 1% (Ramachandra and Shruthi 2007). About 4.4 billion tonnes of solid wastes were generated from Asia every year (Yoshizawa et al. 2004). In subcontinent scenario, India is very rich in biomass where the agro-residues and plantations sources constitute an energy potential of 16,881 MW, bagasse cogeneration amounts to 5000 MW and energy recovery from waste sources makes up to 2700 MW (Subramanian 2007). Bhattacharya (2002) reported that recoverable animal wastes in India could generate energy equivalent to 1046 PJ/year that could be recovered from 60 million digesters of 2 cubic meters capacity. Biomethane potential of some important agro-industrial wastes has been enlisted in Table 4.

7 Measurement of Pollution Level

Every biological waste treatment plant needs to be designed based on the pollution level of the organic wastes that have to be treated. Measurement of the pollution level can be expressed in terms of DO, BOD or COD. A brief description of the aforementioned parameters is discussed in the subsequent sections.

7.1 Dissolved Oxygen (DO)

Dissolved oxygen (DO) refers to the concentration of oxygen present in the water which is represented as mg/L. The concentration of dissolved oxygen often determines the number and type of organisms living in an aquatic environment. For example, fishes are sensitive to low DO levels (<8 mg/L) and thus cannot survive in water bodies which have the DO below this critical level. Organic material that present in the waste after entering into the aquatic environment was degraded by microbial action that can severely deplete dissolved oxygen concentration present naturally. This is the most common cause of fish kills, especially in summer months when warm water holds less oxygen. Untreated wastewater containing high concentrations of nutrients when released into the water bodies results in eutrophication.

Eutrophication is defined as the enrichment of water bodies with mineral and organic nutrients, resulting in excessive proliferation of aquatic plant and algae which lead to oxygen-deprived condition in aquatic ecosystem. Thus, dissolved oxygen is one of the important parameters that have to be considered during wastewater treatment such that the effluent should contain low organic material.

7.2 Biological/Biochemical Oxygen Demand (BOD)

In order to measure the extent to which a wastewater discharge could impact the dissolved oxygen concentration in a receiving stream (i.e. water body that the wastewater is discharged into), a measure of the oxygen-consuming organic matter must be determined.

BOD is the measure of the concentration of dissolved oxygen utilized by aerobic microorganisms during degradation of organic components of the wastewater at constant temperature (20 °C) over a defined time (5 days). BOD is represented in terms of mg O_2 consumed/L of wastewater and used as a standard method to assess the extent of organic pollution in water. A higher BOD of an effluent denotes that it contains high quantity of biodegradable organic matter presents in it. BOD index also helps to decide on the mode of treatment (aerobic or anaerobic).

$$\text{Organic material} + O_2 + \text{nutrients} \rightarrow CO_2 + H_2O + \text{new cells} + \text{nutrients} + \text{energy}$$

The natural oxygen resource may get depleted when water containing high concentration of BOD is released into the environment.

7.3 Chemical Oxygen Demand (COD)

COD is defined as the concentration of oxygen required for complete oxidation of organic pollutant present in the wastewater which is expressed in terms of milligrams per litre (mg/L). COD provides a quantitative measure of organic pollutants found in water bodies (e.g. lakes and rivers) or wastewater.

7.4 Relation Between BOD and COD

BOD:COD ratio is a critical indicator of the waste strength of industrial effluent. Based on this relation, the mode of the treatment process is chosen. Table 5 represents the BOD:COD ratio and their nature of biodegradability. From the table, it has been seen that BOD:COD of >0.5 is suitable for biological pretreatment, and higher the ratio needs physico-chemical treatment process. Since BOD is an index of the biodegradable organic content of the wastes, the different treatment processes can be chosen based on this value. Figure 4 represents the BOD values and its suitable waste treatment process.

Table 5 BOD:COD ratio and their nature of biodegradability

BOD_5:COD	
>0.5	Easily biodegradable
0.4–0.5	Average biodegradable
0.2–0.4	Slowly biodegradable
<0.2	Not biodegradable

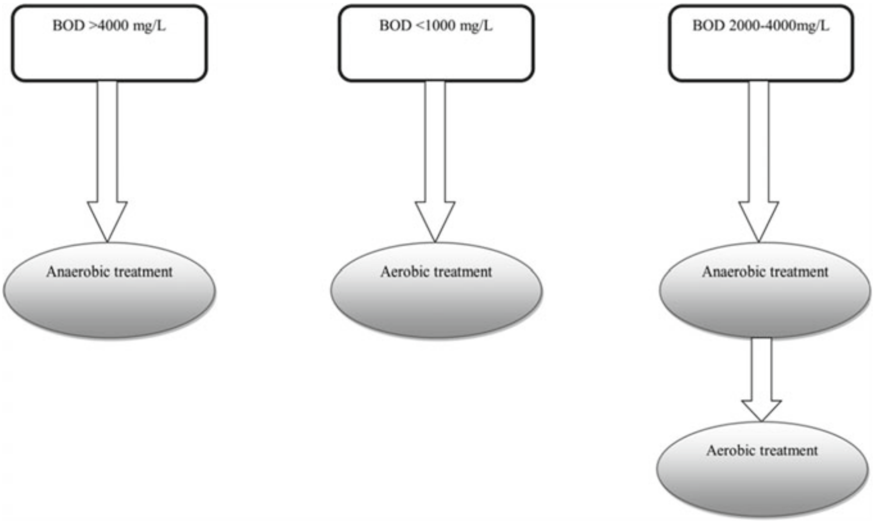


Fig. 4 Selection of treatment based on BOD

8 Types of Treatment

8.1 Aerobic Treatment

Aerobic treatment is the process in which bacteria utilize the oxygen to degrade the organic pollutant present in the waste/wastewater. End product of the aerobic treatment consists of oxidative products such as CO_2, sulphates, nitrates and biomass (microorganisms). The process efficiency can be significantly improved by providing oxygen supply with aerators. Aerobic treatment yields better effluent quality because aerobic bacteria are capable of break down the organic waste products efficiently. During the aerobic process, a significant amount of energy of about 60% is utilized by the microorganisms for growth and synthesis of new cells, and the remaining 40% is released as waste heat. Aerobic processing usually involves the treatment of liquid wastes having relatively very low BOD (<2000 mg/L), whereas the solid wastes are subjected to aerobic composting to degrade the organic material and further convert it into biofertilizer.

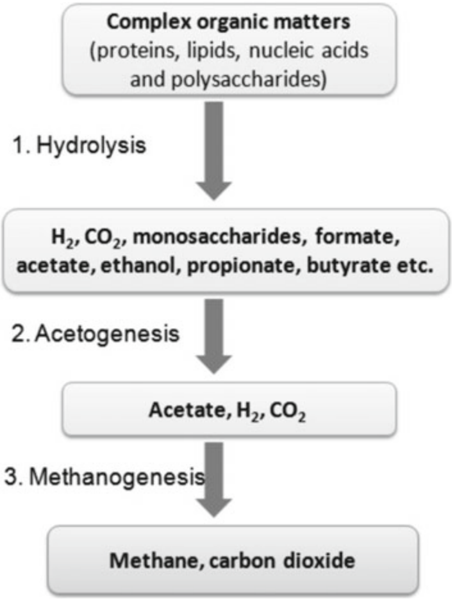
Aerobic composting technology by the processing of municipal solid and agro-industrial wastes plays an important role in conserving soil fertility mainly through physico-chemical and biological activities of compost on soil quality parameters. Compost is being enriched in basic nutrients such as N, P, K, and certain micronutrients help in the restoration of the basic elements utilized during the cultivation of crops/plants. In addition to it, the organic acid such as humic acid that present in the humus acts as chelating agent which minimizes the migration of toxic heavy metals into the environment (Sharma et al. 1996).

Since aerobic treatment of wastes requires oxygen/air supply along with agitation for efficient waste stabilization, it incurs more cost and makes the process uneconomical. As mentioned earlier, liquid and solid wastes having very high BOD or COD were unsuitable for aerobic process.

8.2 Anaerobic Treatment

Anaerobic digestion occurs in the anoxic condition during which different tropical group of bacteria digest organic materials and produce biogas as an end product. Biogas can be used as an energy source which is the main advantage over aerobic treatment. The anaerobic process can typically remove up to 85% of the total COD load from the wastewater. Digestate obtained as a by-product is rich in nutrients and can be utilized as biofertilzer. First step in the digestion process is hydrolysis in which complex insoluble polymers such as carbohydrates, proteins and fats are broken down into simple monomers and make them easily utilizable for other bacteria. Acidogenesis in turn converts the simple monomers like amino acids, simple sugars and fatty acids into carbon dioxide, ammonia, hydrogen and organic acids.

Fig. 5 Stages of anaerobic digestion



Acetogenic bacteria utilize organic acids and convert it into ammonia, hydrogen, acetic acid and carbon dioxide. In the last step, methanogens convert acetic acid, hydrogen and CO_2 to biogas consisting of methane and carbon dioxide. Figure 5 represents the schematic representation of anaerobic digestion process.

The main drivers for the implementation of anaerobic treatment of wastes are:

- Low operating costs
- Biogas production (renewable energy)
- High treatment efficiency in a compact plant
- Positive carbon footprint.

Anaerobic reactor failures occur due to the presence of certain inhibitory compounds in substantial concentrations either present in the input material or produced during the process. A wide array of substances from simple metal component to noxious gaseous product like ammonia has been reported to be inhibitory to the anaerobic digestion processes. These components either interfere with metabolism of the bacteria or hamper its growth rate, thus ceasing the biogas production. Decline in methane production rate and accumulation of organic acid were the main indicators that show the process is inhibited by toxic substances (Kroeker et al. 1979).

9 Pretreatment Strategies

Lignin present in the agro-wastes is recalcitrant in nature, and suitable pretreatment must be employed to degrade the complex structure for efficient bioconversion. Pretreatment aids in the degradation of the cell wall structure of lignocellulose into fragments of cellulose, hemicellulose and lignin. It has been reported that pretreatment of substrates prior to anaerobic digestion could enhance the biogas yield with higher calorific value leading to less effort in purification (Boontian 2013; Ferrer et al. 2008; Yadvika et al. 2004). Minimization of loss of the cellulose and hemicelluloses during pretreatment improves the process economics by reducing the energy input, cost of raw materials, reactors and chemicals used. Different modes of pretreatment include physical, chemical, biological and combined approaches. Mechanical pretreatment mainly involves with size reduction by chipping and grinding. Physical and chemical pretreatments require high-energy for heating and mechanical size reduction, thus increasing the overall cost of the process. Energy consumption for size reduction of crop and forest wood residues may exceed 0.1–0.4 MJ/kg. Increase in lignocelluloses digestibility can be achieved by delinking of acetyl group associated with hemicellulose and lignin, thereby leading to either partial or total solubilization of polymeric structure (Zhu et al. 2008). Separation of lignin and carbohydrates by chemical means can be achieved by the application of acid, alkali and solvents which lead to selective solubilization of lignin. In acid and solvent based pretreatment (organosolv), carbohydrates get solubilized predominantly (Zhao et al. 2009) whereas with alkali, lignin is depolymerized into phenolic compounds whereas with alkali, lignin get degrades and solubilize (Mosier et al. 2005). Chemical process is not selective and thus not recommended as it creates hydrogen sulphide and NOx during the reduction of sulphate and nitrate which not only inhibit the biomethane production but are hazardous to the environment. Presently, researches were focused on developing pretreatment methods through biological mediated which are simple, cost-effective, efficient and eco-friendly.

9.1 Biological Pretreatment

Biological pretreatment is the best-suited method that can be applied for the enhancement of biogas production. During the biological pretreatment, substrate treated with microbial agent such as wood rot fungi and the structure is changed through depolymerization of lignin. Ligninolytic enzymes such as manganese peroxidase (MnP), lignin peroxidase (LiP) and laccase could also serve as a potential biological agent for removal of lignin. Advantages of biological pretreatment include mild operating condition, target specificity, eco-friendly, cost-effective, reusability of microbes/enzymes and do not cause damage to the equipment. Different pretreatment strategies have been given in Fig. 6.

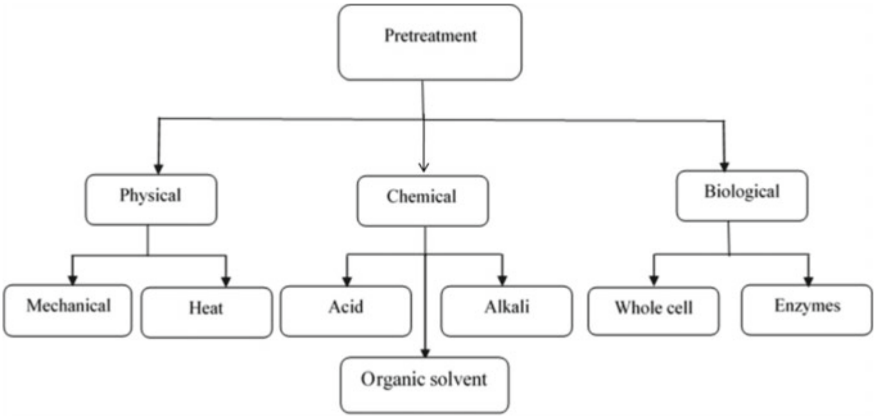


Fig. 6 Different pretreatment strategies for agro-industrial wastes

10 Bottlenecks of Process Parameters that Govern Methane Production Efficiency

Anaerobic digestion process is vulnerable to operational variations, as the microbiology involved and therein is complex which consists of different bacterial groups, each of them characterized with their own optimum process conditions. Intermediate degradation products such as free ammonia, hydrogen, volatile fatty acids (VFA) are the main inhibiting factors sensitive to the microbes involved in degradation. Different process parameters were found to be modulating the concentration of inhibitors. Bottlenecks associated with anaerobic digestion and the ways to mitigate have been discussed in subsequent sections.

10.1 Influence of Inoculum

Anaerobic digestion process is carried by different groups of microorganisms that convert complex macromolecules into simple biomolecules. Inoculum is one of the crucial factors for the AD process, as it plays an important role in optimizing F:M (Food–Microbe) (Lopes et al. 2004; Forster Carneiro et al. 2007). Mostly, cow dung and sewage sludge from wastewater treatment plants are used as an inoculum for treating wastes (Forster Carneiro et al. 2007; Dong et al. 2009). Handling cow dung in large quantity is a limitation for commercial production of methane. It is very unusual for a biological treatment to depend on a single source (Fantozzi and Buratti 2009). Therefore, there is a need for the development of consortia of microorganisms to produce methane without the addition of cow dung for large-scale implementation of biogas plants. At IIT Kharagpur, India, with the prolonged experience of working with anaerobic fermentation process, unique microbial consortia have been developed to meet this demand. Lee et al. (2009) reported that under anaerobic condition *Clostridium* sp. was predominant among the degraders. For the production of VFA, microorganisms such as *Ralstonia Actinomycetes, Thermomonospora* and *Shewanella* were involved, whereas methanogens such as *Methanobrevibacter*, *Methanosarcina* and *Methanobacterium* contribute to methane production (Ike et al. 2010). In case of high rate bioreactors in order to overcome the washout of microbial communities, it is important to operate the reactor with inoculum in the form of cell aggregates such as biofilms, granules, flocs and mats with size that typically range from 0.1 to 100 mm may also be used (Jeong et al. 2010).

10.2 Temperature

Temperature plays a significant role in controlling the growth rate of microorganism and fatty acid concentration in the reactor. Metabolic growth rate of the microorganisms increases with rise in temperature but also results in a higher concentration of fatty acids which could lead to negative effect on biomethane production. It has been reported that anaerobic digestion of waste with high concentration of ammonia was more readily inhibited at thermophilic temperatures as compared to mesophilic condition (Braun et al. 1981; Parkin and Miller 1983). Inhibition caused by higher ammonia concentration was reversed when the operating temperature was reduced from 37 to 60 °C with further increase in biogas yield (Angelidaki and Ahring 1992; Hansen et al. 1998). However, Galler and Winter (1997) reported that methane production was reduced by 50% with fatty acid content of 0.22 g/L at 37 °C and 0.69 g/L fatty acid at 55 °C. This shows that thermophilic microbes tolerated twice as much fatty acid as compared to mesophilic. Thus, maintenance of operational temperatures at ranges conducive for the functioning of microbial consortia is essential. Selection of temperature range should be done during the designing stage depending upon the climatic considerations of the location. During the maintenance of the reactor in thermophilic range, considerable amount of energy is required in such cases, and it is better to operate in mesophilic temperature.

10.3 pH

pH of the substrate and medium is an important factor in the AD of waste as the growth and the proliferation of methanogenic bacteria are inhibited under acidic conditions, thus leading to the cessation of biogas production. Factors such as retention time and loading rate in batch reactors determine the pH of the reaction medium. Steps involved in AD process have different optimal pH and fluctuations that occur due to the biological transformations. During the acidogenic/acetogenesis, pH would fall below 5 which are detrimental for methanogens. This would lead to acid accumulation and digester failure. An excessive rise in the population of methanogens can lead to rapid utilization of volatile fatty acids and causes the accumulation of ammonia and thereby increasing the pH above 8 which is inhibitory for acidogenesis (Lusk 1999). During start-up phase, maintenance of constant pH is essential as freshly added substrate has to undergo the stage of hydrolysis and acidogenesis, which could reduce the pH. In order to maintain equilibrium pH above the acidic level, neutralizing agents such as calcium carbonate or lime have to be added into the system which might incur additional process cost. Optimal pH range 6.5–7.5 is required to attain maximum biogas yield in anaerobic digestion which then depends on type of substrate used and digestion technique (batch or continuous) (Liu et al. 2007). The value of pH in a digester is a function of bicarbonate and volatile fatty acid (VFA) concentration, alkalinity and also the CO_2 level in biogas. It is important to adjust the relationship between the VFA and bicarbonate concentrations for attaining constant pH (Liu et al. 2007).

10.4 Organic Loading

Organic loading rate (OLR) is the measure of quantity of organic material flowing into the digester as influent at a specific interval of time which is expressed in terms of kg COD or VS/m^3/d. Fluctuations in influent flow and substrate loading could lead to imbalance in acid formation and methanogenesis. In case of easily hydrolysable substrates, the acidogenic reactions are rapid at high OLR and may increase the VFA and hydrogen concentrations, causing a decline in the pH. Lower pH can inhibit methanogenesis while higher pH inhibits acid conversion. During peak flow conditions, flow equalization must be provided to overcome the shock loadings. Optimal OLR ranges between 0.5 and 3 kg VS/m^3/d for efficient digestion (Poliafico 2007).

10.5 Macro- and Micronutrients

Advantage of anaerobic processes is low sludge production and hence requires less macronutrients such as nitrogen and phosphorus for the growth of microorganisms. But these nutrients might have to be extraneously added for wastes deficient in them. Depending on waste characteristics, sludge retention time (SRT), typical nutrient requirements for nitrogen, phosphorus and sulphur are in the range from 10–13, 2–2.6 and 1–2 mg/100 mg of biomass, respectively. Further, the trace metals are essential for stimulating the methanogenic activity. Micronutrients such as Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} are recommended at a concentration of 0.02, 0.004, 0.003 and 0.02 mg/g acetate produced, respectively. The exact amount of trace nutrients needed may vary depending on wastes. Higher concentrations of these nutrients may be toxic to the biomethanation process.

10.5.1 Influence of Sodium

Sodium is one of the essential nutrients for the methanogens since it plays an important role in the generation of ATP and oxidation of NADH during metabolic process. Imbalance in its concentration may obstruct the activity of the microbes and hinder their metabolism (Feijoo et al. 1995; Chen et al. 2008). In hydrogenotrophic methanogens, optimal growth takes place at 350 mg Na^+/L. During mesophilic digestion, moderate inhibition is possible at concentrations between 3500 and 5500 mg/L, whereas strong inhibition occurs at 8800 mg/L (Chen et al. 2008). Inhibitory concentration (IC_{50}) of sodium on propionic acid, acetic acid and n-butyric acid utilizing bacteria were found to be 10,500, 7000 and 19,000 mg/L, respectively (Feijoo et al. 1995).

10.5.2 Influence of Potassium

Neutralization of membrane potential occurs due to the passive transport of potassium when their concentration exceeds its critical limit in the reaction medium. Process improvement can be achieved when potassium concentration is maintained below 400 mg/L under mesophilic and thermophilic conditions. When concentration exceeds this limit, it exhibits inhibitory effect, especially to thermophilic microbes. Acclimation effect of bacteria can overcome the inhibition which is influenced by potassium concentration and exposure period. However, bacteria can no longer tolerate beyond the critical level. Potassium toxicity can be moderated effectively by the presence of other cations such as sodium, magnesium, calcium and ammonium.

10.6 Mixing

Efficiency of the anaerobic digestion process can be significantly improved by mixing. Improper or the absence of mixing could lead to the formation of hydraulic dead zones which can cause adverse effects. It has been reported by many researchers that mixing contributed an efficient substrate conversion (Stroot et al. 2001; Kim et al. 2002; Karim et al. 2005; Vedrenne et al. 2007). Factors such as intensity, duration, mixing strategy and location of impeller in the reactor govern the efficiency of the mixing process. However, the performance of anaerobic digesters contradicts with the effect of duration and intensity of mixing. Uniform distribution of substrates, microorganism and enzymes throughout the digester can be achieved through a suitable mixing strategy (Lema et al. 1991), whereas improper mixing would result in phase separation and formation of solid floating layer (Chen et al. 1990). Dolfing (1992) suggested that disruption in the structure of flocks occurs in continuous stirred reactor due to rapid mixing, thereby distorting the synergistic relationships between organisms. Optimal substrate conversion can be attained by an intermediate degree of mixing (Smith et al. 1996).

10.7 Retention Time

Solid retention time plays a pivotal role in the fundamental design and operation of all anaerobic digesters. Anaerobic treatment process requires SRT values higher than 20 days at 30 °C for improved process efficiency.

10.8 Influence of Inhibitory Substances

Inhibitory substances are either found in waste or generated during process. Some of the inhibitory products have been discussed as follows.

10.8.1 Nitrogen Compound and Its Metabolic Products

Nitrogen is required for synthesis of new biomass; at the same time, the improper concentration of nitrogen metabolic products, i.e. ammonia (NH_3), ammonium (NH_4), nitrous oxide (N_2O), nitrite (NO_2) and nitrate (NO_3) often poses problem to anaerobic digestion. Inorganic nitrogen exists in the reactor in the form of ammonia (NH_3) and ammonium (NH_4^+). During anaerobic hydrolysis of organic nitrogen compounds, ammonium ions are released as the main product which causes an increase in pH. The ammonia formation thus counteracts the reduction of the pH, resulting from the acidification step of anaerobic digestion (ATV 1993). Ammonium contributes to the balancing and stabilization of pH in the digester. However, its high concentrations may lead to the inhibition of the process.

Free ammonia was comparatively toxic as it can be transported to the cell through membrane causing imbalance in intracellular proton. Temperature, pH and the presence of ammonia in the reaction medium mainly govern the concentration of free ammonia. Toxic range of ammonia is between 30 and 100 mg/l (at pH < 7 and temperature < 30 °C), whereas in case of ammonium, it was observed between 4000 and 6000 mg/L (ATV 1990).

An increase in temperature would result in improved growth of microbes; consequently, it could lead to the accumulation of free ammonia. Due to this, digestion carried out in thermophilic range is more prone to inhibition than mesophilic. pH of the digestion mixture in alkaline range (>8) would result in increase of unionized VFA which leads to cellular toxicity. This process instability often leads to cell destruction, resulting in an upsurge of VFA, which causes reduction in pH and therefore to a lesser free ammonia concentration. After this, the process attains stationary with reduced methane yield. Due to some inherent changes in predominant methanogenic bacteria or through alteration in methanogenic population, bacteria can acclimatize to free ammonia, thus overcoming its toxicity effect.

10.8.2 Inhibitory Action of Hydrogen

During anaerobic digestion, molecular hydrogen is produced from different metabolic processes. In the hydrolysis stage, carbohydrates are broken down into monomeric sugars along with the formation of VFA, CO_2 and hydrogen. In case of acetogenic bacteria (*Syntrophobacter wolinii* or *Syntrophomonas wolfei*), oxidation of propionate and *n*-butyrate results in the formation of acetate, CO_2 and hydrogen (Mohapatra 2006). In methanogenesis stage, methanogenic bacteria consume hydrogen for the formation of methane, and thus, it does not accumulate. Acetogenesis by reduction of CO_2 could also contribute to the decline of hydrogen concentration in the sludge digesters. This would take place if there is no build-up of hydrogen concentration in the reactor, rather it is consumed by methanogens.

Hydrogen partial pressure (pH_2) plays an important role on the synthesis of short-chain fatty acids such as acetic (C2), propionic (C3) and butyric acid (C4). A stable digester contains very less hydrogen concentration because hydrogenotrophic methanogens utilize it for the reduction of CO_2 to form methane. When there is a decrease in H_2 concentration, it leads to the formation of methane from acetic acid rather than the reduction of CO_2.

10.8.3 Inhibitory Action of VFA

VFAs are the rate-limiting intermediate in the AD process, which are utilized by acetogens to form acetic acid and hydrogenotrophic methanogens. When the concentration of VFA is at 6.7–9.0 mol/m^3, it can inhibit the growth of microorganisms, especially methanogens (Batstone et al. 2000). Increased concentrations of toxic compounds, variation in temperature and organic overloading may cause the accumulation of VFA. Under such circumstances, the methanogens were unable to utilize the VFA and hydrogen rapidly. This leads to acid accumulation followed by decrease in the pH, causing the inhibition of hydrolysis/acetogenesis. Undissociated VFAs can be toxic to microorganisms in which they were transported through the cell membrane and dissociate. This causes a reduction in pH followed by disruption of homoeostasis.

In a batch anaerobic reactor, the presence of increasing concentration of VFA has differential effect on the hydrolytic, acidogenic and methanogenic phases. Increased concentrations of acetate and propionate cause substrate inhibition. Concomitantly, acetate causes non-competitive inhibition towards propionate degradation and uncompetitive inhibits benzoate degradation. This leads to the enhancement of inhibitory effect of pH on methanogenesis.

10.8.4 Action of Long-Chain Fatty Acids (LCFAs)

LCFAs are generated during the fat and lipids metabolism (especially lipid-rich wastes) and reduce into acetate and hydrogen through β-oxidation by acetogens

(Boe 2006; Alves et al. 2001). Gram-positive bacteria were sensitive to LCFAs and cause inhibition at low concentration (Chen et al. 2008). Inhibitory action of LCFAs was mainly due to oleic acid and stearic when its concentration exceeds above 1 g/L (Angelidaki and Ahring 1992). It has also been found that the toxicity due to LCFAs was irreversible in nature. The action of LCFA toxicity mainly involves adhering to the cell wall and affecting the transport of metabolic products (Chen et al. 2008; Alves et al. 2001). LCFAs were found to adsorb onto biomass which causes the flotation of sludge and sludge washout (Chen et al. 2008). Acetate utilizing methanogens are more prone to the inhibition by LCFA than the hydrogenotrophic methanogens (Alves et al. 2001).

LCFAs have been found to exert a bactericidal effect preventing the adaptation to the fatty acid toxicity, whereas sludge acclimatized with lipids showed a higher resistance to oleic acid toxicity. LCFA toxicity is mainly dependent on specific area of sludge and independent of the other biological factors such as sludge origin, acetoclastic methanogenic activity and adaptation to lipids.

11 Bioreactors Used for Anaerobic Treatment

A reactor system that allows efficient mass transfer maintains desired population of microbes, favours product recovery and enables continuous operation of the process with high throughput is a prime requirement of any biologically mediated process. Highly polluting industrial solid and liquid wastes are predominantly treated in an anaerobic digester with an additional benefit such as energy (biomethane) generation and low surplus sludge production.

Application of high rate bioreactors for the treatment of wastes using anaerobic technology makes it suitable for many industries (Barber and Stuckey 1999; van Lier et al. 2001). A number of novel bioreactor designs have been developed in recent years and adopted for biogas production which results in significantly higher conversion efficiency (Borja et al. 1994; Barber and Stuckey 1999). Different modes of anaerobic processes such as single-stage batch continuous and two-stage continuous with a wide range of methane generation reactors like upflow anaerobic sludge blanket (UASB), anaerobic sequencing batch reactor (ASBR), anaerobic filters (AF), continuously stirred tank reactor (CSTR) and tubular fluidized bed reactor (FBR) have been applied to treatment of industrial as well as agro-wastes (Lettinga et al. 1980; Chen et al. 1985; Rajeshwari et al. 2000). The reactor designs were classified based on the retainment of microorganisms in the bioreactor and the separation between the acidogenic and methanogenic bacteria. Broadly anaerobic reactors may be grouped into conventional and high rate reactors. Biogas yield with different bioreactor systems has been represented in Table 6.

An overview of the detailed classification of bioreactors used in anaerobic treatment is given in Fig. 7.

A schematic representation of different reactor configurations that employed in anaerobic treatment has been given in Fig. 8.

Table 6 Different reactor configurations and their biogas yield

Reactor configuration	Type of waste	Yield of biomethane	References
Batch system	Food and vegetable wastes	0.16 m^3 CH_4/kg VS	Rajeshwari et al. (1998)
Anaerobic ponds	Piggery wastes	0.2 m^3 CH_4/kg VS	NIWA (2008)
CSTR	Cane molasses and alcohol sludge Food and vegetable waste	0.19 m^3 CH_4/kg COD_r 0.47 m^3 CH_4/kg VS	Yeoh (1997) Mata-Alvarez et al. (1992)
UASB	Palm oil effluent	0.35 m^3 CH_4/kg VS	Zinatizadeh et al. (2006)
Anaerobic filter	Paper mill	0.24–0.3 m^3 CH_4/kg COD_r	Yilmaz et al. (2008)

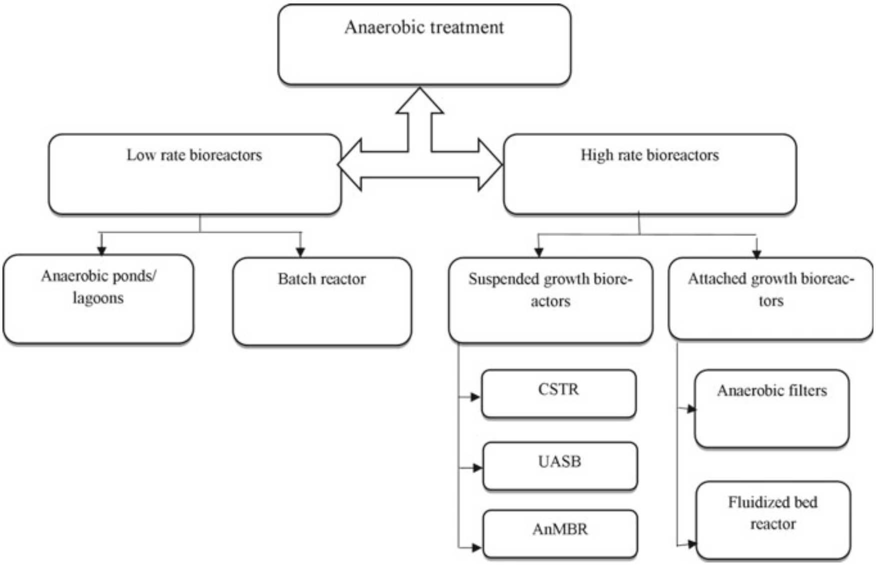


Fig. 7 Classification of bioreactors in anaerobic process

11.1 Reactor Associated Bottlenecks in Biomethanation

In single-stage systems, all three steps of AD used to take place in the same reactor and process conditions (Yu et al. 2002). During initial stages of AD, easily degradable organic substrates undergo rapid hydrolysis, resulting in the formation and accumulation of organic acids. This causes a sharp decline in the pH of the reaction medium, resulting in the inhibition of methane production (Yu et al. 2002; Ghosh et al. 2000). Conditions that are favourable for the growth of acidogenic/acetogenic microorganisms, such as short HRT and acidic pH, are inhibitory to the methanogens (Ghosh

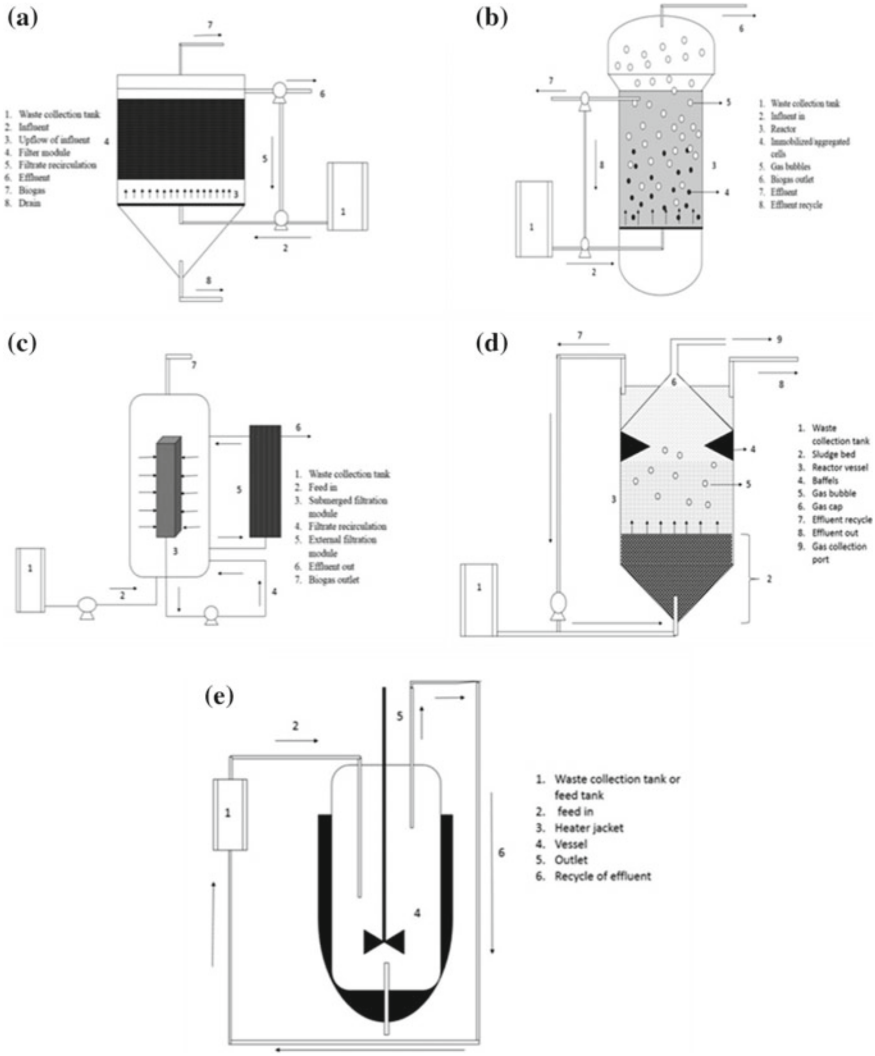


Fig. 8 Schematic diagrams of anaerobic wastewater treatment processes: **a** Anaerobic membrane reactor; **b** Fluidized bed reactor; **c** Anaerobic filter reactor; **d** Upflow anaerobic sludge blanket (UASB); **e** CSTR

1997; Ince 1998). Because of this, single-stage reactors are operated at HRT longer than 15 days with low influent feed concentrations at reduced OLR in high volume reactors such as CSTR (Ghosh 1987). This results in reduced net energy production. Since microorganisms involved in AD require different optimal conditions for efficient functioning, application of single-stage reactors was found to be inefficient and uneconomical. Thus, even more reactor modifications are required to overcome the constraints associated with the existing reactor set up. The modifications should meet both economic and technological perspectives.

11.2 Reactor Modifications

11.2.1 Hybrid Reactors

Acidogenesis and methanogenesis processes are different in nature with respect to their nutritional requirements, growth patterns, physiological conditions, pH, uptake of nutrient and their ability to sustain environmental stress (Weiland 1993). With conventional digestion processes, either of the group may undergo stress condition. In two-phase anaerobic digestion, acidogenesis and methanogenesis were carried out in separate reactors which are connected in series, allowing optimization of both processes (Llabrés Luengo and Mata 1988). A common problem encountered during digestion of wastes, rich in carbohydrates, is that as the organic loading rate increased, the acidogenic phase extends up to methanogenic phase. So there is a need for an effective reactor configuration which can improve both total biogas and methane yield. Thus, combining of two reactors is to separate (two-phase) the different stages of anaerobic digestion process and is termed as hybrid reactors as depicted in Fig. 9 and to distinguish from single-phase reactors.

Advantages of Hybrid Reactors

Advantages of hybrid reactors include improvement in process control and removal of sludge from acidogenic reactor which are in excess without any cell washout from methanogenic reactor; toxic materials can be degraded and attenuated in the

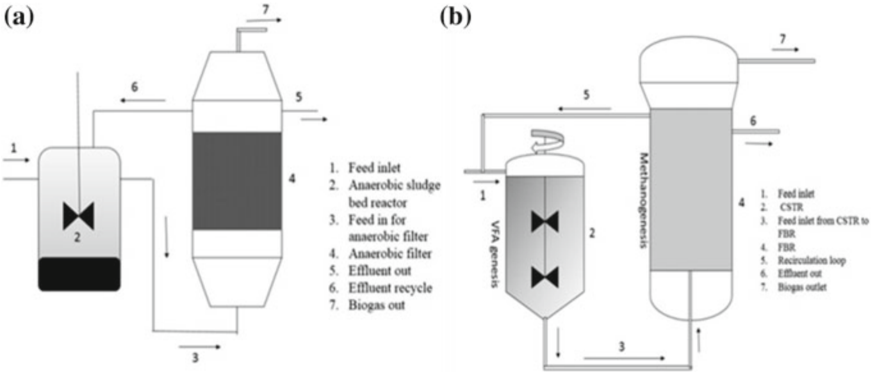


Fig. 9 Two-stage hybrid reactor employed for AD process **a** ASBR + AF; **b** CSTR + FBR

Table 7 Hybrid reactors and their methane yield

Reactor configuration	Type of waste	Yield of biomethane	References
CSTR + AF	Food and vegetable wastes	0.42 m^3 CH_4/kg VS	Verrier et al. (1987)
ASBR + AF	Food and vegetable wastes	0.34 m^3 CH_4/kg VS	Ruynal et al. (1998)
UASB + UASB	Potato processing wastes Palm oil effluent	0.49 m^3 CH_4/kg COD_r 0.3 m^3 CH_4/kg VS	Parawira et al. (2005), Borja et al. (1994)
CSTR + CSTR	Cane molasses	0.19 CH_4/kg VS	Yeoh (1997)

first phase; pH can be controlled precisely in each reactor; composition of CH_4 in biogas from methanogenic phase is relatively higher; loading rate can be increased for methanogenic stage; and treatment plants having balancing tanks can be converted for acidification process. Some of the hybrid reactor configurations and their methane yield have been summarized in Table 7.

12 Methane Enrichment by Carbon Dioxide Removal for Improved Calorific Value

Biogas generated from an anaerobic reactor usually comprised of fuel and non-fuel components. Methane is a fuel part constituting of 45–75% by volume, whereas non-fuel components consist of carbon dioxide (25–55%), hydrogen sulphide, water and other trace gas compounds. As CO_2 proportion increases, it reduces the heating value of the gas which in turn increases the cost incurred for compression and transportation, thus limiting economic feasibility. Calorific value of methane (normal 1 m^3) is about 10 kWh, whereas CO_2 has no heating value (SGC 2012). Hence, the total heating value of biogas is directly proportional to the methane concentration. Purification allows for a wider application of biomethane. The various techniques of carbon dioxide removal have been enlisted in Table 8.

Table 8 Techniques adopted for removal of CO_2 from biogas

Technique	Function
Pressure swing adsorption	Adsorption of CO_2 on activated carbon
Water scrubber	Adsorption of CO_2 in water
Chemical absorption	Chemical reaction between CO_2 and amine-based solvents
Membrane separation	Separation of CO_2 through membrane
Cryogenic separation	Cooling until condensation and sublimation of CO_2

13 Utilization of CO_2 Enriched Liquid for Blue-Green Algae Cultivation

Cyanobacteria, blue-green algae, are receiving wide attention because of their ability to sequester CO_2, thereby reducing the effect of increased CO_2 level in the atmosphere. In addition to sequestration, these organisms can provide pollution-free methane, hydrogen, bioethanol, biodiesel and other valuable biomolecules. Flue gas or biogas containing large proportion of CO_2 could be used as a carbon source for the production of microalgae (*Chlorella* sp.) without any deleterious effects using a photobioreactor. Utilization of CO_2 from biogas for the cultivation of blue-green algae is a zero-waste concept, thereby incurring a complete utilization of the products. Traviesco et al. (1993) demonstrated that bubbling of biogas into a deep algal pond could reduce the CO_2 content from 44–48% to 2.5–11% generating enriched methane of 88–97%.

14 Conclusions

The anaerobic digestion of agro-industrial wastes is a widely accepted and adapted technology for environmental protection and resource preservation. Disadvantages in aerobic treatment of wastes such as high sludge production and additional cost incurred for treatment could be effectively overcome by adopting anaerobic process, where low sludge production and additional biogas output that increase the overall techno-economic feasibility of the process. It demonstrates a sustainable method for waste treatment and disposal in developed and developing nations. The effective application of anaerobic digestion for the treatment of solid waste and wastewater is based on waste characteristics and application of suitable bioreactors. It has been recommended that anaerobic co-digestion, adaptability and resistance of microorganisms to inhibitors and inclusion of methods to either eliminate or detoxify the toxicants before start-up phase can significantly improve the efficiency of waste treatment. Hence, there exists a pressing need for the scientific community to venture into the obstacles faced in the anaerobic digestion. Mitigation of the problems would not only enhance the biogas yield as fuel but also create new economic avenues for both farmers and industries. This would precisely encourage the full-fledged adoption of the technology by a wider spectrum of community.

Glossary

Anaerobic digestion It is a biochemical process carried out by three distinct groups of microorganisms under oxygen limited or oxygen deprived condition to degrade complex organic compounds into gaseous by-products such as methane and carbon dioxide.

Biogas Biogas is a mixture of methane, carbon dioxide, hydrogen sulphide, hydrogen and traces of other components produced during anaerobic digestion of organic compounds. Methanogens are the prime source of production of methane which is the fuel part of biogas. This methane can be used as source of energy for generation of heat, electricity, etc.

Co-digestion Co-digestion is the simultaneous digestion of a homogenous mixture of two or more substrates. Traditionally, anaerobic digestion was a single substrate, single purpose treatment. Recently, it has been realized that AD as such became more stable when the variety of substrates applied at the same time is increased. The most common situation is when a major amount of a main basic substrate (e.g. manure or sewage sludge) is mixed and digested together with minor amounts of a single, or a variety of additional substrate.

Questions

1. How wastes are classified?
2. Difference between aerobic and anaerobic treatment?
3. What is the basis for choice of treatment of wastes?
4. What are the different functionalities of single-stage and two-stage bioreactors in anaerobic digestion?

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Oleaginous Lipid: A Drive to Synthesize and Utilize as Biodiesel

S. P. Jeevan Kumar, Althuri Avanthi, Anjani Devi Chintagunta, Anamika Gupta and Rintu Banerjee

Abstract Turmoil of petroleum oil prices, energy, and environmental security, and its finite sources has made biodiesel a more attractive renewable fuel. Biodiesel, a mixture of fatty acid methyl esters (FAMEs) is conventionally derived from either vegetable oils or animal fats. However, using these conventional sources has raised food security concerns and their succinct supply can serve only for a small fraction of existing demand for transport fuels. Furthermore, the cost and acreages needed for the production of vegetable oils has impeded its use as a feedstock and necessitated to look for an alternative feedstock. Recently, much emphasis has been laid on oleaginous microorganisms for their ability to synthesize lipids under stress conditions. In comparison to vegetable oils, microbial oils have many dividends, such as short life cycle, less industrious, less land requirement, independent of season and climate, and easier to scale-up. This chapter attempts to focus light on recent research on oleaginous yeast, mold, bacteria, and microalgae as prospective oil resources for biodiesel production in the near future. In addition, the biochemistry of lipid accumulation, lipid enhancement via biochemical, metabolic and transcription factor engineering approaches, and fermentation processes have been discussed.

Keywords Oleaginous microorganisms · Biodiesel · Biochemical engineering · Fermentation process · Triacylglycerols (TAGs)

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1 Introduction

One among the major mind wrenching concerns of today's world is the depletion of crude oil reserves due to increasing industrialization, motorization, and the unpredictable political issues raised by the oil-producing countries ultimately leading to a steep increase in the cost of crude oil. The savior in such a situation could only be an alternate to the non-renewable fuel, viz. biodiesel which apparently has the potential to secure the future energy supplies without any emission of CO_2 upon its use. Also, CO emissions are more limited than that evolved from burning of conventional diesel (Santori et al. 2012). Biodiesel is defined as a mixture of fatty acid methyl esters (FAMEs) derived from transesterification of either animal fats or edible/non-edible plant oils. It is a clean renewable fuel (less sulfur and aromatic content), eco-friendly, non-toxic, and biodegradable and can be used to run any compression ignition engine with no further modifications (Benavide and Urmila 2012). These properties of biodiesel have inspired the researchers across the globe to explore a plethora of feedstocks for biodiesel production. The initial attempts were made using edible plant oils such as rapeseed, palm, corn, canola, and sunflower. However, using edible plant oil accounts for about 70–85% of the final market price of the biodiesel. In addition, extensive use of edible plant oils can inevitably create starvation in developing countries (Liang and Jiang 2013). These problems associated with edible plant oils can be addressed by the utilization of non-edible plant oils as a promising substrate for biodiesel production. Some of the non-edible plants are *Jatropha curcas, Sterculia feotida, Pongamia glabra, Linseed, Pongamia pinnata, Hevea brasiliensis, Camelina sativa, Deccan hemp, Simmondsia chinensis, Croton megalocarpus, Garcinia indica*, etc. (Atabani et al. 2013). However, cultivating of non-edible plants leads to "food versus fuel dilemma" as it occupies major fertile land acreages to grow. Therefore, potential renewable resources prospected in today's time are the oleaginous microbes which include bacteria, microalgae, and fungi/yeast (Wang et al. 2012). The present chapter showcases various aspects of oleaginous microbes, biochemistry of lipid accumulation, factors affecting lipid biosynthesis, types of fermentation process for large-scale production, and various strategies for enhanced lipid production.

2 Oleaginous Microorganisms

Although, most of the microorganisms are competent enough to deposit lipids in their membranous structures some exceptional microbes referred as "oleaginous microorganisms" can accumulate up to 20% of lipid on dry cell weight basis and under stress conditions they can hoard up to 70–80% of their biomass (Meng et al. 2009; Christophe et al. 2012). The various microbes capable of producing the single cell oil (microbial lipid) are bacteria, microalgae, yeast, and fungi (Ma 2006). Among these eukaryotic yeasts, molds and microalgae are accomplished with the synthesis of

TAGs which are comparable in composition with vegetable oils, whereas prokaryotic bacteria synthesizes lipoid. In the presence of alkali or acid catalyst, TAGs react with alcohol to produce fatty acid methyl ester and glycerol through transesterification process. Production of microbial oil is beneficial than animal fats and vegetable oils due to their independency on season and climate, fast growth, effortless scale-up, minimum labor, and less requirement for land (Li and Wang 1997). Therefore, the focus has been laid toward the investigation of microbial oils, which might emerge as a potential feedstock for biodiesel generation in the mere future.

2.1 Oleaginous Bacteria

Several bacteria can amass oil under specific environmental conditions but the composition of lipid varies from other microbial oils. Only limited bacteria are capable of generating oils desirable for biodiesel production (Xue et al. 2005) while the majority of them produce complex lipoids (Yi and Zheng 2006). In most of the bacteria, the neutral lipid (lipoid) like polyhydroxyalkanoic acids is generated in the outer membrane which serves as a source for carbon and energy. The extraction of lipoid is difficult as it is synthesized in the outer membrane. The knowledge of gene regulation mechanisms in bacteria for fatty acid synthesis made easy to employ biological, genetic, and metabolic engineering approaches to improve its oil accumulation. In one such attempt using renewable carbon sources, metabolically engineered *Escherichia coli* could generate 1.28 g/L of fatty acid esters through fed-batch fermentation process (Kalscheuer et al. 2006). Although the yield attained from oleaginous bacteria was meager, it has presented a new avenue for biodiesel production. Some of the oleaginous bacteria along with respective carbon source and their lipid content are given in Table 1.

Table 1 Lipid content of oleaginous bacteria

Strain	Carbon source	Lipid content	References
Gordonia sp. DG	Agro-industrial waste	57.8 mg/L (culture medium)	Gouda et al. (2008)
Mycobacterium tuberculosis H37Rv	Limiting nutrient (iron, IL1)	11.9% (dry weight)	Bacon et al. (2007)
Nocardia globerula 432	Acetate and pristine	>49.7% (dry weight)	Alvarez et al. (2001)
Rhodococcus opacus PD630	Agro-industrial wastes	88.9 mg/L (culture medium)	Gouda et al. (2008)
Streptomyces coelicolor	Glucose	83.0 ± 0.5% (dry weight)	Arabolaza et al. (2008)

2.2 *Oleaginous Microalgae*

Microalgae are another feedstock for biodiesel production which can accumulate lipid content up to 60% of dry weight under particular climatic conditions (Araujo et al. 2011) Among the microalgae, Bacillariophyceae and Chlorophyta have higher oil content with lipid profile rich in C16 and C18 fatty acids showing Δ^9, Δ^{12}, and Δ^{15} desaturation which is similar to that of vegetable oils (Chisti 2007). Presently, *Chlorella* is attracting the attention of international energy research institutions as it is suitable for breeding in large scale for biodiesel production (Miao and Wu 2004). The cultivation parameters which influenced oil production in algae are temperature, pH, light intensity, salinity, nitrogen sources, and minerals (Solovchenko et al. 2008; Illman et al. 2000).

Autotrophic microalgae can be transformed into heterotrophic microalgae through genetic engineering techniques or by changing the cultivation conditions to accumulate oil with high organic carbon content. Microalgae can accumulate lipid content naturally up to 5–20% (w/w), whereas "engineering *Cyclotella*" developed by National Renewable Energy Laboratory (NREL) can amass oil content up to 60% (w/w) and 40% (w/w) in the laboratory and outdoor culture conditions, respectively (Dunahay et al. 1992). The oil accumulation can be enhanced by employing "engineering microalgae" having economic as well as ecological significance. Although microalgae are high lipid producers, their need for large acreages, exorbitant photobioreactors, longer fermentation periods, and intensive downstream processing steps hindered them from being an ideal feedstock for industrial-scale production. The lipid content of some oleaginous microalgae is given in Table 2.

Table 2 Lipid content of oleaginous microalgae

Strain	Culture conditions	Lipid content (% dry weight)	References
Chlorella vulgaris	Phototrophic	20–42	Feng et al. (2011)
Dunaliella sp.	Phototrophic	12.0–30.12	Araujo et al. (2011)
Chaetoceros gracilis	Phototrophic	15.5–60.28	Araujo et al. (2011)
Crypthecodinium cohnii	Heterotrophic	19.9	Couto et al. (2010)
Chlorella protothecoides	Heterotrophic	49.0	Gao et al. (2010)
Phaeodactylum tricornutum F&M-M40	Phototrophic	18.7	Rodolfi et al. (2009)
Chlorella	Heterotrophic	55.0	Miao and Wu (2004)

2.3 Oleaginous Yeast and Mold

Since 1980, yeasts and fungi have gained importance as favorable oleaginous microorganisms for biodiesel production (Ratledge 1993). *Rhodosporidium toruloides* showed a biomass concentration of 26.7 g/L and intracellular lipid content of 70% using crude glycerol as substrate when cultivated in 5-L batch fermenter. It has also been reported that broad range substrates can be utilized for lipid accumulation. Another report on oleaginous yeast *Cryptococcus curvatus* showed that it can accumulate storage lipids up to >60% (w/w) when grown under N-limiting conditions, with the major proportion of triacylglycerol and saturated fatty acids similar to vegetable oils. On the other hand, a filamentous fungus *Mortierella alliacea* strain YN-15, accumulated arachidonic acid (AA, C20:4n-6) in its mycelia in the form of triglyceride, which lead to an yield of 46.1 g/L dry cell weight, 19.5 g/L total fatty acid upon 7 days of incubation in a 50-L fermenter (Meng et al. 2009).

Many mold species are explored not only for oil utilized for biodiesel production but also for special lipids, such as gamma-linolenic acid (GLA, $C_{18}H_{30}O_2$, C18:3, $\Delta^{6,9,12}$), docosahexaenoic acid (DHA, $C_{22}H_{32}O_2$, C22:6, $\Delta^{4,7,10,13,16,19}$), arachidonic acid (ARA, $C_{20}H_{32}O_2$, C20:4, $\Delta^{5,8,11,14}$), and eicosapentaenoic acid (EPA, $C_{20}H_{30}O_2$, C20:5, $\Delta^{5,8,11,14,17}$) (Yi and Zheng 2006). In the light of this information, it can be projected that oleaginous yeasts/fungi could be the most potential alternative oil resources for biodiesel production (Meng et al. 2009). Lipid content of some oleaginous yeast and molds are given in Table 3.

It can be concluded that (Table 3) the oleaginous microorganisms can be considered as one among the various potent candidates for the production of biodiesel which can meet the industrial demand in the future. Thus, the primary concern is to boost up the yield of microbial oils by combining the traditional fermentation with modern biotechnological methods such as media engineering, mutation, and genetic

Table 3 Lipid content of oleaginous yeast and molds

Strain	Carbon source	Lipid content (% dry weight)	References
Yeast			
Rhodosporidium toruloides Y4	Glucose	67.5	Li et al. (2007a)
Lipomyces starkeyi	Glucose and xylose	61	Zhao et al. (2008)
Trichosporon fermentans	Glucose	62.4	Zhu et al. (2008)
Mold			
Mortierella isabellina	Glucose	83	Meng et al. (2009)
Cunninghamella echinulata	Xylose	57.5	Fakas et al. (2009)
Mucorales fungi	Sunflower oil	42.7–65.8	Certik et al. (1997)

engineering techniques. Utilization of all these techniques requires the insights of biochemistry, genetics and related metabolic pathways for lipid accumulation.

3 Biochemistry of Lipid Accumulation

As mentioned in the earlier sections, the biochemistry of lipid biosynthesis in oleaginous microorganisms slightly differs when compared to non-oleaginous microorganisms. Acetyl-CoA, malonyl-CoA, and glycerol-3-phosphate, the three important precursors for lipid synthesis in the presence of some specific co-factors, such as NADPH play a significant role in biosynthetic pathway. The cytoplasmic citric acid is cleaved by ATP-citrate lyase (ACL) into acetyl-CoA and oxaloacetate (OAA) which is a unique feature of oleaginous microorganisms. The acetyl-CoA thus formed and further converted into fatty acid in the presence of fatty acid synthetase (FAS) resulting in the formation of triacylglycerols (TAGs). Thus, lipid accumulation is a two-step process which involves synthesis of long-chain fatty acid (FA) followed by synthesis of triacylglycerol (TAG).

The fatty acid synthesis takes place in the cytosol of the cell. The two forms of FAS, namely type I and type II are playing a significant role. Type I is commonly found in yeast, fungi, algae, and some special bacteria, where, the acyl carrier protein is not in bounded form but perhaps integrated into the multienzyme complex (Magnuson et al. 1993; Schweizer 1980). An intensive study reveals that the complex has hexameric structure ($\alpha_6\ \beta_6$) with two non-identical multifunctional subunits in yeast (Schweizer et al. 1978). Subunits α and β are encoded by two different independent genes with molecular weight 185 KDa and 180 KDa, respectively. Studies revealed that α-subunit is responsible for acetyl- malonyl- and palmityl-transferase, enoyl reductase, and dehydratase activities, whereas β-subunit is responsible for β-ketoacyl synthase, β-ketoacyl reductase, and acyl carrier protein activities (Schweizer 1980). Type II FAS complex is mostly found in bacteria and cyanobacteria, where each individual reaction is carried out by different proteins participating in the pathway (Magnuson et al. 1993).

Fatty acid biosynthesis starts in the presence of acetyl-CoA carboxylase (ACC) which converts acetyl-CoA into malonyl Co-A with biotin as prosthetic group. In the presence of FAS, four reaction steps such as condensation, reduction, dehydration, and reduction systematically take place resulting in the elongation of carbon chain. Acetyl-CoA is converted to malonyl Co-A by the condensation process followed by the reduction of β-keto group into alcohol. Further, the elimination of one water molecule takes place through dehydration followed by reduction to form the corresponding saturated fatty acid. As a result, the length of carbon chain is increased by two carbons after each cycle and the process is repeated until palmitic acid (16-C), stearic acid (18-C), archidic acid (20-C), behenic acid (22-C), and melissic acid (30-C) is formed.

Although, the elongation of fatty acid chain is similar to the normal palmitic acid synthesis, but unsaturated fatty acids are formed by the introduction of double bond catalyzed by fatty acyl–CoA desaturase, an oxidase which is a flavoprotein by nature. Most of the desaturases are membrane-bound multienzyme complex except fatty acyl carrier protein (ACP) desaturase found in plant chloroplast which is soluble enzymes (Sommerville and Browse 1996). For palmitoleic/oleic acid biosynthesis, the first double bond is introduced into the alkyl chain at Δ^9 position. And for other unsaturated fatty acids desaturation takes place in different carbon of alkyl chain at Δ^6, Δ^{12}, Δ^{15}, and so on resulting in the production of different unsaturated fatty acids (18-C linoleic acid, Δ^9 and Δ^{12}; 20-C arachidonic acid, Δ^5, Δ^8, Δ^{11}, and Δ^{14}; 22-C erucic acid, Δ^{13}) in presence of respective desaturases. A recent report says that in psychrophilic oleaginous yeasts, an introduction of Δ^6 and Δ^{15} desaturases resulted in the production of γ- and α-linolenic acids, respectively (Rossi et al. 2011).

For TAG biosynthesis two possible routes are adopted either by glycerol kinase from glycerol or from dihydroxyacetone phosphate (DHAP) in presence of G3P dehydrogenase in a reversible reaction. G3P and DHAP are the intermediates of EMP pathway which are also formed in several other biosynthetic pathways of the cell. The triacylglycerol (TAG) is formed by consecutive acylation of glycerol-3-phosphate (G3P), which is catalyzed by a variety of acyltransferases which lead to the formation of lysophosphatidic acid (LPA), 1,2-diacyl G3P (phosphatidic acid, PA) and ultimately TAG (Rossi et al. 2011).

Lipid accumulation in oleaginous microbes is regulated mainly by ATP: citrate lyase (ACL) and malic enzyme (ME). It is found that the lack of nitrogen in the medium leads to activation of cellular AMP deaminase which reduces the mitochondrial AMP concentration. This decrease in AMP limits the activity of AMP-dependent NAD^+-Isocitrate dehydrogenase (NAD^+-ICDH) (Christophe et al. 2012). Loss of ICDH activity leads to a build-up of citrate within the mitochondria which is then translocated by malate/citrate translocase system to cytosol (Evans et al. 1985), and further cleaved by ATP: citrate lyase (ACL) into oxaloacetate and acetyl-CoA which is a precursor for fatty acid synthesis (Botham and Ratledge 1979). During the course of reaction for one mole of palmitic acid, 14 mol of NADPH are required, which is supplied by another crucial enzyme called malic enzyme (ME). Lipid accumulation is profoundly influenced by ME in nitrogen-deficient condition in the medium. For example, *Mucor circinelloides* and *Mortierella alpina* have been reported to accumulate lipid up to 25 and 50% of its dry weight and their corresponding ME was active till 20–40 and 60–85 h, respectively (Wynn et al. 1999). Therefore, these two key enzymes can be up-regulated using typical nitrogen-deficient medium to enhance lipid accumulation in oleaginous microorganisms.

A special mention of acetyl-CoA synthase (ACS) is needed as it catalysis the conversion of acetate into acetyl-Co A which is a precursor for lipid biosynthesis. It was found that overexpression of *acs* gene in *E. coli* led to nine-fold increase in ACS activity due to increased assimilation of acetate in the medium. This increase in acetate assimilation subsequently contributed to lipid synthesis (Lin et al. 2006). Thus, ACS exerts its effect by supplying the precursor such as acetyl-CoA into the lipid synthesis pathway.

The lipid accumulated in the oleaginous microorganisms can be extracted and subjected to transesterification process to obtain FAMEs (biodiesel), where not only the metabolic enzymes are playing a significant role on the synthesis of saturated/unsaturated lipid but also some environmental parameters such as carbon, nitrogen, DO, temperature, pH, and reactor configuration are also playing a significant role on the type of lipid biosynthesized and its enhanced amount. The quality of the biodiesel can be determined by the carbon chain length, degree of saturation and/or unsaturation of fatty acids. In general, the fatty acids in triacylglycerol are saturated (Cn:0), monounsaturated (Cn:1), and polyunsaturated (Cn:2,3) possessing two or three double bonds, respectively. Long-chain SFA (Cn:0) reduces NOx emission, increases cloud point, cetane index, and enhanced oxidative stability. In contrary, PUFA reduces oxidative stability, cloud point, cetane index, and increased NO_x emissions. Ironically, no fatty acid profile meets the optimal fuel properties as the cloud point and the rest parameters are opposed to one another. Hence, the conciliation can be deduced with higher monounsaturated and meager content of saturated and polyunsaturated fatty acids, respectively. On the other hand, the cetane number is a yardstick for the ignition quality of biodiesel which increases with increased fatty acid chain length and decreases with increased branch chain (Mazumdar et al. 2012).

4 Strategies for Enhanced Lipid Production

Oleaginous microorganisms accumulate lipids mainly in the form of TAGs which is the feedstock for biodiesel production. Nevertheless, biodiesel from oleaginous microorganisms is exorbitant which is crippling the future prospects. The straight forward approach to combat the cost issues is to enhance the lipid content which can be achieved either by genetic manipulation of lipid biosynthetic pathways, repression of lipid competitive pathways, and transcription factor engineering. Thus, an emphasis has been given to highlight the lipid enhancement by adopting the various approaches for genetic manipulations. The schematic diagram of lipid enhancement approaches has been given in Fig. 1.

4.1 Biochemical Engineering Approaches for Lipid Enhancement

The biochemical engineering approach emphasizes on imposing physiological stress to the microbes to streamline the metabolic flux to lipid synthesis. The various physico-chemical parameters such as carbon, nitrogen, C/N ratio, and physiological conditions which influence lipid production are discussed below.

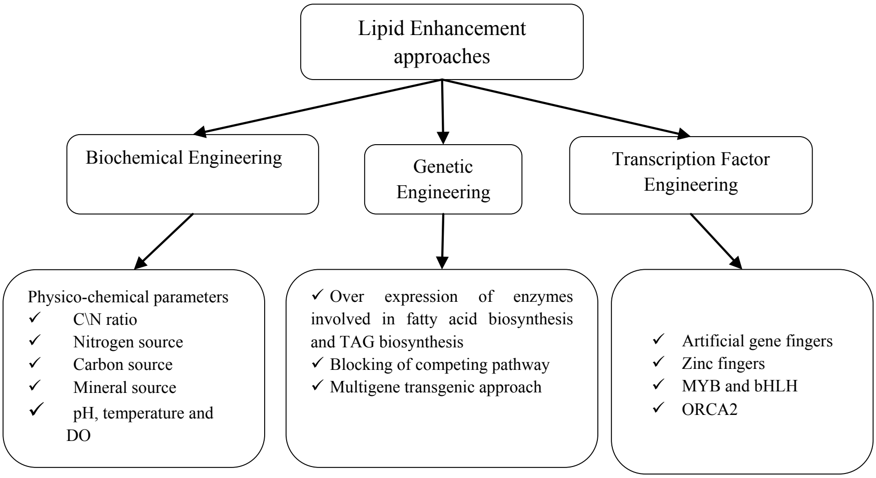

Fig. 1 Schematic diagram of lipid enhancement approaches

4.1.1 Effect of Carbon

Though glucose is an ideal carbon source for lipid production in most of the oleaginous microbes, assimilation of cheap feedstocks like glycerol and lignocellulosic substrates is predominantly investigated to make the process economical. Under carbon limited conditions, the oleaginous microorganisms utilize the stored intracellular lipids for cell proliferation, whereas under surfeit carbon conditions, a part of carbon will be utilized for cell proliferation and rest will be channeled toward the lipid synthesis (Ratledge 2004).

Lignocellulosic biomass is abundant in nature with low value which makes it compatible substrates for biofuel production. For instance, *Mortierella isabellina* accumulated 39.4% of lipid content on non-detoxified lignocellulosic hydrolysate (NDLH). In addition, NDLH with some precipitate facilitated biomass to form pellets (diameter of 0.11) which helps in easy harvest of biomass by simple filtration technique (Zheng et al. 2012). Apart from lignocelluloses biomass, glycerol obtained from biodiesel manufacturing process can be utilized to make competitive edge with plant oils. *Candida freyschussii* assimilated crude glycerol and accumulated 33% of lipid content at a rate of 10% of glycerol conversion with similar fatty acid profile of vegetable oils. Thus, it clearly envisages that the oleaginous microbes are promising in the near future for high lipid accumulation using cheap substrates (Amaretti et al. 2012).

4.1.2 Effect of Nitrogen

Nitrogen is one of the important parameters for accumulation of neutral lipid mainly TAG. The organic and inorganic nitrogen sources showed varied influence on oil accumulation during the cultivation of yeast (Liu et al. 2000). It was found that inorganic nitrogen sources mostly influence cell growth than that of oil production, whereas organic nitrogen sources promote oil production rather than cell growth (Huang et al. 1998). From fungal growth studies conducted using *Pellicularia* under various nitrogen sources, a significant decrease in triglyceride content (19–31%) was observed when grown on the medium containing ammonium sulfate, ammonium nitrate, and ammonium chloride. While, a significant increase in the triglycerides (65–85% of the neutral lipids) was found when grown on the medium containing urea due to increase in concentration of citrate, a precursor of lipid biosynthesis (Evans and Ratledge 1984). Thus, it can be concluded that nitrogen is one of the important parameters which not only fulfills the elemental nitrogen requirement but also participates in different metabolic activities of the cell, including the pathways which are active for lipid accumulation/enhanced lipid biosynthesis in the cell.

4.1.3 *C*/*N* Ratio

Lipid accumulation in oleaginous microorganisms mostly takes place under stress conditions. It was reported that nitrogen limitation or variation in the carbon and nitrogen ratios (*C*/*N*) led to the downregulation of Kreb's cycle. In the presence of surplus carbon and meager nitrogen source in the medium the cell's lipid content boosts up and becomes obese due to prevented cell proliferation. The nutrient starvation predominantly led to the enhanced lipid accumulation due to the reduced cell division (Ratledge and Wynn 2002). An increase in *C*/*N* ratio from 25 to 70, led to enhanced oil content from 18 to 46% in microalgae (Mainul et al. 1996). Studies conducted on *Chlorella*, revealed that *C. pyrenoidosa*, *C. vulgaris*, *C. minutissima,* and *C. emersonii* accumulated 23%, 40%, 57%, and 63% of lipid, respectively, under low-N medium, whereas under normal conditions these organisms accumulate starch as repository material (Illman et al. 2000).

4.1.4 Physiological Conditions

Along with the other factors temperature, dissolved oxygen, micronutrients, pH, and inorganic salts also govern the triglyceride formation. The different lipid constituents are biosynthesized in different metabolic pathways but each fraction has got different characteristics and the variation of any one of them may have a different impact on the overall biodiesel quality. The composition of polar lipids (phosphatidylinositol, phosphatidylserine, phosphatidylethanolamine, and phosphatidylcholine) and neutral lipids (steryl esters and triacylglycerols) varied under different temperatures in oleaginous microorganisms. The temperature lower than the optimal growth temperature enhances the lipid content. Dissolved oxygen concentration had a profound effect on composition of fatty acids. The oxygen stress led to variation in triglyceride fraction and decrease in sterol and phospholipids, thereby showing a positive effect on accumulation of TAG (Yi and Zheng 2006). In another report, it was stated that lipid production in fungi occurred over a wide range of pH (Jeffery et al. 1999). In case of *Trichoderma reesei* grown on glucose substrate, the highest growth was observed at pH 4.0, whereas maximum lipid accumulation was found at pH 3.2 (Brown et al. 1990). It was already reported that the addition of inorganic salts like NaCl (1.0 M) during the log phase of *Dunaliella* cultivation resulted in 70% increase of TAG (Takagi et al. 2006).

Oil accumulation varied extensively due to trace metal ions and minerals (Mainul et al. 1996; Wang et al. 2005). The presence of metal ions such as Mg^{2+} and Mn^{2+} influence the malic enzyme which is a key regulator for lipid accumulation (Savitha et al. 1997), whereas lipogenesis was inhibited by Zn^{2+} (Jackson and Lanser 1993). Phosphorus is an essential mineral for photophosphorylation process in microalgae. Photosynthesis requires a large quantity of Rubisco protein which is synthesized by ribosomes rich in phosphorus (Wang et al. 2008). The deficiency of nutrients such as phosphorous and iron causes termination of cell growth and channels metabolic flux to fatty acid biosynthesis. Enhanced accumulation of lipid was found in *Monodus subterraneus* due to the limitation of phosphorous (Khozin-Goldberg and Cohen 2006). Under favorable conditions, the deficiency of iron stimulates lipid accumulation in *C. vulgaris* up to 56.6% of biomass (dry weight) (Liu et al. 2008).

4.2 Genetic Engineering Approaches for Lipid Enhancement

Besides the biochemical engineering, there are some other approaches for enhancing lipid accumulation. Genetic engineering (GE) approaches have great potential for lipid enhancement in long-term perspective. The various genetic engineering strategies employed for lipid enhancement are discussed below.

4.2.1 Overexpression of Enzymes Involved in Fatty Acid Biosynthesis

As mentioned above (Sect. 3), fatty acid biosynthesis starts with a carboxylation reaction catalyzed by acetyl-CoA carboxylase (ACC) which converts acetyl-CoA into malonyl Co-A. This reaction is an important committing step in fatty acid synthesis pathway (Courchesne et al. 2009). Therefore, several researchers made attempts to overexpress and/or co-express ACC. For instance, co-expression of *E. coli* ACC (*accA*, *accB*, *accC*, *accD*) and thioesterase I (encoded by *tes A* gene) in another strain of *E. coli* resulted in a six-fold augment in the synthesis fatty acids (Liang and Jiang 2013).

Another key regulatory stride of fatty acid metabolism is the one catalyzed by malonyl-CoA:ACP transacylase (MAT) which converts malonyl Co-A to malonyl-ACP (Liang and Jiang 2013). It is envisaged that overexpression of *fabD* gene encoding MAT can increase the malonyl-ACP availability, concomitantly improving free fatty acid production.

Yet, another crucial control point in fatty acid synthesis is the condensation reaction of acetyl-CoA with malonyl-ACP catalyzed by β-ketoacyl-ACP synthase III (KAS III). Therefore, the overexpression of KAS subunit of FAS can enhance fatty acid synthesis. It is reasoned from these reports that the fatty acid biosynthesis is shared by various component enzymes of the pathway with each having a definite role to play.

Although, FAS is an important entity of fatty acid synthesis pathway, lipid enhancement by genetic engineering of FAS may not be feasible due to its complexity in structure, interdependent activity, and differences in multipoint controls (Liang and Jiang 2013; Courchesne et al. 2009). The lipid enhancement by deploying various genetic engineering strategies are given in Table 4.

Table 4 Lipid enhancement by various genetic engineering strategies

Genes	Source	Receiver	Observation	References
ACC1 (ACC)	*Mucor rouxii* (mold)	*Hansenula polymorpha* (yeast)	+40% fatty acid content	Ruenwai et al. (2009)
FAT, *fab*D (MAT)	*E. coli*	*E. coli*	Fatty acid content (+11%)	Zhang et al. (2012)
DGAT	*Arabidopsis*	Yeast	200–600 X DGAT activity, 3–9 X TAG content	Bouvier-Nave et al. (2000)
GPD1, *DGUT2* (GPDH)	*Yarrowia lipolytica*	*Yarrowia lipolytica*	5.6 X TAG content	Dulermo and Nicaud (2011)
Antisense PEPC	*Anabaena* sp.	*E. coli* DH5α	+46.9% lipid content	Hou et al. (2008)
ΔAGPase	*Chlamydomonas reinhardtii* BAFJ5	*Chlamydomonas reinhardtii* BAFJ5	+46.4%, 3.5 X lipid content	Li et al. (2010)
POX1-6 (AOXs), MFE1, GPD1, Δ GUT2	*Yarrowia lipolytica*	*Yarrowia lipolytica*	+lipid accumulation	Dulermo and Nicaud (2011)

4.2.2 Overexpression of Enzymes Associated with TAG Biosynthesis

Overexpression of enzymes related to biosynthesis of TAGs is a straight forward approach to directly increase the biodiesel yield as TAGs are precursor molecules for diesel production. As discussed earlier, lysophosphatidate (LPA) is the rate-limiting step in the TAG synthesis pathway which is catalyzed by acyl-CoA: glycerol-*sn*-3-phosphate acyl-transferase (GPAT) (Cao et al. 2006). This enzyme is subjugated to regulation at both transcriptional and post-transcriptional levels. Thus, overexpression/co-expression of GPAT gene can increase oil content (Jain et al. 2000).

From the TAG biosynthesis pathway, it is well understood that diacylglycerol (DAG) is a common precursor for the formation of either TAG or phospholipid. Therefore, another important regulatory enzyme in the TAG formation is diglyceride acyl-transferase (DGAT) which inserts the third acyl-CoA into DAG for the formation of TAG and fatty acyl-CoA (Oelkers et al. 2002). Thus, the overexpression of DGAT would channel DAG to TAG formation rather than phospholipid. In one such study, it was found that the transformation of yeast with *Arabidopsis* DGAT resulted in 200–600-fold increased activity of DGAT with concomitant three- to nine-fold increase in TAG formation (Bouvier-Nave et al. 2000). This indicates the existence of direct relation between the DGAT activity and TAG formation (Olukoshi and Packter 1994).

4.3 Blockage of Competing Pathways

Lipid biosynthesis can be enhanced either by up-regulation of genes involved in either TAG and fatty acid synthesis or by downregulation of concerned genes in competing pathways such as β-oxidation pathway and blocking of other competing pathways such as phosphoenolpyruvate and starch biosynthesis.

Complete repression of β-oxidation pathway or deactivation by modification in the lipid mobilizing genes may enrich the lipid content. For example, the downregulation of β-oxidation genes in *Saccharomyces cerevisiae* has enhanced both intracellular and extracellular lipid content (Michinaka et al. 2003). Another study on deactivation of β-oxidation pathway showed that the modifications in the *POX* genotype (mainly *POX1*–*POX6* genes) that encode AOX proteins which regulate lipid mobilization led to increased level of G3P and subsequently increased fatty acid content (Dulermo and Nicaud 2011).

In the light of above-mentioned fatty acid synthesis pathway, it can be interpreted that the TAG biosynthesis requires fatty acids which are in turn produced via series of intermediates arising from phosphoenolpyruvate (Song et al. 2008). Phosphoenolpyruvate acts as a common precursor molecule for both competing oxaloacetate flowing into Kreb's cycle and the mainstream pyruvate leading to free fatty acid synthesis. Thus, the strategic point for repression is clearly the downregulation of the phosphoenolpyruvate carboxylase (PEPC) which catalyzes the conversion of phosphoenolpyruvate to oxaloacetate.

On the other hand, in autotrophic microalgae, photosynthetic carbon is streamlined to starch synthesis under stress conditions. Starch synthesis takes place in the plastid and the enzyme ADP-glucose pyrophosphorylase (AGPase) catalyzes the conversion of glucose 1-phosphate and ATP to ADP-glucose and Pi. Further starch synthases (SS) and branching enzymes (BE) utilize this ADP-glucose to form polysaccharide starch via intermediate glucans. Therefore, it is evident that the repression of key enzymes in starch synthesis could enhance the lipid accumulation by streamlining the photosynthetic carbon into lipid synthesis. Li et al. (2010) reported that the downregulation of the key enzyme AGPase in a *Chlamydomonas* starchless mutant resulted in ten-fold increase in TAG formation.

4.4 Multigene Transgenic and Transcription Factor Engineering Approaches

From the above discussion, it can be interpreted that GE approach targets only a single gene at a time, whereas multigene transgenic approach and transcription factor (TF) engineering emphasize on tailoring more than one gene at a time aimed to up-regulate lipid biosynthesis (Grotewold 2008). A recent study by Tai and Stephanopoulos (2013) states that the co-overexpression of two genes, namely ACC 1 and DGAT 1 in *Yarrowia lipolytica* resulted in five-fold increase in lipid content (62%, w/w) than the control. This clearly envisages multi-transgenic approach has the potential to enhance the lipid accumulation.

Other promising strategy foreseen for improved lipid production is TF engineering. Transcription factors are proteins that bind to specific DNA sequences which establish DNA–protein and protein–protein interactions, and thereby regulate transcription. Although TFE in oleaginous microorganisms is in infancy, exploring TFs for overproduction of metabolites as well as regulation of lipid biosynthesis has been identified in animals, plants, and microorganisms. Moreno-Risueno et al. (2007) identified the Dof-type (DNA binding with one finger) TF family sequences from various organisms of different taxonomic groups such as *Chlamydomonas reinhardtii* (alga), *Physcomitrella patens* (moss)*, Pinus taeda* (gymnosperm) and angiosperms *Arabidopsis thaliana* (dicotyledon), *Oryza sativa,* and *Hordeum vulgare* (monocotyledon). Thus, in-depth research in TF engineering may serve as a conduit for enhanced oil production.

5 Fermentation

Oleaginous microorganisms, including bacteria, fungi, microalgae, and yeasts are capable of lipid acquisition and thus accumulate lipid up to 60% of dry cell weight (Meng et al. 2009). In comparison to above-mentioned microbes, yeast presents the best candidature since it grows faster than others and is very easy to culture on large scale (Ratledge and Cohen 2008).

Yeast species, such as *Cryptococcus albidus, Lipomyces lipofera, Lipomyces starkeyi, R. toruloides, Rhodotorula glutinis, Trichosporon pullulan,* and *Y. lipolytica* are able to accumulate lipids, and hence biodiesel production. Lipid components accumulated within yeast include fatty acids like myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. These lipids require either lipase or a chemical catalyst for biodiesel production (Li et al. 2007b). Apart from the above-discussed parameters (Sect. 4), reactor configuration has a sound effect on lipid accumulation for large-scale biodiesel production and thus critical evaluation of the reactors is necessary. There are basically two types of reactor configurations: batch and continuous.

5.1 Batch Fermentation

Batch fermentation is the simplest mode of operation in which the entire substrate and inoculum are added at once and then the reaction is allowed to occur for a definite period of incubation time. During this period, the concentration of substrate, microbial biomass, and product change with progress of the time. Following the reaction, all the contents are withdrawn at once and further purified to recover the desired product. Batch fermentation has the following characteristics:

1. Flexible with various biological entities
2. Low level of contamination as growth period is short
3. One-time investment as compared to continuous mode of operation
4. Efficient for processes targeting both highly expensive and quality product
5. Since, the mode of production is non-continuous, downtime is needed between two consecutive loadings.

A study was conducted by Liang et al. (2012) under batch mode using *C. curvatus* for fermenting the hydrolysate derived from sweet sorghum bagasse (SSB) obtained after enzymatic hydrolysis. In this study, the SSB hydrolysate used for fermentation was pretreated with dilute sulfuric acid (0.5%, v/v) at a solid loading of 11% (w/v), for a period of 1 h at 121 °C. After pretreatment, the solid biomass was subjected to enzymatic hydrolysis using cellulase (15 IU/g) and cellobiase (60 IU/g) at 50 °C in a shaking incubator maintained at 150 rpm. The reducing sugars obtained after saccharification were fermented at 37 °C using the three days old culture of *C. curvatus* at a dosage of 10% (v/v) of the hydrolysate. After 6 days of fermentation, it was observed that the SSB hydrolysate supported the growth of *C. curvatus* up to 10.8 g/L which had a lipid content of 40% of dry cell weight.

The short comings of the batch fermentation have been studied further in order to overcome the difficulties faced during this process through a different mode of operation such as fed-batch fermentation.

5.2 Fed-Batch Fermentation

Fed-batch system is different from batch where the medium components along with the substrate are added with an intermittent loading program so that the raw materials are gradually utilized by the microbes for conversion to products. This mode of operation is aimed at overcoming the limitations of the batch fermentation such as substrate utilization, feedback inhibition, substrate inhibition, and utilization of nutrients.

A recent study was conducted by Chang et al. (2013) on co-production of biodiesel and omega-3 oils using *Aurantiochytrium* sp. with glucose as a carbon source under fed-batch mode. For which two fed-batch experiments were conducted in 2-L capacity reactors. In the first set of experiment, the media initially contained 100 g/L of glucose with a supplementation of 660 g/L of glucose after 29 and 46.5 h. While in the second set of experiment, the media initially contained 40 g/L glucose and the subsequent feeding (660 g/L) was done after 26 h of incubation time. It was observed that the higher initial glucose concentration did not lead to any improvement in the rate of biomass production (48 g/L) or fatty acid yield (12–14 g/L) when compared to the lower initial glucose levels. From this study, it is clear that initial higher concentration of glucose in the fermentation media does not have any positive effect on lipid accumulation. Thus, a systematic study on lipid accumulation and substrate utilization is one of the gray areas for drawing any conclusion on the metabolism of carbon utilization and fat synthesis.

5.3 Continuous Fermentation

Continuous fermentation means the continuous flow of input media and continuous output of the fermented broth, including product where a definite flow rate is maintained so as to keep the total volume constant. In case, there is a disturbance of either of this flow the problem of reactor flooding or non-maintenance of required volume takes place, affecting the entire fermentation system. This system has the following characteristics:

1. Production is continuous
2. Steady state is attained after certain start-up period
3. No fluctuation of concentration with time and space within the reactor

4. Reaction rate is constant
5. No downtime required.

According to a study conducted by McGinn et al. (2012), biomass productivity of *Scenedesmus* sp., was observed to be two times greater in a continuous mode (130 mg/L/d) than in batch mode (65 mg/L/d). In a continuous mode, dilution rate has the major influence on biomass productivity. This fact is clearly substantiated in a recent study conducted by Tang et al. (2012) on *C. minutissima.* They reported that the biomass yield has been varied from 39 to 137 mg/L/day as the dilution rate increased from 0.08 to 0.64 d^{-1} where the maximum productivity was observed at 0.33 d^{-1}. In another study, Yoon and Rhee (1983) had observed that dilution rate also has an influence on the *R. glutinis* fatty acid profile. As per their observations, the concentration of PUFA increased with an increase in dilution rate while saturated and monounsaturated fatty acids showed reverse trend.

As perceived the theme for lipid enhancement is to produce biodiesel. The process by which the lipids are converted into biodiesel is known as transesterification. Microbial lipids have to undergo transesterification process in order to reduce the viscosity of the oil. Hence, a brief overview has been discussed on transesterification and glycerol valorization.

6 Transesterification

Transesterification is a process in which TAGs present in oil are converted into simple alkyl esters with short-chain alcohols like methanol and ethanol (Fig. 2). This reaction is reversible and proceeds considerably in the presence of catalysts, which are either acidic, basic or enzymatic in nature. The cost of the entire process depends on quantity and type of catalyst used in the process.

Base-catalyzed transesterification is faster, less corrosive than the acid catalyzed for which it is industrially favored. On the contrary, it requires high energy and posses difficulties during glycerol recovery. Also, saponification by the feedstocks with high acid value can deteriorate the quality of biodiesel when base is used as a catalyst. On the other hand, acid-catalyzed transesterification is very slow and

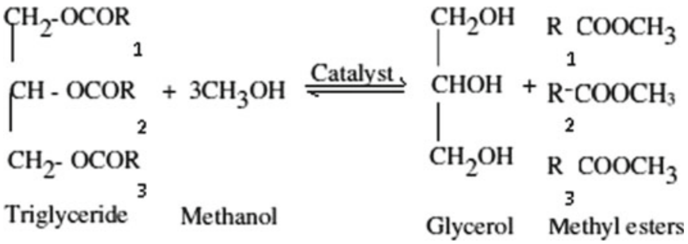

Fig. 2 Typical transesterification reaction (*Source* NREL 2004)

Table 5 Biodiesel properties to assess its quality as fuel

Parameters	USA (ASTM)	India (BIS)	Europe (EN)
Viscosity (mm^2/s) at 40 °C	1.96	1.9–6	3.5–5
Pour point (°C)	15–18	–	–
Cetane number (min)	47	≥40	51
Flash point (°C)	130	130	120
Density (g/cm^2) at 15 °C	0.88	0.87–0.89	0.86–0.89

corrosive compared to base-catalyzed transesterification and is found to be suitable only for oil with high free fatty acids (FFAs). These limitations hinder the industrial application of acid-based transesterification.

Entirely, a new realm is set by yet another method of biodiesel production called as enzymatic transesterification which falls under biological and environment friendly stretch. A report on enzyme-mediated transesterification stated that significant conversion (98.5%) of fatty acid methyl ester was reported through ethyl esterification of docosahexanoic acid by employing immobilized lipase from *Candida antarctica* (Shimada et al. 2001). In this study, immobilized lipase was used so as to sustain the inhibition of enzyme activity due to high concentration of methanol and water generated during the course of reaction. The FAMEs thus obtained should reach the significant standards in order to be considered as good quality biodiesel. Even though different standards for comparing the quality of biodiesel were developed in various countries like USA (ASTM), India (BIS), Europe (EN) (Table 5), etc. ASTM standards are followed throughout the world (Jain and Sharma 2010).

As discussed earlier, glycerol is a by-product of transesterification reaction, and thus valorization of glycerol is essential to make the process more economically viable.

6.1 *Conversion of Crude Glycerol: By-Product Utilization*

Although the emphasis on the current chapter is biodiesel production, one cannot ignore the fact that the transesterification of TAGs generates significant amount of a primary by-product known as glycerol which accounts 10% (w/w) of biodiesel produced, creating a serious disposal issue for the biodiesel refinery. Recent report projected that world biodiesel production by 2016 would reach up to 37 billion gallons. But, the irony is that this is accompanied with 4 billion gallons of crude glycerol (Yang et al. 2012). Owing to this huge production, the global market price

Table 6 Conversion of crude glycerol to high-value industrial compounds

S. No.	High-value compound	Microorganism/method	References
1.	Poly-3-Hydroxybutyrate	*Cupreavidus necator*	Posada et al. (2011)
2.	Lactic acid	*Escherichia coli* AC-521	Fan et al. (2010)
3.	Ethanol	*Klebsiella planticola*	
4.	Citric acid	*Yarrowia lipolytica* NCIM 3589	
5.	Hydrogen	Steam reforming	
6.	1,3-Dihydroxyacetone (DHA)	*Schizochytrium limacinum*	
7.	1,3-Propanediol (1,3-PD)	*Klebsiella pneumonia*	
8.	Dichloro-2-propanol (DCP)	Second-order nucleophilic substitution mechanism using acetic acid catalyst	
9.	Acrolein	Low-pressure packed bed gas-phase dehydration of glycerol	

of pure glycerol took a steep fall. Thus, it is necessary to channel crude glycerol to other value-added products to uplift the overall process economics and co-generate various commercially viable compounds.

Extensive research to streamline crude glycerol waste from biodiesel production found its application as a raw material for manufacturing the various high-value industrial compounds, such as citric acid, lactic acid, ethanol, poly-3-hydroxybutyrate, hydrogen, 1,3-dihydroxyacetone (DHA), 1,3-propanediol (1,3-PD), dichloro-2-propanol (DCP), and acrolein, through different microbial intervention and mostly as pure culture process. Glycerol can also be utilized through chemical means.

Table 6 summarizes the applications of crude glycerol in production of different value-added compounds (Table 6). Thus, this approach of glycerol utilization ensures environmentally friendly, sustainable, and profitable market for biodiesel negating the necessity of waste disposal.

7 Conclusion

Environmental concerns, the exhaustion of finite resources have spurred to search for alternative fuels. On the other hand, the limited supply and exorbitant cost of vegetable oils and animal fats have crippled for the development of other sources for biodiesel production. Oleaginous microorganisms capable of producing a significant amount of lipid are the potential candidates for sustainable biodiesel production. However, engineering the available oleaginous strains for higher lipid yield is desirable to cater the growing demand for oil. The three promising approaches discussed above pave a way for lipid enhancement. The theme of biochemical engineering approach is to impose physiological stress on the strain, whereas GE targets one and TF engineering targets more than one enzyme involved in the lipid biosynthetic pathway. These lipids are further subjected to transesterification in the presence of alcohol and catalyst to form FAMEs/ biodiesel. It is speculated that in order to make the process commercially viable various value-added products can be synthesized from crude glycerol, a by-product from lipid transesterification. Therefore, biodiesel production from oleaginous lipids is no exaggeration but is rather a step closer to renewable fuel-powered motor engines.

Glossary

Acetyl-CoA Acetyl coenzyme A is the thioester between coenzyme A and acetic acid. It is formed by pyruvate decarboxylation in cellular respiration process

Acetyl-CoA citrate Lyase Acetyl-CoA citrate Lyase is an enzyme that catalyzes the conversion of citrate to Acetyl-CoA

Acetyl-CoA Carboxylase Acetyl-CoA carboxylase is an enzyme which catalyzes the carboxylation of acetyl-CoA to form malonyl-CoA

Biodiesel Chemically it is defined as "fatty acid methyl esters" derived either from plant oils, animal fats or from microbial lipids

Batch Fermentation Batch fermentation process refers to the process that starts with the inoculation and end with the retrieval of the product happens inside a single fermenter with no intermediate steps

Continuous Fermentation Sterile nutrient solution is added to the bioreactor continuously and an equivalent amount of converted nutrient solution with microorganisms is simultaneously removed from the system

***C/N* ratio** Carbon to nitrogen is a ratio of the mass of carbon to the mass of nitrogen in a substance. *C/N* ratio is the indicators for nitrogen deficiency in the fermented broth

Fatty Acid Synthetase (FAS) Fatty acid synthetase is a multienzyme system which is responsible for the de novo synthesis of fatty acids

Fed-batch Fermentation A biotechnological process when one or more nutrients are fed to the bioreactor while cultivation and the products remain in the bioreactor until the end

Glycerol-3-Phosphate Glycerol-3-Phosphate is the major component in glycerol phospholipids formed by the reaction catalyzed by glycerol kinase

Lipoid Lipid bodies formed in the form of inclusions of poly (hydroxyalkanoic acid) (PHA) in prokaryotes

Lysophosphatidic acid Lysophosphatidic acid is the intermediate in the triacylglycerols synthesis which is formed by the addition of first acyl group to glycerol-3-phosphate

Malonyl Co-A Malonyl-CoA is a coenzyme A derivative of malonic acid which plays a key role in chain elongation in fatty acid biosynthesis

Phosphatidic Acid Phosphatidic acids are the simplest diacylglycerophospholipids which are major constituent of phospholipids

Saturated Fatty Acid Saturated fatty acids are fatty acid which is devoid of double bonds in the fatty acid chain

Transesterification Transesterification is used to describe where an ester is transformed into another through interchange of the alkoxy moiety

Triacylglycerols (TAGs) Triacylglycerol is an ester derived from glycerol and three fatty acids

Unsaturated Fatty Acid Unsaturated fatty acids are fatty acid which possesses at least one or more double bonds in the fatty acid chain

Questions

1. Describe different types of reactor configurations possible for effective lipid fermentation?
2. Enumerate the factors responsible for an effective design of a bioreactor for improved lipid production?
3. What is meant by oleaginicity? Mention the advantages of yeasts/molds over other microbes?
4. Describe the biochemistry of lipid accumulation in oleaginous microorganisms?
5. What is genetic engineering? How can it enhance lipid accumulation in oleaginous microbes?

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Photobioreactors for Bioenergy Systems and Lipid Extraction Methods from Microalgae

Madhumi Mitra, Xavier Henry, Abhijit Nagchaudhuri and Kalyani Maitra

Abstract Biofuels, especially those derived from plant materials, are being heavily investigated as an alternative to fossil fuels. Unfortunately, issues related to the use of food crops and arable land have plagued biofuel production efforts. In response, algae are touted as a suitable biofuel feedstock: they exhibit high growth rates, readily metabolize fossil fuel combustion products, and thrive well in marginal environments or intensive systems. Despite this, the efficiencies of the current algal production systems, their scalability, and the eventual price of the final product still require much research. The following review will attempt to chronicle the evolution of algal photobioreactors and also discusses the methodologies for oil extraction through the current state-of-the-art technologies. In particular, it aims to identify the contemporary and emerging issues involved in culturing algae for nutrient recycling and production of biofuels and ultimately compile and highlight the proposed solutions for the optimization of these systems.

Keywords Algae · Bioenergy · Biofuels · Nutrient recycling · Photobioreactors

1 Photobioreactor

A bioreactor is a containment vessel which allows its user to exercise a certain degree of control over the biotic and abiotic parameters most influential to an organism's growth. In essence, a bioreactor creates an artificial environment which can be manipulated for the culturing of selected species. Depending on their design, the

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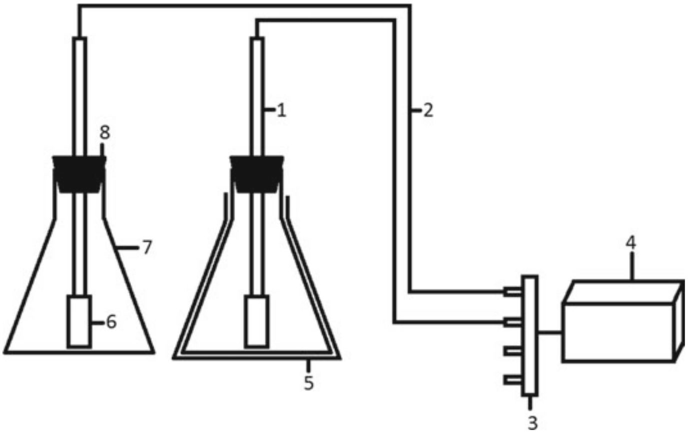

Fig. 1 Schematic of a simple Erlenmeyer PBR array; (1) 1 ml pipette, (2) airline hosing, (3) gang valve, (4) air pump, (5) optical filter, (6) rod air diffuser, (7) Erlenmeyer flask, and (8) rubber stopper

bioreactor may afford its operator the ability to culture their target organism with certain specific attributes or to densities not normally possible under natural conditions. Consequently, a photobioreacor (PBR) is a vessel that permits the growth of phototrophs (plants and certain bacteria), and as such, it seeks to mimic and or optimize the internal conditions to be suited to the process of photosynthesis (Fig. 1).

Typically, the conditions present within a given bioreactor are optimized to improve metabolic efficiency. For any PBR, considerable attention is given to the availability of light and carbon, the elements most critical for the synthesis of biomass. Additionally, considerations should also be given to other ecological aspects integral to the success of that organism. For microalgae, such factors may include temperature, pH, salinity, and the availability of certain micro- and macronutrients. In some instances, however, less than the optimum conditions may become desirable. Consider the parameters that might be varied during the course of experimentation to ascertain their effects on a given response. For example, an investigator may want to determine an alga's lipid accumulation response by severely limiting its access to nitrogen, a tactic integral for improving eventual biodiesel yields. In fact, it is the ability to perform these types of precise manipulations that has made PBRs indispensable in experimentation and research.

2 Desirable Characteristics for Algal PBRs

Culturing microalgae represents one of the most exciting yet challenging prospects for reshaping our energy future. Our continued reliance on energy derived from petroleum and even first-generation bioenergy crops has proven difficult to manage given their social, economic, and environmental implications. This is not to say that a shift toward microalgae will equate to a walk in the park either. A greater understanding of microalgal metabolism and how this may be enhanced by the culturing apparatus is needed in order to facilitate its large-scale production.

The most common systems in use today are open raceway ponds (ORPs) and closed PBRs (Fig. 2). ORPs consist of shallow ponds with a motorized paddle to move the culturing medium along a specified pathway (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Wang et al. 2012; Xu et al. 2009). The flow is maintained to prevent sedimentation of the microalgae and to encourage mixing of CO_2 which is sparged from the bottom of the pond. ORPs are one of the simplest and least expensive methods to cultivate algae, but they are plagued by high evaporation rates and contamination issues because of the "openness" of their design (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Wang et al. 2012). PBRs, on the other hand, offer more precise control of environmental conditions and are widely regarded as the better method of cultivating axenic cultures (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Wang et al. 2012).

As previously mentioned, most of the future success of algal biofuels will depend on how its raw material is produced. According to Lam and Lee (2012), based upon a survey of several culturing systems (Lee et al. 2014; Xu et al. 2009), effective microalgae production requires the following:

1. Adequate illumination area.
2. Optimal gas–liquid transfer.
3. Low contamination levels.
4. Low capital and production cost.
5. Minimal land area requirement.

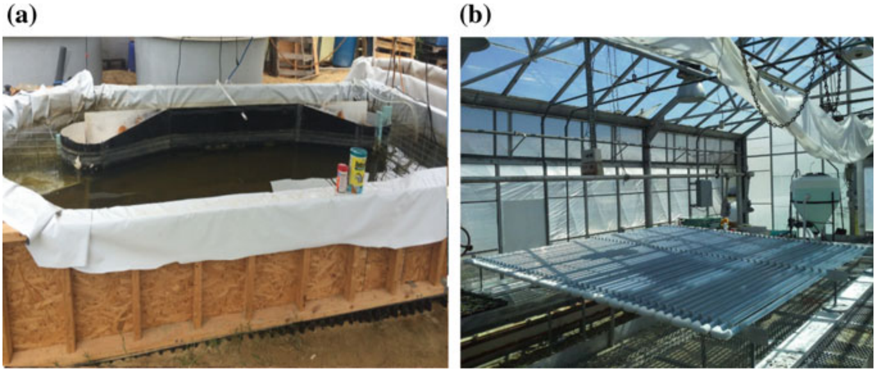

Fig. 2 Generalized characteristics of an ORP (**a**) versus a horizontal tubular PBR from Culturing Solutions, both at University of Maryland Eastern Shore, MD (**b**)

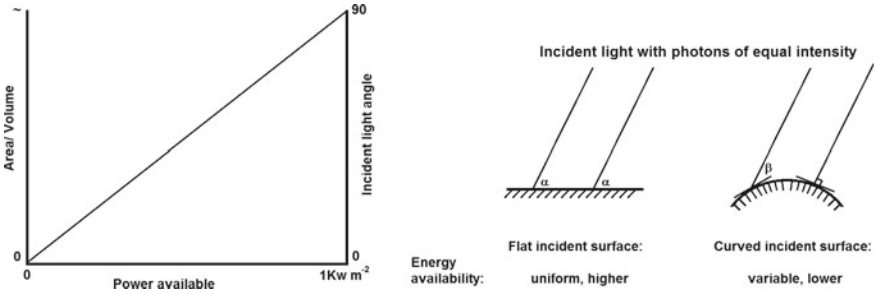

Fig. 3 Graph depicting relationships between culture system surface area-to-volume ratio, incident light angle, and power available as well as the effect of system surface shape on PFD

2.1 Adequate Illumination Area

As most microalgae are obligate phototrophs, it stands to reason that providing the maximal area for photon acquisition will be integral to culturing success. Therefore, for any productive PBR, there must exist some optimization between the system's light incident surface area, its incident surface angle and shape, as well as its eventual volume for retaining the algal medium (Fig. 3) (Saeid and Chojnacka 2014; Wang et al. 2012). All of these parameters will have some bearing on the consequent photon flux density (PFD) available to the alga's photochemical machinery. Anecdotely, most PBRs are designed to have a high surface area-to-volume ratio ensuring that each cell has reasonable exposure to the incident photons and to reduce losses via attenuation. Coincidentally, results from a study conducted in 1999 proved that efforts to restrict the incident light path to 10 cm resulted in optimal culturing conditions (Zou and Richmond 1999). Alternately, in more voluminous PBRs, culture agitation to ensure proper exposure to all cells or supplemental light from an embedded or strategically placed source may become necessary for production (Burgess and Fernández-Velasco 2006; Wang et al. 2012). In certain instances, this artificial light may be the only source of illumination and its quality and quantity may also be controlled to foster specific metabolic outcomes (Kuwahara et al. 2011; Pawlowski et al. 2014; Wang et al. 2014).

2.2 Optimal Gas–Liquid Transfer

The production of biomass in any PBR is predicated on the ability of the alga to draw from an adequate supply of carbon. This is facilitated by ensuring that there is optimal dissolution of CO_2 or a range of gases for that matter, within the algal medium (Cheng-Wu et al. 2001; Richmond and Cheng-Wu 2001; Wang et al. 2012; Zittelli et al. 1999; Zou and Richmond 1999). Equally as important is the off-gassing of O_2 from reactors. Under high concentrations of dissolved O_2 and high illumination levels, the propensity to liberate oxygen radicals which can damage algal cell structures increases (Wang et al. 2012). In the typical PBR, the effective management of gases will be dependent on several factors including

Gas type: This will determine its solubility within the PBR medium and ultimately the pool available for the alga. Most commonly, CO_2 is sparged into PBRs from an array of sources including pressurized cylinders, waste streams from industrial processes, and even combustive flue gases (Kao et al. 2014; Pawlowski et al. 2014). In scenarios where the PBR serves a dual function of biomass production and bioremediation, the scope of gases broadens to include oxides of nitrogen, sulfur, and even volatile organic compounds (Kao et al. 2014).

Surface area available for mixing at gas–liquid interface: In this context, what matters most is increasing the surface area of gas bubbles in relation to the volume of gas dispensed within the medium (Fernandes et al. 2014). Therefore, it is typically more desirable to achieve smaller diameter bubbles in higher densities than fewer larger ones to maximize the dissolution capability of the gas (Fernandes et al. 2014). Furthermore, significant efforts should be made to prolong the contact time between gas and medium by optimizing bubble path within the reactor. Increasing this residence time by orienting paths with the greatest distance ensures adequate opportunity for gas dissolution and limits off-gassing losses from the system (Fernandes et al. 2014; Pawlowski et al. 2014).

Mixing forces: Without the application of mixing forces, the PBR would either quickly equilibrate with ambient conditions or depending on the alga's growth phase, may be quickly exhausted (CO_2) or elevated (O_2) (Fernandes et al. 2014; Saeid and Chojnacka 2014). In most PBRs, this factor is directly related and controlled by the sparging or gas delivery system.

PBR temperature: As many PBRs essentially function as greenhouses, one undesirable effect is that of heat gain (Wang et al. 2012). This is especially observed under direct illumination by sunlight in addition to the inadequacy of regular heat dispersion pathways due to high algal densities within the system (Burgess and Fernández-Velasco 2006; Pereira et al. 2014; Wang et al. 2014). Another area where temperature plays a major role in PBR efficiency is that of gas dissolution. Following Henry's law, the solubility of a gas is highly dependent on temperature. Referring to the solubility graph for CO_2, it becomes apparent that for the large majority of targeted algae, optimum culturing temperature will be at odds with maximizing gas retention and utilization (Fig. 4) (Caroll et al. 1991). This especially proves problematic in instances where the management of process materials is of the highest priority, such as in PBRs for flue gas remediation. It may become necessary to cool gases down, through either storage or heat exchangers, to increase solubility while also recapturing and recycling non-dissolved gas to improve the remediation capability of the system and maximize biomass production (Kao et al. 2014).

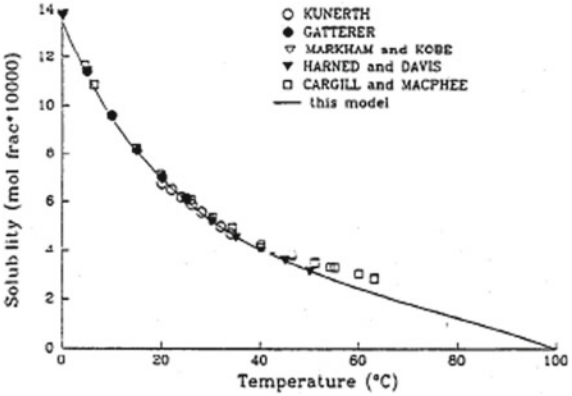

Fig. 4 Solubility of carbon dioxide in water as reported by Caroll et al. (1991)

2.3 Low Contamination Levels

Traditionally, open raceway ponds (ORPs) are used to culture algae in extensive operations. ORPs are typically comprised of shallow ponds with a motorized paddle to move the culturing medium along a specified pathway (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Xu et al. 2009). Due to their simplicity, ORPs continue to be one of the least expensive methods to cultivate algae. Due to the "openness" of their design, significant efforts are usually required to deter grazing and limit contamination by unwanted organisms (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Saeid and Chojnacka 2014; Wang et al. 2012). In certain instances, this problem may be mitigated by the addition of substances to control pests or even the growth of extremophiles under certain conditions. PBRs, which are typically self-contained units, are widely regarded as the better method of cultivating and maintaining axenic cultures (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Saeid and Chojnacka 2014). Since no system will ever be completely fail-proof, it is necessary to employ methods to actively prevent and manage contaminations during culture.

2.4 Low Capital and Production Cost

Arguably one of the most dissuasive factors for the proliferation of PBR in the algal production sector is the significant capital investment required to commence a program (Fernandes et al. 2014; Holtermann and Madlener 2010; Kovacevic and Wesseler 2010; Lam and Lee 2012; Malcata 2011; Oltra 2011; Singh and Olsen 2011; Sun et al. 2011; Wijffels and Barbosa 2010; Slegers et al. 2011; Zittelli et al. 1999). When comparing the typical costs over a project's lifetime, it becomes clear why most extensive algal production systems prefer ORPs to PBRs (Fernandes et al. 2014; Saeid and Chojnacka 2014). While there is still significant variation in the cost of PBRs due to intrinsic system characteristics, the startup and maintenance costs clearly overshadow that required for simply digging a hole in the ground. In fact, the majority of the costs associated with extensive PBR operations are linked directly to scale-up (Christenson and Sims 2011; Demirbas and Demirbas 2011; Lam and Lee 2012; Rawat et al. 2011; Singh and Olsen 2011; Subhadra 2010; Vyas et al. 2010; Wang et al. 2012; Wijffels and Barbosa 2010). Consider a bench-scale PBR of 1L producing 2 g L^{-1} d^{-1} of biomass versus an industrial scale reactor producing enough biomass to fuel hundreds of vehicles daily! Imagine the sheer volume of such an operation, its complexity, and then finally the capital required to see it through construction. It is no wonder why significant efforts are being undertaken to incorporate low-cost materials and simplify fabrication to improve the eventual economics. Yet still, many modern PBR designs still struggle with efficiencies concerning illumination, heat management, surface area—volume ratio, and gas exchange (Cheng-Wu et al. 2001; Richmond and Cheng-Wu 2001; Slegers et al. 2011; Zittelli et al. 1999; Zou and Richmond 1999). Despite this, there are indications that gains are still possible through the use of novel designs and tools used in cross-cutting applications (Richmond and Cheng-Wu 2001; Slegers et al. 2011; Zou and Richmond 1999).

2.5 Minimal Land Area Requirement

Minimizing the physical footprint of any algal production system is key to increasing efficiency and reducing costs (Holtermann and Madlener 2010). In addition to efficiency and cost concerns, the competition with acreage for food production, urbanization, and even other renewable energy activities can heavily impact the decision with algal operations. The use of PBR technologies can significantly reduce space requirements over ORPs by increasing volumetric productivity. The production levels necessary to sustain any impactful biofuel venture will still demand considerable land use (Holtermann and Madlener 2010; Kandilian et al. 2014; Saeid and Chojnacka 2014). At the center of high spatial requirement issue, it is the need for uniform and consistent exposure of all algal cells to the PAR (Saeid and Chojnacka 2014). This poses a problem even more in PBRs since these are expected to increase cell densities beyond what is capable in ORPs. As a result, to support the large volumes required, a balance must be struck between energy inputs for equal illumination and the available illuminable surface area of the installation (Kandilian et al. 2014).

3 PBR Inputs

Culturing microalgae represents one of the more exciting and challenging aspects related to changing our energy future. As previously illustrated, reliance on fossil fuels and even biofuels from first-and second-generation fuel crops can be unsustainable without any social, economical, and environmental implications (Demirbas 2009; Russi 2008; Subhadra 2010; Timilsina and Shrestha 2011; Zidanšek et al. 2009). However, a switch toward microalgae will not likely equate to a “walk in the park” either. Instead, much research and experimentation (beyond what is currently being undertaken) are needed to make the widespread adoption of algal bioenergy a reality. A greater understanding is needed of the metabolic processes used to convert nutrients into viable substances, including the effects of light, C, and other nutrients, in addition to the equipment that will allow for algae’s large-scale production.

3.1 Light

As plants, microalgae need light to convert CO_2 and water into the substances necessary for their survival. Depending on the type of microalgae, the products of this reaction range from starches to low-density lipids that accumulate within their cells (Chen et al. 2011a, b; Phukan et al. 2011; Singh and Olsen 2011). Studies have actually indicated that microalgae are more efficient at harnessing photosynthetically available radiation (PAR) than higher plants (Chen et al. 2011a, b; Smith et al. 2010). Yet it is interesting to note that the photochemical conversion of light energy in microalgae is not an efficient process (6% efficiency), owing to only partial absorption (400–700 nm) of total incident radiation (Lee et al. 2014; Stephenson et al. 2011; Wang et al. 2012). The methods to improve this aspect of photosynthesis will prove valuable in increasing biofuel yields.

Accordingly, there has been much experimentation on the effects of light varied characteristics on algae. Tests with *Dunaliella tertiolecta* were carried out to determine the effects that light source, intensity, and photoperiod had on algal performance (Tang et al. 2011). For the test, three light sources (white and red light-emitting diodes and a fluorescent light), three intensities (100, 200, and 350 $\mu E/m^2\ s^{-1}$), and three photoperiods (15 h light: 9 h dark, 12 h light: 12 h dark, and 24 h light: 0 h dark) were investigated. The results indicated that greater light intensities and longer photoperiods yielded the greatest biomass accumulations. Unexpectedly, light source was deemed insignificant, and this result was corroborated by a similar experiment with *Arthrospira platensis* (Tang et al. 2011). The researchers did make efforts to explain the observed behavior, stating that it likely resulted from the relatively low light intensities used during the trial. Regularly, the effects of pigmentation are manifested above 3000 $\mu E/m^2\ s^{-1}$ (Tang et al. 2011). In other trials testing the effects of light pigmentation, acetate filters were successfully used to cultivate or maintain algal cultures by selectively filtering incident light (Fig. 5) (Chen et al. 2011a, b; Mohsenpour et al. 2012; Ko and Noike 2002).

Fig. 5 Trial investigating the effects of spectral filtering using acetate films on *Chlorella vulgaris,* University of Maryland Eastern Shore, MD

3.2 Carbon

In a similar fashion, much experimentation has been undertaken to identify the optimal CO_2 concentration for maximum algal productivity. There is a general misconception that the higher the CO_2 concentration, the more is the eventual biomass. Investigations have shown that in most reactions, there is a point of diminishing returns. The same holds true for CO_2, although this limit is highly species-dependent as shown in Table 1 (Kumar et al. 2010; Larkum et al. 2012; Tang et al. 2011). As reported by Tang, maximum growth rates for *Dunaliella tertiolecta* were experienced between two and six percent CO_2 concentrations, while percentages outside this range resulted in decreased yields. What is certain, however, is the fact that regular atmospheric CO_2 concentrations will support microalgal growth, although better yields will require slightly higher concentrations (Kumar et al. 2010). This realization is partly responsible for the impetus to develop microalgal production in tandem with anthropogenic C sources (Christenson and Sims 2011; Demirbas and Demirbas 2011; He et al. 2012; Holtermann and Madlener 2010; Kao et al. 2014; Kumar et al. 2010; Lee et al. 2014; Markou and Georgakakis 2011; Malcata 2011; Nigam and Singh 2011; Odlare et al. 2011; Rawat et al. 2011). The anticipation is that flue gases could be scrubbed of their C, thus reducing GHG emissions. At the same time, the microalgae are supplied with a source of C at levels suitable for large-scale biofuel production (Demirbas and Demirbas 2011; He et al. 2012; Holtermann and Madlener 2010; Kao et al. 2014; Kumar et al. 2010; Lee et al. 2014; Markou and Georgakakis 2011; Malcata 2011; Odlare et al. 2011; Rawat et al. 2011).

Table 1 Maximum published CO_2 tolerances for selected species of alga as reported by Kumar et al. (2010), Larkum et al. (2012), and Tang et al. (2011)

Species	Known maximum CO_2 concentration (%)	References
Cyanidium celdanum	100	Seckbach et al. (1971)
Scenedesmus sp.	80	Hanagta et al. (1992)
Chlorococcum littorale	60	Kodama et al. (1993)
Synechococcus elongates	60	Miyairi (1997)
Euglena gracilis	45	Nakano et al. (1996)
Chlorella sp.	40	Hanagta et al. (1992)
Eudorine spp.	20	Hanagta et al. (1992)
Dunaliella tertiolecta	15	Nagase et al. (1998)
Nannochloris sp.	15	Yoshihara et al. (1996)
Chlamydomonas sp.	15	Miura et al. (1993)
Tetroselmis sp.	14	Matsumoto et al. (1995)

3.3 Water

One input often overlooked but is critical to any algal production system is water. For large-scale production of algal biomass to be feasible, it should compete neither for sources geared toward consumption nor for food production (Holtermann and Madlener 2010). This, in effect, has driven much research toward using sources that are beyond the scope of normal societal use including brackish or full strength seawater, as well as process effluents to include treated and untreated wastewater and even animal slurries (Christenson and Sims 2011; Holtermann and Madlener 2010; McGinn et al. 2012; Guerrero-Cabrera et al. 2014). In fact, sources such as these are even more desirable since nutrients, which would otherwise have to be supplemented, are often readily available in excess. This removes the additional costs and complexities from the operation while simultaneously providing bioremediation or ecosystem services to activities which could otherwise negatively impact the environment (Christenson and Sims 2011; McGinn et al. 2012; Guerrero-Cabrera et al. 2014).

3.4 Other Nutrients

In addition to C, there are several other nutrients required for the metabolic processes of microalgae that are not directly involved with photosynthesis. The most notable are N and P (Kumar et al. 2010). These nutrients are made available to microalgae from a myriad of sources (Flynn and Butler 1986; Kumar et al. 2010). Nitrates and phosphates are readily available to wild microalgae, largely through the misuse of agricultural fertilizers (Noh et al. 2004; Randall and Mulla 2001). Also available, in increasing quantities, is ammonium due to either the reduction of atmospheric N or the activity of the enzyme urease on urea (Bekheet and Syrett 1977; Flynn and Butler 1986; Glibert et al. 2006; Kumar et al. 2010).

The efflux from the combustion of fossil fuels are a significant source of atmospheric N-containing compounds (He et al. 2012; Holtermann and Madlener 2010; Kao et al. 2014). Through the processes of atmospheric wet and dry depositions, aerial fertilization is becoming increasingly relevant in determining N fluxes and concentrations at the land-air-water margins (EPA 2012).

Another promising avenue for algaculture is through the bioremediation of effluents from other nutrient-rich activities. At the forefront are wastewater treatment facilities, animal production systems, and more recently, aquaculture operations whose effluents tend to have elevated levels of N- and P-containing compounds (McGinn et al. 2012; Guerrero-Cabrera et al. 2014). This allows operators to make use of resources which would have otherwise been discarded; therefore, reducing input costs while minimizing the end-of-process effects of these compounds had made their way into the natural environment (McGinn et al. 2012; Guerrero-Cabrera et al. 2014).

3.5 Power

While algae naturally utilize the sun's energy to produce biomass, increasing their productivity beyond that which is naturally possible, such as in PBRs, will require a concomitant increase in power. This power may be attributed to many systems of complex PBRs which may include power for mixing paddles, spargers, heating and cooling systems, supplemental lighting, and in some instances, the controls and instrumentation systems (Chen et al. 2011a, b; Wang et al. 2012). In large-scale PBR operations, this power requirement may be significant and inevitably may determine the economic viability of the activity (Chen et al. 2011a, b; Holtermann and Madlener 2010). It is in the operator's best interest to keep the system's power requirements low which is typically achieved in one of several ways. The first method typically involves utilizing the effects of one process to meet several system needs. Vertical lift PBRs, for example, were borne out of this particular strategy. For that, the sparger at the base of a small diameter column is used as the primary source of aeration while simultaneously providing mixing forces to ensure adequate illumination of all algal cells within the medium and to deter cell aggregation or sedimentation (Wang et al. 2012).

Incorporating renewable energy technologies either as the sole power source or to supplement a portion of the system's total power requirement is another method for reducing dependence on the traditional grid (Burgess and Fernández-Velasco 2006; Saeid and Chojnacka 2014). This trend, however, is highly dependent on the availability of these renewable energy resources in the vicinity and the ability to outlay the initial capital required to install such facilities on site.

4 PBR Designs

PBRs are usually enclosed tanks or tubes made of glass or acrylic sporting a variety of structural arrangements (Demirbas 2010; Demirbas and Demirbas 2011; Lam and Lee 2012; Xu et al. 2009). Commonly seen arrangements include helical tubes and vertical and near-horizontal tubular arrays with flat plate reactors becoming increasingly popular (Figs. 6, 7, 8, and 9) (Cheng-Wu et al. 2001; Chisti 2007; Demirbas 2010; Demirbas and Demirbas 2011; Richmond and Cheng-Wu 2001; Slegers et al. 2011; Zou and Richmond 1999).

The upsurge in flat plate reactors is credited to their approach in dealing with light path issues experienced in the other PBR designs (Richmond and Cheng-Wu 2001; Slegers et al. 2011; Zou and Richmond 1999). Results from a study conducted in 1999 proved that decreasing the light path to 10 cm through flat plate PBR resulted in optimal culturing conditions (Zou and Richmond 1999). Despite this, more research

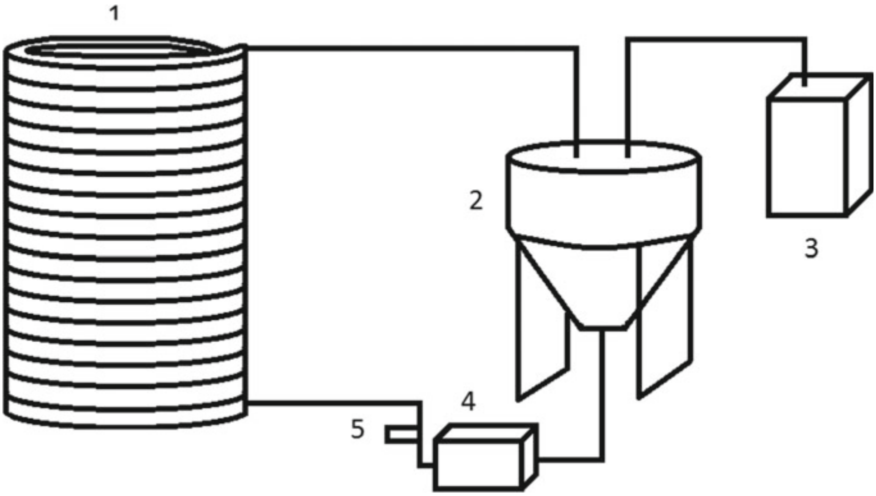

Fig. 6 Basic schematic of a helical tube PBR; (1) helical tube photo array, (2) recirculation tank, (3) controller and module, (4) recirculation pump, and (5) harvesting outlet

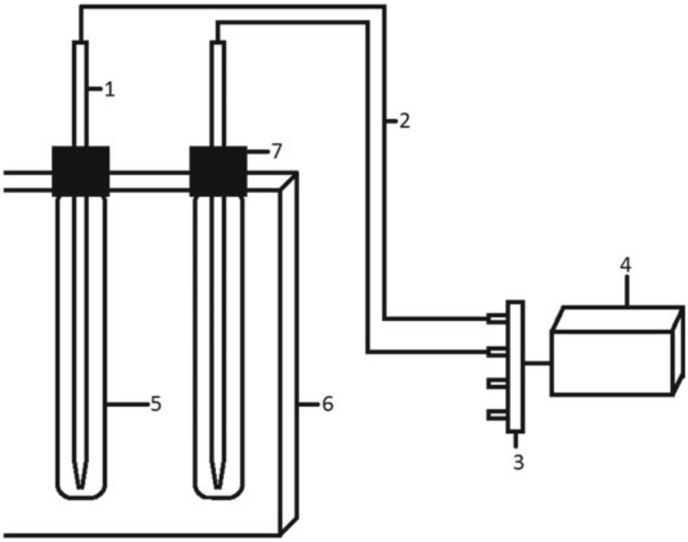

Fig. 7 Basic schematic of a vertical tubular (test tube) bubble column PBR; (1) 1 ml pipette, (2) airline hosing, (3) gang valve, (4) air pump, (5) 15 ml test tube, (6) test tube cradle, and (7) modified screw cap with off-gassing vent

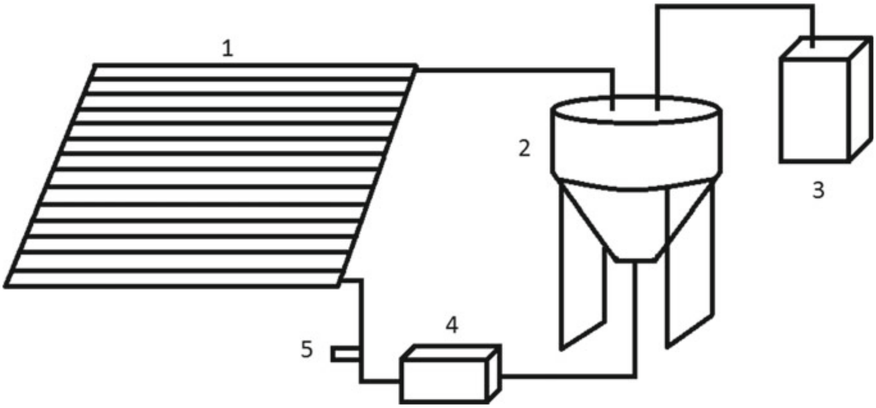

Fig. 8 Basic schematic of near-horizontal tubular PBR; (1) tubular PVC photo array, (2) recirculation tank, (3) controller and module, (4) recirculation pump, and (5) harvesting outlet

leading to PBRs improvements is still needed. The issues with respect to cooling, system cost, and scalability still pose significant challenges to large-scale production (Cheng-Wu et al. 2001; Richmond and Cheng-Wu 2001; Slegers et al. 2011; Wang et al. 2012; Zittelli et al. 1999; Zou and Richmond 1999). Nevertheless, with the aid of sound scientific principles, it seems as though the imagination will be the only limit concerning the final structural arrangement of a PBR.

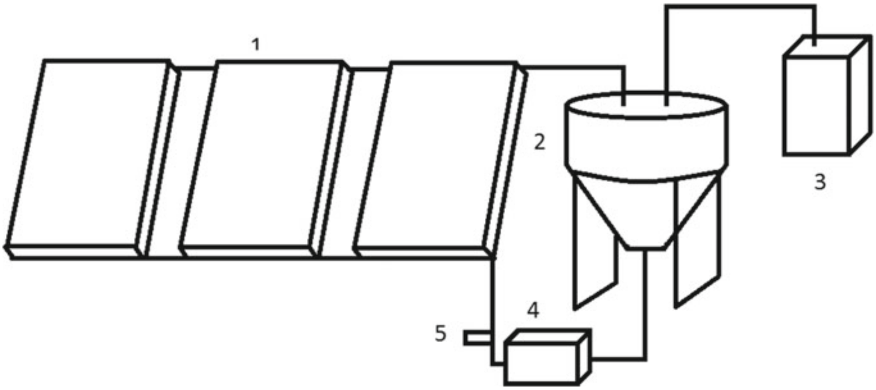

Fig. 9 Basic schematic of a flat plate PBR; (1) flat plate photo arrays, (2) recirculation tank, (3) controller and module, (4) recirculation pump, and (5) harvesting outlet

5 Instrumentation and Control Systems

Since one of the key advantages of PBRs is the level of environmental control they allow, it is no surprise that increasing numbers of PBRs are being outfitted with sophisticated microprocessor systems and a wide array of sensors. This is advantageous as the management of multiple parameters is greatly simplified (Pawlowski et al. 2014). Sensors typically integrated in instrumented PBRs include pH, temperature, conductivity, REDOX, and in certain instances, selective ion devices. Many times, the instrumentation can be achieved through relatively inexpensive sensors and probes which can serve to significantly reduce system costs. Invariably, these types of systems tend to be those developed for bench-scale studies although the data quality may even rival their more expensive counterparts. Through the integration of microprocessors, additional functionalities are also possible such as continuous data logging for making on-the-fly decisions or even active control of environmental and chemical conditions within the PBR (Pawlowski et al. 2014).

6 PBR Productivity

When deciding the suitability of one species over another for biofuel production, their ecologies need to be considered. Under high nutrient loads (eutrophy), both micro- and macroalgae display opportunistic behaviors forming expansive blooms. However, phytoplankton blooms will manifest more quickly due to faster growth rates and more efficient nutrient uptake mechanisms (De Paula Silva et al. 2008). Macroalgae usually require the presence of substrate, which may introduce challenges with locating suitably large areas for cultivation. Microalgae, on the other hand, do not have such requirements and are perfectly suited to growth in shallow or confined spaces such as open ponds or PBRs, although decreased yields are likely in smaller culturing environments (Cheng-Wu et al. 2001; Chisti 2007; Richmond and Cheng-Wu 2001). Most importantly, between the two groups, it is microalga that exhibits the highest growth rate, a key for any biofuel feedstock (Wang et al. 2012). In fact, under certain manipulations of nutrient loading, some species can be made to attain lipid contents approaching 80% their weight (Chisti 2007).

The effect of nutrient limitation on microalgal lipid production is increasingly gaining significance. It is documented that limiting N concentrations in microalgal production systems results in increased lipid formation as a natural response to stress (Chen et al. 2011a, b; Dragone et al. 2011; Flynn and Butler 1986; Illman et al. 2000; Jiang et al. 2012; Kumar et al. 2010; Řezanka et al. 2011). When the effects of varied N concentration on *Dunaliella tertiolecta* were investigated, it was found that low levels of ammonium and nitrate resulted in rapid and significant accumulations of neutral lipids (Chen et al. 2011a, b). It was also noted that high nitrate concentrations produced the most algal biomass (Chen et al. 2011a, b). Similar results were reported for N limitation on the microalga, *Chlorella* sp.; low nitrates reduced biomass accumulations but also increased lipid content by 63% (Illman et al. 2000). While limiting the availability of N induces a response to increase lipid production, it simultaneously reduces the capacity of cultures to increase biomass. Therefore, striking a balance between these two conditions will be essential for increasing the efficient production of feedstock for bioenergy applications.

7 Microalgal Oil

Microalgae thrive in water bodies and are excellent potential feedstock for the production of next-generation biofuels. These simple photosynthetic organisms contain pigments that directly harvest sunlight and assimilate atmospheric carbon dioxide in an aquatic environment to produce biomass for its growth (Hu et al. 2008). Microalgae also store and accumulate neutral lipids in their thalli as triacylglycerides (TAG) that can be extracted to be transformed into fatty acid methyl esters (FAMEs), which is the main component of biodiesel (Sheehan et al. 1998). The high oil content of several naturally occurring algal species ranges from 15 to 80% of its dry biomass and are, therefore, very promising sources for biofuel production than conventional oil crops, which produce only 5% oil of its dry mass (Zhou et al. 2013). Microalgae have less water and land requirements for their growth when compared to land growing crops. Moreover, their flexible metabolism allows them to produce and store lipids, carbohydrates, and proteins in different amounts depending on the nutrient available in the cultivating environment (Shifrin and Chisholm 1981; Cho and Thompson 1986; Sukenik and Carmeli 1990). Several studies have been done targeting to boost the lipid storage ability of microalgae, which includes nutrient limitation (Suen et al. 1987), heterotrophic growth model (Ceron Garcia et al. 2005), and genetic engineering (Kilian et al. 2011). Efforts of engineering microalgae with high lipid biosynthesis ability by blocking or disrupting competing pathways have been successful but showed decreased growth rate of the strains and hence less biomass accumulation (Wang et al. 2009; Li et al. 2010; Work et al. 2010; Radakovits et al. 2011). To circumvent this issue, researchers have targeted knockdown of lipid metabolism by engineering of lipid catabolism without disrupting the carbohydrate pool, which is the primary carbon storage product for these organisms (Trentacostea et al. 2013). There is also a report on the use of bioactive small molecules that trigger protein function on desired phenotype and modulate its lipid productivity (Franz et al. 2013).

Although microalgae offer an attractive pathway as a renewable energy source for the biofuel industry, there are several challenges yet to be tackled for their production at a commercial scale to meet the energy need of the future. The science of algal biofuel is still at its infancy, and rapid growth of this feedstock will require substantial investment in research and development (Scott et al. 2010). For the viability of the biofuel value chain, there is a great demand and need for the optimization of all steps involved—starting from the generation of the raw material to product delivery. One such area in this pipeline involves determining and/or screening of these oleaginous microalgae for their lipid content. Some of these protocols routinely used for determining the oil content of microalgae are discussed in the following sections.

8 Lipid Extraction Methods

Due to their taxonomic and ecological diversity, an estimated 300,000 naturally occurring algal species flourish in the aquatic environments (Guarnieri et al. 2013; Radakovits et al. 2010). Moreover, genetic engineering offers different tools to produce new strains of microalgae with improved, desired traits. It is imperative to have dependable, rapid, accurate, and reliable screening methods for algal oil content determination. Both qualitative and quantitative estimations of lipid content are crucial for identifying the suitable strain for the production of biofuels. The neutral lipid content of microalgae comprises mainly of triacylglycerides (TAGs), the most desired component of biodiesel (Sheehan et al. 1998). There are considerable variations among microalgal species differing in shape, size, cell membrane composition, and the type of lipid stored in their cells. Thus, the process of lipid extraction, methods of quantification, or screening of algal oil content may have variable responses and often vary among species. There is yet any mention in the literature of a single, unique standardized method that can accurately quantify and detect the composition of algal oil across the spectrum universally.

The initial disruption of cell wall in microalgae can be achieved by mechanical means such as sonication, grinding, bead beating, freezing, or ultrasound (Prabakaran and Ravindran 2011; Medina et al. 1998; Araujo et al. 2013). The dual step involved in the conventional *gravimetric* technique of oil quantitation consists of cell disruption to expel the oil from the lipid bodies following its extraction using a mixture of chloroform/methanol and water mixture. The general extraction methods for lipid recovery were separately devised by Folch et al. (1957) and by Bligh and Dyer (1959) using a varying ratio of chloroform–methanol mixture, different sample quantity, and the presence or absence of sodium chloride in the purification step with water. In both the methods, the monophasic solvent system extracts and dissolves the lipids following the addition of water that creates the biphasic layer leading to the separation of the polar and non-polar molecules into the upper and the lower non-polar phases, respectively. Due to its toxic effects, replacement of chloroform with dichloromethane or other solvent systems proved to be less efficient for the extraction process (Kumari et al. 2011; Go et al. 2012). Another method for lipid extraction uses supercritical carbon dioxide (SC-CO_2) for the extraction of non-polar molecules, and if needed, isopropanol acts as a modifier to increase the solvents' polarity (Halim et al. 2011).

9 Lipid Analysis

The "lipid" obtained from microalgae mainly comprises of neutral triglycerides and saturated, unsaturated, or polyunsaturated fatty acids. Algal oil's potential as biodiesel is dependent on the nature of the saturated and polyunsaturated fatty acids present, and this ranges from 14 to 18 carbon chain length, such as C14:0, C16:0, C16:1, C18:0, C18:2, and C18:3. To maintain certain standards for biodiesel used in the transportation industry, the presence of some fatty acids is undesirable as these lower the efficiency of the fuel and engine compatibility (ASTM International, ASTM D6751–15ce1, http://www.astm.org/Standards/D6751.htm). To qualify for these specific physical and chemical properties, knowing the chemical composition and structure of the algal lipid is crucial for assessing its fuel potential. Profiling of the extracted lipid and its identification and quantification of the different components are often achieved by traditional techniques of *chromatography*, such as thin-layer chromatography (TLC), gas chromatography-mass spectroscopy (GC-MS), or high-pressure liquid chromatography (HPLC) (Eltgroth et al. 2005; Gu et al. 2011; Barupal et al. 2010). In all these chromatographic separation methods, the individual components present in the lipid extract are characterized by comparison to different known fatty acid standards. The GC-MS and HPLC are very robust and are often used for lipid quantification.

Transesterification is the commonly used method evidenced in the literature where the lipids in the biomass are directly converted to their methyl esters (biodiesel) by reaction with methanol in the presence of an acid or a base as a catalyst (Johnson and Wen 2009). Glycerol is a by-product formed in this process, and the fatty acid methyl esters (FAMEs) obtained are routinely characterized by gas chromatography (GC), liquid chromatography-mass spectroscopy (LCMS), and GC-MS. This is one of the most commonly employed methods for quantification of the composition of algal oil.

Studies detecting the algal oil components have used *Raman spectroscopy* with lasers to alter vibrational energy state of the molecule, which in turn provides information about the nature of the chemical bonds present in the molecule and its structure (Wu et al. 2011; Samek et al. 2010).

Nuclear magnetic resonance (NMR) spectroscopy is another spectral technique that has been widely used for exploring the biodiesel potential of microalgae produced on a small scale. This technique usually involves the extraction of the oil from the biomass, following its screening and profiling to determine its composition by running several proton (^{1}H), carbon (^{13}C) one- and two-dimensional (1D, 2D) NMR experiments (Gao et al. 2008; Sarpal et al. 2016a, b).

The use of *Fourier-transform infrared spectroscopy* (Stehfest et al. 2005; Dean et al. 2010) enables the qualitative detection of the carbonyl group vibration present in esters (typical carbonyl group C=O assignment at 1740 cm^{-1}) derived from lipids and fatty acids.

Colorimetric techniques use the sulfo-phospho-vanillin (SPV) color developer (Cheng et al. 2011) to estimate the lipid content, and the degree of color change is proportional to the lipid content. The use of triethanolamine-copper (TEA-Cu) salts replacing SPV turned out to be less time consuming, more sensitive, and minimal labor (Chen and Vaidyanathan 2012; Wawrik and Harriman 2010).

The growing demand for robust method to monitor algal growth and its rapid screening to quantify its oil content has introduced the two most viable, rigorously used *fluorescent lipid probes*—Nile Red and BODIPY (boron-dipyrromethene) as evidenced in the literature.

Nile Red is a fluorescent neutral lipid binding dye that permeates through the cell wall to bind lipid droplets and allows rapid qualitative determination of lipid (Cirulis et al. 2012). The dye fluoresces yellow or red under the emission and excitation filters of the fluorescence microscope, and this range can vary with the protocol being used involving staining time, temperature, and cell wall rigidity. The cells are stained in the presence of a carrier solvent (dimethyl sulfoxide or ethanol), which helps the permeation of the dye into the interior of the cell. The Nile Red fluorescence response varies for each algal species and strain, and therefore, each protocol requires optimization. This experiment when done on a microplate (96-well plate) can monitor several reactions at the same instant very efficiently and produce high throughput data (Franz et al. 2013).

The BODIPY is a green lipophilic neutral fluorophore that binds to a wide range of both neutral and polar lipids, and unlike Nile Red, the presence of chlorophyll a is distinct and does not interfere with the fluorescence of the dye (Cirulis et al. 2012). Moreover, unlike Nile Red, BODIPY does not localize in the cytoplasmic compartments other than lipid bodies. Optimization of BODIPY staining method is required for different species of algae, and these parameters are dependent on the nature of the microalgae undergoing the screening process.

From the discussions of the several methods cited in the literature, it is clear that lipid content analysis is typically a function of the viability of the selected method for the microalgae species and strains under investigation. It is imperative that the suitability of the method of choice will be dependent on the type of information required from the assay for that particular strain. For high throughput efficient screening of algal oil as potential biofuel, the method of choice for analysis should be robust, optimized with reproducibility for both qualitative measurements and quantifying the composition of the algal oil. Usually, one or more of these methods are adapted in conjunction for the analysis process. One such example can be rapid qualitative screening of a particular algal species by the Nile Red technique for its oil content following the extraction of the neutral lipid by Bligh and Dyer (1959) technique and its quantification by running the FAME analysis to determine the components present in the extracted lipid.

Ultimately, the availability of instrumentation, facility support, amount of the algal biomass present, and information needed is a crucial deciding factor for the choice of a particular method employed for lipid analysis. The algal biofuel research is still rapidly growing every day, and ambitiously one can predict that with this progression rate, suitable techniques with broader scientific adaptability are going to be in place in near future.

10 Commercialization

Commercialization represents one of the greatest challenges to the widespread adoption of PBR technologies to large-scale algaculture (Holtermann and Madlener 2010; Kandilian et al. 2014). As with many new technologies, especially those in the energy sector, significant capital investments are necessary to get projects off the ground with very little return on investment before its tenth year in operation (Holtermann and Madlener 2010).

Another aspect requiring much attention is yield production and scalability, areas where most PBR designs pose significant challenges (Chisti 2007). It is for this reason that the largest commercial algaculture operations utilize ORPs for their inherent simplicity and often rely on extremophilic algae and cyanobacteria, such as *Arthrospira platensis,* to limit contamination (Saeid and Chojnacka 2014). The simplification of PBR structures, as well as the adoption of low-cost materials for construction, may offer some reprieve in the area of scalability. However, increasing yield may still remain a function of reactor size and optimizing of harvest volume percentage (Cheng-Wu et al. 2001; Richmond and Cheng-Wu 2001; Saeid and Chojnacka 2014; Zittelli et al. 1999; Zou and Richmond 1999).

11 Future Trends

With the resurgence of interest in algal culturing for biofuels, bioremediation, and bioproducts, many are attempting to make improvements at various stages of its life cycle. The following are a few of the strategies identified as keys to the success of algal culture operations in the future.

11.1 Algae Production in Tandem with Industry, a Bioremediation Model

Bioremediation is a concept where living organisms are utilized to effect positive change within a polluted system. It is often regarded as the “greener” method for returning an ecosystem to healthier conditions with minimal negative impacts. Organisms normally used for this process exhibit certain biological traits, which make them suitable as bioremediation agents. These characteristics include rapid growth rates, high degree of environmental tolerance, and the ability to safely metabolize the targeted pollutants (Chisti 2007; Demirbas and Demirbas 2011; He et al. 2008). Christensen and Rorrer (2009) have reported that some algae are capable of absorbing several organic pollutants, and yet these represent only a fraction of the compounds possible for uptake. Numerous reports have also indicated their affinities for N-, P-, and S-containing compounds (Christenson and Sims 2011; Demirbas and Demirbas 2011; Kumar et al. 2010; Markou and Georgakakis 2011; Malcata 2011; Nigam and Singh 2011; Odlare et al. 2011; Perelo 2010; Rawat et al. 2011). So it is therefore not surprising to learn that microalgae are considered excellent bioremediative agents, especially when the act of remediation can lead to products of significant economic value. As a consequence of the dual benefit, remediation will continue to find its way into increasing numbers of algal production systems (Fig. 10) (McGinn et al. 2012; Guerrero-Cabrera et al. 2014).

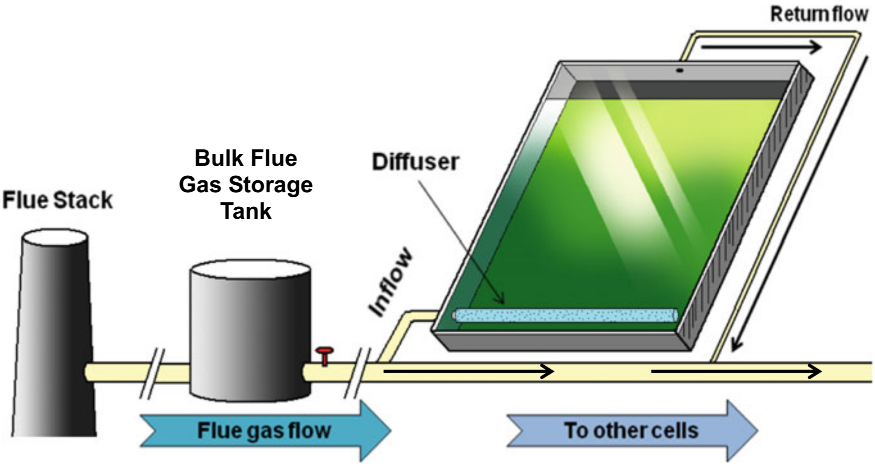

Fig. 10 Basic schematic of an integrated PBR flue gas stack system for bioremediation

11.2 *Increasing PBR Efficiency Through Process and Structures Optimization*

There are several challenges facing the use of PBRs for large-scale microalgae cultivation. As previously stated, issues with respect to yield, light attenuation and quality, cooling, and scalability still require attention (Cheng-Wu et al. 2001; Richmond and Cheng-Wu 2001; Slegers et al. 2011; Zittelli et al. 1999; Zou and Richmond 1999). Spectral filtering has been shown to impact microalgal yield and therefore has the potential to improve PBR designs (Ko and Noike 2002). The optimization of the photosynthetic properties of reactors by only transmitting useful radiation is something not well documented for microalgal production. Furthermore, the removal of wavelengths below 300 nm and above 700 nm may also aid in maintaining optimal culture temperatures (Chen et al. 2011a, b).

In addition to spectral improvements, the adoption of novel configurations, including flat plate and helical bioreactors, may also address some of the aforementioned shortcomings. The use of polyethylene bags and other inexpensive construction materials has also made inroads in improving the economics of PBRs and their viability in large-scale operations (Wang et al. 2012). Some of these strategies have been demonstrated in large commercial ventures. Furthermore, advances in event-based process control can aid in increasing PBR efficiency by reducing energy usage, increase accuracy, and therefore reducing waste of critical inputs such as CO_2 (Pawlowski et al. 2014; Saeid and Chojnacka 2014).

11.3 *Biorefineries*

Realizing that the economics for the large-scale cultures of algae for bioenergy is simply not there, it has been suggested that biorefineries could temporarily improve the outlook until the infrastructure is in place (Taylor 2008). The biorefinery approach would allow for other high-value products to be produced in tandem with the basal algae activities (Kandilian et al. 2014; Taylor 2008). The products suited toward this strategy include nutraceuticals, pharmaceuticals, pigments and chemicals, fish, shrimp, and other shellfish (Kandilian et al. 2014; Saeid and Chojnacka 2014). This allows the risk to be distributed across all facets of the operation, while allowing the natural evolution of technologies or the market to take place. Once this maturation has been achieved, additional energies may be focused toward up-gauging algae production either to meet the newly developed demand or for further diversification of the refinery portfolio.

Glossary

Axenic Culture a culture where only one specific species is present.

Open Raceway Pond a shallow “racetrack” shaped pond that consists of a raised central berm (which creates two distinct but connected channels) and utilizes a motorized paddle to move the cultured algae through its channels. A shallow pond with a motorized paddle to move the culturing medium along a specified pathway.

Photobioreactor a vessel that permits the growth of phototrophs (plants and certain bacteria), and as such, it seeks to mimic and or optimize the internal conditions to suited to the process of photosynthesis.

Questions

1. Design a qualitative model to describe the most important variables and dynamics found within an algal photobioreactor.
2. Given the concerns over the commercial viability of PBRs for algal production, debate their suitability within the energy, pharmaceutical, or environmental sectors. Which, in your opinion, will offer the greatest return on investment?
3. What are the different methods of lipid extractions for microalgae? Which one would you apply for microalgal species like *Chlorella* and *Spirulina*?

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Thermochemical Conversion of Biomass

Serpil Guran

Abstract Sustainable biomass, with number of environmental and economic advantages, has enormous potential in reducing fossil fuels usage to mitigate climate change and achieving low-carbon economy. Because of variety of biomass species with numerous physical and chemical properties, conversion of biomass feedstocks into bioenergy and bio-based products involves a broad diversity of existing and emerging pre-treatment and conversion technologies. Biomass conversion into power, heat, fuels and bio-based products, based on the specific feedstock, is generally categorized into two major conversion pathways—biochemical and thermochemical. Thermochemical conversion technologies to convert sustainable biomass and organic waste into energy forms (heat, power, fuels and bio-based materials) can be categorized as direct combustion, gasification and pyrolysis based on the amount of oxidizing agent present. In this chapter, biomass thermochemical conversion to low-carbon energy and bio-based product production pathways is discussed.

Keywords Sustainable biomass · Thermochemical conversion · Combustion · Gasification · Pyrolysis

1 Introduction

Sustainable biomass, with number of environmental and economic advantages, has enormous potential in reducing fossil fuels usage to mitigate climate change and achieving low-carbon economy. The price volatility of high-carbon fossil fuels proves that there is need for renewable, secure and reliable, low-carbon feedstocks and efficient, scalable biomass conversion technologies for clean energy generation to secure sustainable growth and stay resilient.

In order to achieve effective biomass-to-energy and bio-products pathways, the clean energy industry needs access to information that can reduce start-up risks,

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including strategies and information for securing local feedstocks, efficient conversion technologies that are tested and verified and policies to stimulate market demand for low-carbon biofuels and bio-products (Brennan-Tonetta et al. 2014). This stresses the importance of biomass sustainability that has been long discussed and a debated matter.

1.1 Sustainable Biomass

In addition to the social concerns over the food to fuel pathway and diverting food crops to energy generation, the utilization of corn ethanol and soybean biodiesel is still been debated and researched for their environmental impacts such as increased greenhouse gas (GHG) emissions, land use change, loss of carbon sinks and increased carbon release from soils (Fargione et al. 2008; Hertel et al. 2010; Searchinger et al. 2008). Further concerns stress that the impacts of traditional energy crops such as clearing additional land for agriculture, increasing the net carbon footprint by releasing stored soil carbon and eliminating the carbon sink function of the once intact ecosystem should be avoided (Hertel et al. 2010; Searchinger et al. 2008). Therefore, it is critical to utilize "Sustainable Biomass" for clean energy development to avoid unintended negative impacts.

Sustainable Biomass: Biomass feedstocks do not follow food to fuel pathways and do not result in forest conversion and/or land clearing for biomass production plantations. Organic matter includes agricultural crop residues (i.e., straw, husks, corn cobs, leaves, brunches), dedicated and non-invasive fuel crops (fast-growing trees and grasses, i.e., aspen, poplar, willow, switchgrass), native vegetation, forest residues, animal manure (i.e., equine, dairy and poultry), aquatic species (i.e., algae, duckweed) and unrecycled biomass in waste streams (food waste, yard waste, unrecycled waste paper, cardboards, untreated waste wood, landfill gas, biogas from digester including wastewater treatment facilities) used as feedstocks and inputs in bioenergy and bio-products industries for low-carbon energy (low-carbon power and heat, advanced biofuels, drop-in fuels, compressed natural gas (CNG) and liquefied natural gas (LNG) applications) and bio-based products manufacturing to displace petroleum-based counterparts.

Because of the variety of biomass species with numerous physical and chemical properties, conversion of biomass feedstocks into bioenergy and bio-based products involves a broad diversity of existing and emerging pre-treatment and conversion technologies. Biomass conversion into power, heat, fuels and bio-based products, based on the specific feedstock, is generally categorized into two major conversion pathways—biochemical and thermochemical (Fig. 1).

This chapter focuses on "Thermochemical Conversion Technologies" of biomass into useful energy forms and bio-based products.

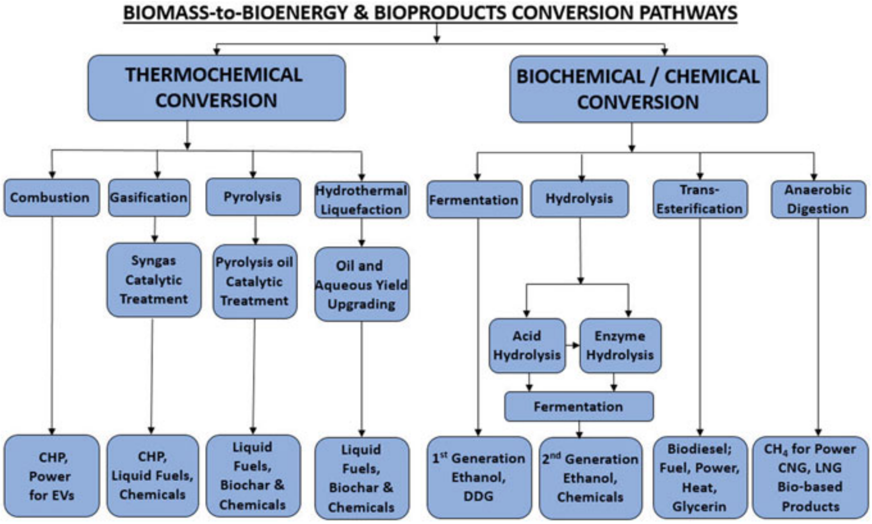


Fig. 1 Biomass conversion pathways (Brennan et al. 2014)

2 Thermochemical Conversion Technologies

Terrestrial biomass species consist of major structural components, namely cellulose, hemicellulose and lignin and non-structural extractives. The concentration of each class of compound varies depending on the species, type of plant tissue, stage of growth and growing conditions (Table 1) (Khan et al. 2009; Agblevor and Besler-Guran 2002). Thermochemical conversion pathways have a major advantage of converting all these major components simultaneously. Especially, lignin conversion through biochemical conversion has been proven to be difficult (Binod et al. 2011; Harris 1949; Kumar et al. 2009; Mosier et al. 2005). Thermochemical conversion technologies to convert sustainable biomass and organic waste into energy forms (heat, power, fuels and bio-based materials) can be categorized as direct combustion, gasification and pyrolysis based on the amount of oxidizing agent present. Combustion is carried out with excess amount of oxygen; whereas, gasification and pyrolysis are carried out with limited amount of oxygen and no oxygen present, respectively. In addition, hydrothermal liquefaction appears to be viable conversion technology in the absence of oxygen (Fig. 2).

Thermochemical conversion pathways utilize solid and low moisture biomass. The diverse nature of biomass feedstocks, agricultural wastes, dedicated energy crops, forestry wastes and agro-industrial wastes can reduce efficiency if the most suitable conversion technology is not selected.

Table 1 Cellulose, hemicellulose and lignin contents in common agricultural residues and wastes (Prasad et al. 2007)

Lignocellulosic material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15–20	80–85	0
Cotton seed	80–95	5–20	0
Newspaper	40–55	25–40	18–30
Waste papers	60–70	10–20	5–10
Primary wastewater solids	8–15		
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Coastal bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12
Swine waste	6.0	28	NA

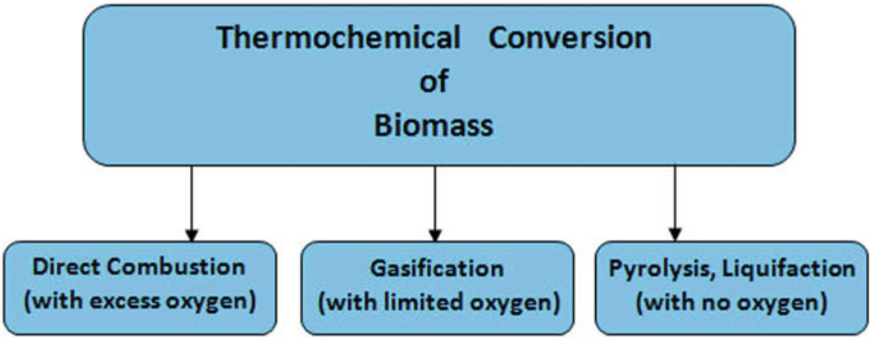


Fig. 2 Thermal conversion pathways of biomass

2.1 Direct Combustion

Combustion is an exothermic chemical reaction of a fuel with oxygen. Common products of combustion are carbon dioxide and water with the release of heat (Naik et al. 2010). Direct combustion systems oxidize biomass to generate hot flue gas which can be used for heat or fed into a boiler to generate steam. The steam can then be used in a steam turbine to generate electricity (Naik et al. 2010; Peterson and Haase 2009).

Biomass fuel properties are the defining parameters for the technology to combust them. The most important fuel properties for combustion are the proximate analysis and heating value of biomass. Proximate analysis provides fixed carbon (char), volatile, moisture and ash content assessment of biomass, while ultimate analysis examines elemental percentages of C, H, O, N, S and Cl in a given biomass sample (Table 2).

2.1.1 Fundamentals of Combustion

Combustion of biomass consists of a complex series of homogenous and heterogeneous oxidation reactions including drying, devolatilization, gasification, char formation, char gasification, combustion and gas phase reactions. The decomposition products of cellulose, hemicellulose and lignin first undergo partial and complete oxidation reactions. When biomass is heated, its components start to dehydrate, hydrolyze, pyrolyze and oxidize, with increasing temperatures, forming combustible volatiles, tarry substances and char. Composition and physiochemical properties of biomass are the determining parameters for duration and rate of the steps of the oxidation process (Fig. 3) (Khan et al. 2009; Naik et al. 2010). It is important to achieve complete combustion in which the 100% of the energy in fuel is harvested. Ensuring the sufficient amount of oxygen supply is critical. Additional oxygen/air is also important for complete combustion and reducing the CO formation in the flue gas (Peterson and Haase 2009).

Presence of stoichiometric amount of oxygen is considered to be the ideal fuel-to-air ratio. However, in reality, stoichiometric combustion is considered to be unattainable due to various factors including process conditions such as temperature, heating rate and residence time. Increasing the amount of excess air will avoid incomplete combustion and help harvest all the energy present in the fuel. Typical excess air requirement for various systems is in the range of 5–50% depending on the fuel characteristics and system configuration (Sadaka and Johnson 2017).

2.1.2 Combustion Emissions

Research shows that combustion of biomass is a common source of particulate matter (PM) and gaseous emissions such as polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOC) and carbon monoxide, nitrogen oxide, sulfur oxide (Naik et al. 2010; Tissari et al. 2008). Biomass combustion flue gas may include unburnt compounds and also compounds produced during the combustion.

Table 2 Ultimate and proximate analysis of various lignocellulosiôc biomass (adapted and revised from Werther et al. 2009)

Biomass	Proximate analysis				Ultimate analysis				
	Moisture	Volatile	FC	Ash	C	H	O	N	S
Sunflower husk	9.1	69.1	19.9	1.9	51.4	5.0	43.0	0.6	0.0
Cotton husk	6.9	73.0	16.9	3.2	50.4	8.4	39.8	1.4	0.0
Mustard husk	5.6	68.6	22.0	3.9	46.1	9.2	44.7	0.4	0.2
Palm fiber	36.4	46.3	12.0	5.3	0.851.5	6.6	40.1	1.5	0.3
Pepper waste	9.7	58.4	24.4	7.4	45.7	3.2	47.0	3.4	0.6
Soya husk	6.3	69.6	19.0	5.1	45.4	6.7	46.9	0.9	0.1
Groundnut shell	7.88	68.1	20.9	3.1	50.9	7.5	40.4	1.2	0.02
Coconut shell	4.4	70.5	22.0	3.1	51.2	5.6	43.1	0.0	0.1
Sewage sludge	6.9	44.6	7.0	41.5	52.0	6.3	32.1	6.3	3.1
Coffee husks	11.4	64.6	20.0	4.1	43.9	4.8	49.6	1.6	0.1
Wood	40.0	46.7	12.8	0.5	50.7	5.9	43.1	0.2	0.04

FC: fixed carbon

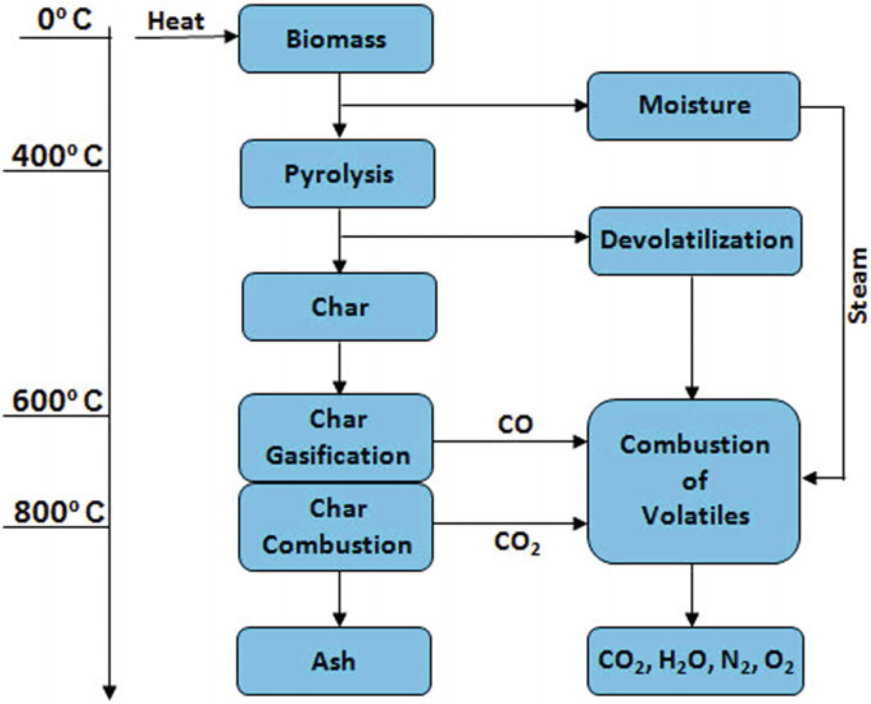


Fig. 3 Stages of biomass oxidation during the combustion

The unburnt compounds—These compounds include CO, hydrocarbons, tar, PAH and char particles. These compounds in the flue gas are the result due to incomplete and inefficient combustion which can be attributed to low combustion temperature, poor fuel and oxygen mixing and insufficient length of residence time in the combustion zone (Khan et al. 2009).

Compounds formed during the combustion—These compounds are mostly particulates which are formed by vapor–molecule collision with resulting molecular clusters. These clusters even combine and reach critical size that undergo further molecular collisions to form stable particles. In flue gases, the saturation of fine particle forming vapors is considered the result of low temperature (Sippula 2010; Kulmala et al. 2000; Seinfeld and Pandis 2006). Also, oxidation of the vapor leads to the formation particulates. The growth mechanisms of particles involve vapor condensation, coagulation, agglomeration, surface reactions and adsorption (Jokiniemi et al. 2001; Christensen and Livbjerg 2009). From these mechanisms, condensation causes the growth of particles based on particle size and saturation ratios (Jokiniemi et al. 2001; Christensen and Livbjerg 2009). Particle size growth by coagulation and agglomeration occurs as a result of collision of aerosol particles that stick together. Particle size, chemical composition and process conditions determine the properties of these particles (Dayton et al. 1995; Johansson et al. 2003; Alauddin et al. 2010;

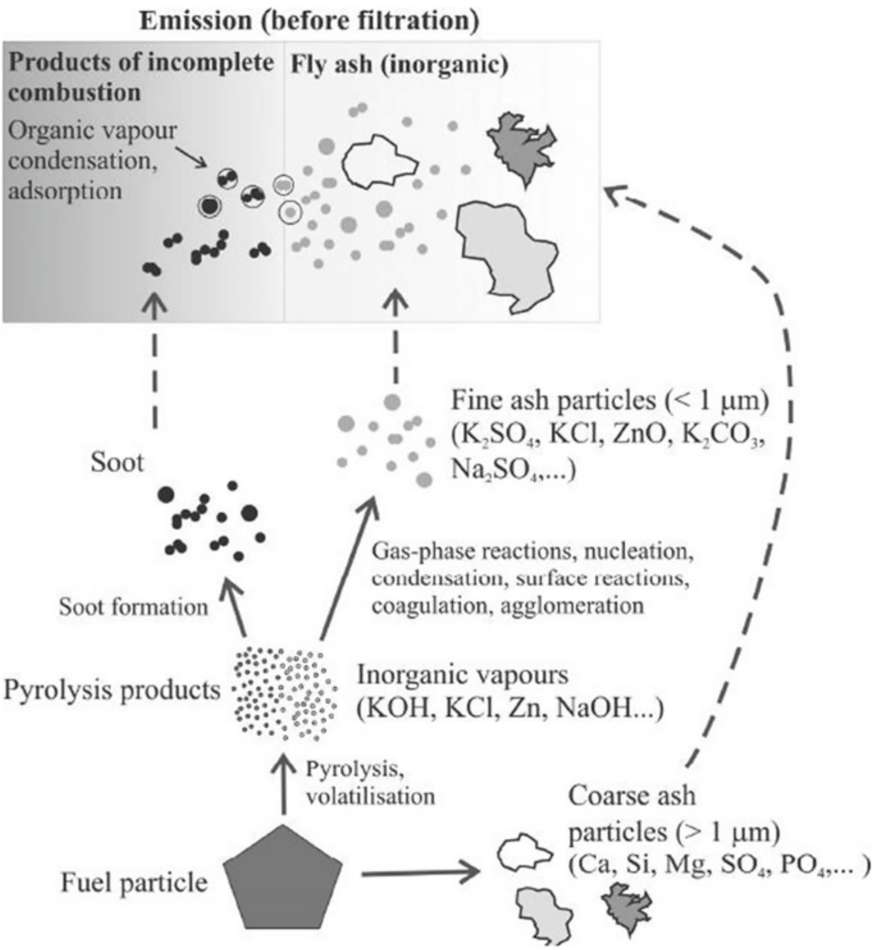


Fig. 4 Particle formation in biomass combustion (Sippula 2010)

Wiinikka and Gebart 2005). Literature suggests that biomass fly ash and particulate fraction are mainly formed by alkali compounds (Fig. 4).

2.1.3 Particle Emission Control Technologies

Formation and uncontrolled emissions from biomass combustion are raising growing health concerns about using direct combustion as a technology option. In any size application, emissions should be controlled for pollutants to meet air quality regulations. Particle control technologies include

- Cyclones
- Multi cyclones
- Core Separators
- Cartridge Filters
- Electrostatic Precipitator (ESP)
- Fabric Filters (Bag houses)
- Rotating Particle Separators.

2.1.4 Types of Direct Combustion

Direct combustion of biomass can be categorized as follows:

- fixed-bed combustion;
- fluidized-bed combustion and
- pulverized biomass combustion.

Fixed-bed Combustion—systems burn biomass on a grate or underfeed stokers and release the hot flue gases into a heat exchanger system to generate steam. When primary air passes through the fixed-bed, biomass drying, partial gasification and initial charcoal combustion take place. The combustible gases then are burned in a separate zone. Underfeed stokers feed biomass into the combustion chamber by screw conveyors from below and transfer biomass upward on a grate.

Fluidized-bed Combustion—systems utilize an incombustible suspended bed (usually sand) where the biomass is burned to release flue gas. Fluidized-bed boilers can be further classified according to fluidization type, namely bubbling or circulating fluidized-beds. In bubbling fluidized-bed applications, the bed particles are suspended by the primary air at comparatively lower fluizidation velocities (~1–3 m/s). Whereas in circulating bubbling fluidized-bed designs, higher gas velocities (~3–6 m/s) are applied, and solids leave the combustion zone. Additional bed materials are reintroduced by circulating the material again (Khan et al. 2009; Vakkilainen et al. 2013). Fluidized-bed application increases heat transfer to achieve improved efficiency and close to complete oxidation reactions with reduced emissions. However, this method has greater standby power needs than fixed-bed boilers (Obaidullah et al. 2012).

Pulverized Biomass Combustion—Combustion of pulverized biomass fuel is injected into the hot zone of the combustion chamber. The oxidization of combustible gases is also achieved by the addition of secondary air. This type combustion is efficient with small biomass particles with low moisture (Sippula 2010; Van Loo and Koppejan 2008; Obernberger et al. 2001).

2.1.5 Biomass Co-firing

Co-firing technology refers to the combustion of mixture of two fuels in one chamber. Co-firing biomass with fossil fuels is receiving increased attention as a way to reduce the adverse environmental effects of coal burning for energy, including greenhouse gas mitigation. Research reviews report over 100 successful co-firing demonstrations in 16 countries that use biomass species including herbaceous woody and waste biomass in various types of boilers (tangential, wall and cyclone fired) (Khan et al. 2009; Tissari et al. 2008; Johansson et al. 2003; McDonald et al. 2000; Baxter 2005). Co-firing biomass with coal can generate a reduction in NO_x, SO_x and GHG emissions from direct coal combustion based on the blend percentage of biomass and coal. Generally, up to 15% biomass can efficiently be co-fired with coal without drastic reduction in efficiency or technology retrofitting (Hein and Bemtgen 1998).

2.2 Gasification

Gasification is a thermochemical conversion process in which carbonaceous substances such as biomass are partially oxidized in the presence of a gasifying agent (air, steam and oxygen) converted into gaseous products (Alauddin et al. 2010; Ruiz et al. 2013; Devi et al. 2003). The product gas, commonly referred to as producer gas or syngas, consists mainly of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O) and small amounts of hydrocarbons such as methane (CH_4) (Alauddin et al. 2010; McDonald et al. 2000; Devi et al. 2003). The gas leaving the gasifier also consists of ashes, tars and small amount of unburnt char. In addition, the syngas can also contain alkali metal compounds, sulfur, nitrogen, carbonyl sulfide, ammonia and cyanide (HCN). Following gasification, syngas needs to be cleaned prior to further utilization. Syngas is best used as a fuel for stationary power and heat generation or to manufacture a range of fuels, chemical intermediates and end products (Ruiz et al. 2013).

Gasification is one of the promising technologies that is being widely researched to convert sustainable biomass and waste biomass into energy forms, as it adds value to low or negative value feedstocks into marketable fuels and products (Ruiz et al. 2013; Guran et al. in press).

2.2.1 Fundamentals of Biomass Gasification

The reaction mechanism of biomass gasification consists of four consecutive substages which take place in a partial oxidation process at high temperatures between 500 and 400 °C. These reactions are considered to take place consecutively; however, they usually overlap without any definitive limits. The overlap occurs mostly during the oxidation and final gasification steps (Fig. 5) (Alauddin et al. 2010; Ruiz et al. 2013; Devi et al. 2003; Basu et al. 2010; Pereira et al. 2012).

Fig. 5 Biomass gasification stages (Ruiz et al. 2013)

- **Dehydrating (Drying)**: The moisture content of biomass is highly variable and can range from 30 to 60%. When solid biomass enters the gasifier, first dehydration takes when the particles are heated from ambient temperature up to 150 °C. This stage is influenced by particle size and the heating rate of the particle. It is critical to reduce biomass moisture level down to 10–15% to achieve an efficient conversion.
- **Pyrolysis**: At this stage, the breakdown of biopolymers occurs at 150–400 °C along with the formation of char and condensable and non-condensable gases. This stage is influenced by type and particle size of biomass, heating rate and maximum temperature, residence time and pressure.
- **Oxidation**: During oxidation, the char, formed in the pyrolysis stage, is oxidized to CO_2 and water. This stage releases a large amount of heat as a result of the oxidation of carbon and hydrogen. The energy needed for the next stage of gasification is generated at this step.
- **Gasification**: The sub-stoichiometric amount of oxygen initiates partial oxidation of char and carbon releasing carbon monoxide and hydrogen. Char gasification occurs through gas–solid and gas–gas reactions in which solid carbon is oxidized to carbon monoxide and carbon dioxide, Further, H_2 is generated through water–gas shift reaction. The gas–solid reactions of char oxidation are the slowest, and they limit the overall rate of the gasification mechanism. Further, many reactions are catalyzed by the alkali metal compounds present in the biomass. The syngas composition is influenced by biomass composition, moisture content, heating rate, temperature and the residence time which defines the oxidation duration of the pyrolysis products (Bridgwater 2003). Several reduction reactions occur as follows (Puig-Arnavat 2010):

  - Water-Gas Shift Reaction $CO + H_2O \rightarrow CO_2 + H_2$ $-42\,\text{kJ/mole}$
  - Bounded Reaction $C + CO_2 \leftrightarrow 2CO$ $-172, 6\,\text{kJ/mol}$
  - Methane Reaction $C + 2H_2 \leftrightarrow CH_4$ $+75\,\text{kJ/mole}$

Providing a valid theory to describe the entire biomass gasification process is very complex due to the variety of biomass feedstocks that can be used and their specific characteristics, reaction thermodynamics, pressure and temperature conditions (Pereira et al. 2012). In addition to air, pure oxygen and steam can be used as a gasifying agent. It has been shown that gasification with air results in a gaseous product with low to medium heating value (4–7 MJ/Nm); whereas, gasification with oxygen or steam results in medium heating value (10–14 MJ/Nm) (Alauddin et al. 2010). Although steam gasification leads to higher amounts of H_2 yields, it requires higher operating temperatures to vaporize water and is proven to be an expensive approach.

Research indicates that a mixture of air/steam at variable ratios would contribute to more efficient syngas production (Damartzis and Zabaniotou 2011; Skoulou et al. 2008). The following operating parameters define efficient gasification of biomass: the type of gasifying agent, gasifying agent/biomass ratio, biomass moisture content, residence time, reaction temperature, pressure, air-fuel ratio and catalyst additives (Guran et al. in press).

2.2.2 Gasification Reactor Types

A gasification reactor is a chamber in which the biomass and gasifying agent are mixed at certain ratios and at certain temperatures, and in some applications with inert materials such as catalysts. Reactor design and operation require understanding of the effects of various biomass characteristics and operating conditions on the performance of the system. Gasifier designs are categorized by (Bridgwater 2003; Puig-Arnavat 2010; Rauch 2003)

- Gasifying agent: Air-blown, steam and oxygen;
- Heating type: direct or auto-thermal, indirect;
- Reactor pressure: atmospheric or pressurized;
- Reactor design: Fixed-bed, fluidized-bed and entrained flow.

The most common classification of gasifiers is based on the design of the reactors (Alauddin et al. 2010; Ruiz et al. 2013; Devi et al. 2003; Pereira et al. 2012; Bridgwater 2003; Puig-Arnavat 2010).

1. Fixed-bed gasifiers are also known as moving bed reactors. Depending on the air flow in the chamber, they can be further grouped as updraft fixed-bed, downdraft fixed-bed, cross-draft fixed-bed and open-core fixed-bed gasifiers. These work by piling the biomass on top of a grate inside the gasification chamber, and the fuel bed moves slowly down the reactor as the gasification reactions proceed. These types of gasifiers are simple, inexpensive and proven to be easy to operate. However, they produce gas with low energy content, and tar elimination is needed (Fig. 6).
2. Fluidized-bed gasifiers utilize a hot, suspended inert bed where biomass is fed and gasified. Fluidized-bed technology offers better performance and yield since it provides better heat and mass transfer for efficient conversion of various types of biomass and wastes with different compositions and heating values (Table 2) (Alauddin et al. 2010; Nemtsov and Zabaniotou 2008). Inert bed material provides improved heat transfer to the biomass particles. Usually, synthetic olivine, which is calcined magnesium silicate is used for heat transfer. Research suggests that small amount of MgO present will reduce the glass-like bed agglomerations that would result from the biomass potassium interaction with the silicate compounds. The MgO titrates the potassium, and without MgO the potassium will form glass K_2SiO_4, cause the bed to become sticky, agglomerate and eventually de-fluidize (Dutta and Phillips 2009). Research has shown that fluidized-bed

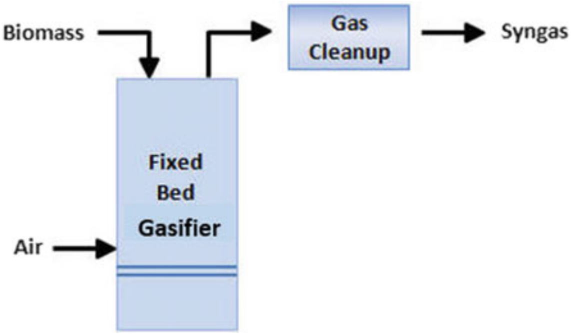


Fig. 6 Fixed-bed gasification reactor

reactors are promising for lignocellulosic biomass due to their lower gasification temperature requirements (Alauddin et al. 2010). Fluidized-bed reactors generally operate at 800–1000 °C to prevent ash from becoming too sticky and depositing on the internal parts of gasifiers. Fluidized-bed reactors are not fully efficient to convert all the char into volatiles due to the continuous mixing of solids. The mixing of solids helps to maintain homogeneous temperature profile throughout the gasifier; however, partially gasified particles may leave the gasification zone before complete conversion (Ruiz et al. 2013). Depending on the operational mode of the heat transfer medium in the gasification chamber, fluidized-bed gasifiers can be further grouped as circulating fluidized-bed, bubbling fluidized-bed and twin-bed fluidized-bed gasifiers.

Bubbling fluidized-bed gasifiers are the simplest and most cost-effective type of continuous gasification (Alauddin et al. 2010). These reactors provide high rates of heat transfer between the bed material and the biomass to generate uniform syngas with a low amount of tar. However, it has been reported that because of back mixing of solids, high conversion is not attainable, and improved mixing is required. In some cases, slow oxygen diffusion rates may occur, which can hinder gasification efficiency (Alauddin et al. 2010; Devi et al. 2003; Guran et al. in press) (Fig. 7).

Circulating fluidized-bed gasifiers operate in a way such that the solids (biomass and bed material) move in a circulating manner to avoid bubble formation, which prevents the gasifying agent from bypassing the bed and solids. High thermal inertia and vigorous mixing enable gasification of various types of biomass; it is therefore one of the recommended technologies for large-scale biomass gasification (Ruiz et al. 2013; Devi et al. 2003; Basu et al. 2010; Puig-Arnavat 2010) (Fig. 8).

Twin-bed fluidized-bed gasifiers use two separate fluidized-bed gasification chambers. The biomass is gasified with steam in the first reactor, and remaining char is transported into the second reactor and combusted fully with air to supply heat for the first reactor (Alauddin et al. 2010; Ruiz et al. 2013; Devi et al. 2003; Pereira et al. 2012) (Fig. 9).

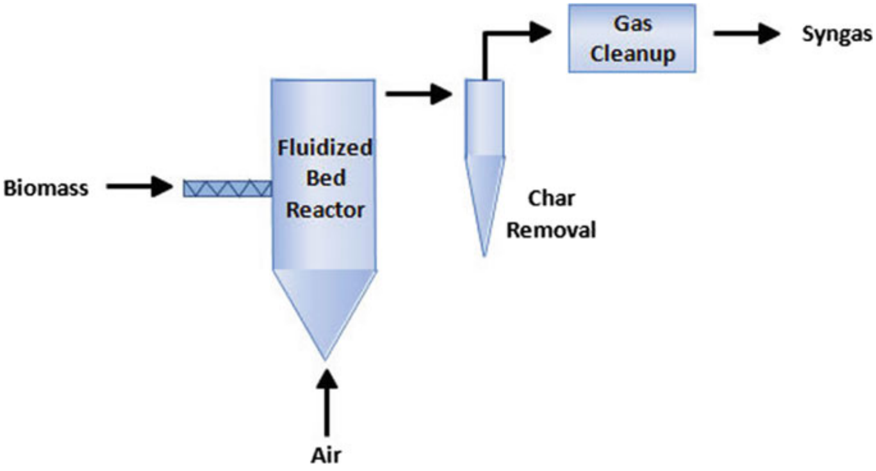


Fig. 7 Fluidized-bed gasification reactor

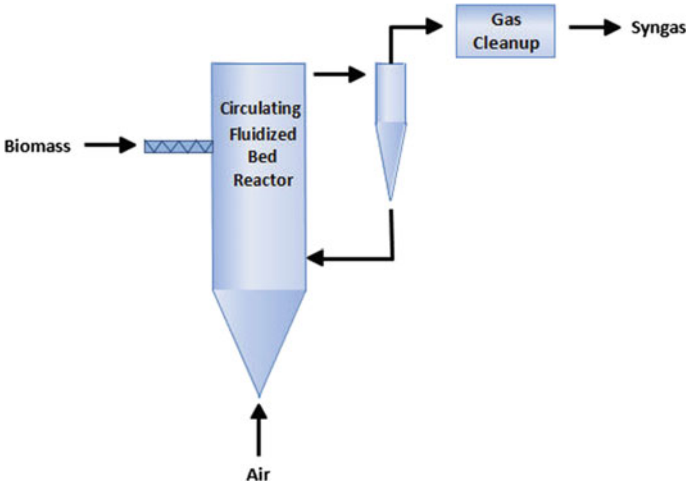


Fig. 8 Circulating fluidized-bed gasification reactor

3. Entrained-flow gasifiers were originally designed for coal gasification for the integrated gasification combined cycle (IGCC). They operate at high temperatures (approximately 1400 °C) and pressures of 20–80 bar. The fuel feed for the gasifier is a slurried powder which facilitates inexpensive feeding of solid fuel. These reactors consume 20% more oxygen than dry feeding due to their high draft demand (Ruiz et al. 2013; Guran et al. in press; Damartzis and Zabaniotou 2011; Skoulou et al. 2008; Rauch 2003). Oxygen rapidly reacts with volatile

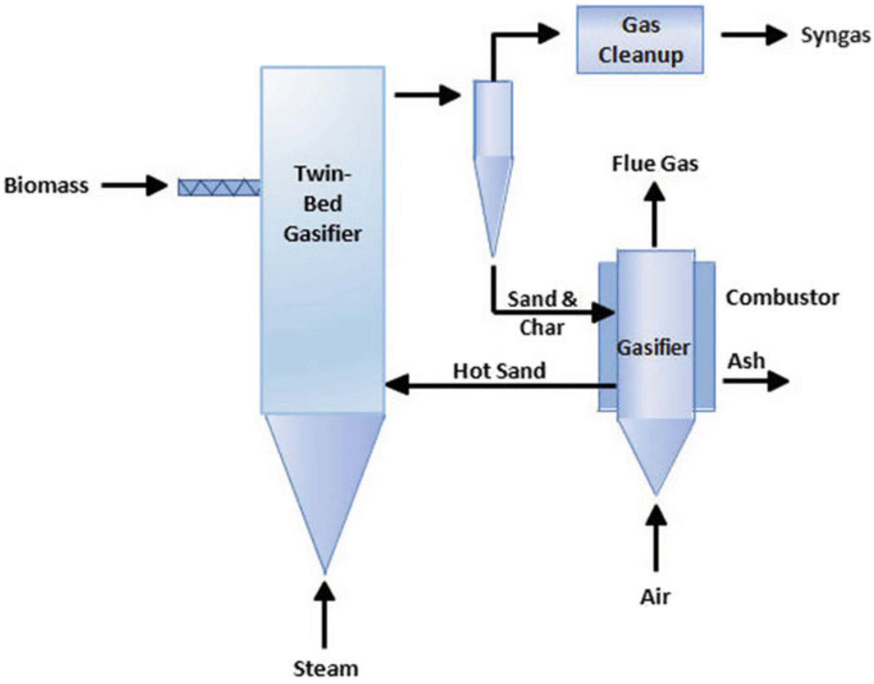


Fig. 9 Twin-bed gasification reactor

materials and the char and produces exothermic reactions which raise the temperature above the melting point of the ash and completely destroys the tars (Basu et al. 2010; Nemtsov and Zabaniotou 2008; Valero and Uson 2006). The high temperatures also result in a higher level of conversion of carbon (Basu et al. 2010).

2.2.3 Syngas Cleaning

Syngas generated by biomass gasification contains some impurities such as tars, carry over char particles and acid gases (CO_2 and H_2S). Syngas has to be cleaned and conditioned to be utilized efficiently. In order to reduce the tar formation in syngas, the operating parameters should be optimized. Biomass tar is a light hydrocarbon and phenolic mixture, and it can be converted into gaseous products through steam reforming and various types of catalysts which can enhance the conversion. Catalysts are categorized into three groups: (1) naturally occurring catalysts (i.e., dolomite, olivine); (2) metal catalysts (i.e., nickel, and alkali metals) and (3) alkalis (i.e., potassium, potassium hydroxide (KOH), potassium bicarbonate ($KHCO_3$)). In some cases, the char also is used in reforming the syngas (Ahrenfelt et al. 2013; Wang et al. 2008; Sutton et al. 2001).

$$\mathrm{CnHm\ (tar)} + n\mathrm{H_2O} \rightarrow (n + m/2)\mathrm{H_2} + n\mathrm{CO} \quad \text{(tar steam reforming reaction)} \tag{1}$$

$$\mathrm{CnHm\ (tar)} + n\mathrm{CO_2} \rightarrow m/2\mathrm{H_2} + 2n\mathrm{CO} \quad \text{(tar dry-reforming reaction)} \tag{2}$$

The main gas cleaning systems for the removal of dust, particles and tars from syngas are as follows: (Ruiz et al. 2013; Wang et al. 2008)

- Cyclones
- Ceramic, textile bag filters
- Rotating particle separators
- Electrostatic precipitators
- Scrubbers.

2.2.4 Syngas Utilization for Power Generation and Liquid Fuels Manufacturing

The syngas generated by biomass gasification can be utilized both for power and heat generation and also converted into second generation biofuels and chemicals.

Syngas for Power and Heat Generation

Biomass gasification power generation is currently being considered because biomass gasification can reduce the potential ash slugging or other ash-related problems since the gasification temperature is lower than combustion. Gasification of biomass is proven to be a fuel for small-scale power plants and heat generation; however, the technology still needs to be optimized to be technically and economically viable on a larger scale. Gasification in power generation plant operations is more complex than combustion, and the processes are more sensitive to operating parameters. Gasification of biomass for power generation has only been proven in small scales. Most biomass gasification applications demonstrated to date for electric power have power output less than 10 MW (Heschel and Klose 1995). Biomass is also being investigated for co-gasification with coal to reduce fossil-based CO_2 emissions. Analysis of integrated gasification combined cycle (IGCC) oxy-co-gasification of straw and coal has shown that up to 10% biomass co-gasification in an oxygen-blown entrained-flow gasifier was technically feasible (Valero and Uson 2006; Bain et al. 2005). Low heating value clean syngas is suitable for use in internal combustion engines, gas turbines or other applications requiring a high-quality gas. The clean gas mixture can also be utilized in microturbine systems and fuel cells. Fuel cells can utilize the hydrogen fraction of syngas with oxygen to generate electricity and heat in the presence of an electrically conductive electrolyte medium (Guran et al. in press; Wang et al. 2008; Hernandez-Pacheco et al. 2005; Iaquaniello and Mangiapane 2006; Jurado et al. 2004; Karellas et al. 2008).

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO + 292.41\ \text{kJ mole}^{-1} \quad \text{(dry methane reforming reaction)} \tag{3}$$

$$CO + H_2O \rightarrow H_2 + CO_2 - 41.98\ \ \text{kJ mole}^{-1} \quad \text{(water−gas shift reaction)} \tag{4}$$

$$CaO + CO_2 \rightarrow CaCO_3 \tag{5}$$

Syngas generated via biomass gasification is a mixture of H_2, CO and CH_4 and methane—water reforming (Eq. 3) and water–gas shift (Eq. 4) reactions result CO, H_2 and CO_2 mixture. With a novel catalysts such as copper–zinc, CO_2 adsorption and pure hydrogen generation is possible (Wang et al. 2008). In addition, nickel-based catalysts have shown efficiency for the reduction in tar and increased hydrogen levels. Research stated that hydrogen production was increased from 30.1 to 50.6 vol% when the Ni loading on the catalyst was increased from 5 to 40% (Pereira et al. 2012; Wu et al. 2011).

Syngas for Advanced Liquid Fuels Manufacturing—Fischer–Tropsch (FT)

Biomass gasification end products of syngas can be converted into various long chain liquid hydrocarbons to displace fossil-based counterparts. The conversion reaction is widely known as the Fischer–Tropsch (FT) reaction which was developed originally for coal gasification into liquid fuels (Schulz 1999; Dry 1996).

$$CO + 2H_2 \rightarrow -CH_2 - + H_2O - 165\ \text{kJ/mole} \quad \text{(Fischer−Tropsch reaction)} \tag{6}$$

Liquid hydrocarbons such as biomass-based diesel, kerosene and gasoline production can be optimized by temperature, pressure and ratio of H_2 to CO. The desired ratio should be close to 2:1. Because syngas produced by biomass gasification contains CH_4 and CO_2, a steam reforming and water–gas shift reaction can be performed to achieve desired H_2 to CO ratios. Another technical challenge is to remove inerts such CO_2 and other contaminants such as H_2S from syngas before the syngas goes thorough FT conversion. These impurities will reduce FT catalysts activity by causing catalyst poisoning. Cobalt is the widely used as a catalyst for FT conversions at pressures of 20–40 bar and temperatures between 180 and 250 °C (Wang et al. 2008; Tijmensen et al. 2002).

Syngas from biomass gasification can be converted into numerous fuels including fossil diesel and fossil gasoline like fuels. Additionally, methanol and dimethyl ether (DME) appear as advanced fuels alternatives to gasoline and diesel fuels (Eqs. 7, 8, 9) (Ng et al. 1999; Tao et al. 2001).

$$CO + 2H_2 \rightarrow CH_3OH \tag{7}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{8}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (9)$$

Alcohol Synthesis

The syngas from biomass gasification should be reformed, quenched and treated to have reduced acid gas concentrations (H_2S, CO_2). Literature suggests that alcohol synthesis reactions take place at 1000 psia and 300 °C. The fixed-bed catalytic reactor consists of specifically designed novel molybdenum disulfide (MOS_2)-based catalysts. This type of particular catalysts also is enhanced with alkali metal salts (i.e., potassium carbonate) and cobalt (COS). Research also suggests that these compounds shift the product from hydrocarbons to alcohols. The presence of CO_2 and H_2S in the syngas also should be controlled since CO_2 may cause catalyst deactivation, and higher than 100 ppmv H2S levels inhibit both the reaction and the higher alcohol selectivity (Dutta and Phillips 2009).

Overall stoichiometric reaction for alcohol synthesis is as follows:

$$n\mathrm{CO} + 2n\,\mathrm{H}_2 \rightarrow \mathrm{C}_n\mathrm{H}_{2n+l}\mathrm{OH} + (n-1)\mathrm{H}_2\mathrm{O}$$

H_2:CO ratio varies from 2:0. 2:1.5 and 2:1 (Dutta and Phillips 2009; Herman 1991).

Syngas for Bio-based Products Manufacturing

Biomass gasification generated syngas can also be chemically and biologically converted into bio-based products including organic acids, alcohols and polyesters (Wang et al. 2008; Brown 2006; Maness and Weaver 1994). The biological conversion of syngas has numerous potential advantages over chemical catalysis. Various bacteria for fermentation have been tested, and *Butyribacterium methylotrophicum* for butanol and ethanol, *Clostridial bacteria* for ethanol and *Rhodospirillus rubrum* for H_2 and polyesters have shown remarkable results. Most bacteria for syngas fermentation are sulfur-tolerant and not sensitive to H_2: CO ratio. Therefore, biological conversion processes do not require expensive gas cleaning and control of H_2: CO ratio. Further biological conversions are not carried out under high pressure and high temperature, and product selectivity of biocatalysts is higher than that of chemical catalysts. However, low growth rates of these anaerobes and difficulty of maintaining the anaerobic conditions and product inhibition can be listed as primary barriers (Wang et al. 2008; Maness and Weaver 1994; Vega et al. 1989; Datar et al. 2004; Hanaoka et al. 2005; Grethlein and Jain 1993).

2.2.5 Plasma Gasification

Plasma gasification (PG) technology originally was developed for metal melting applications. Recently, it is being considered as an emerging alternative technology that can be used to convert waste material and biomass materials into energy source. Acceptable feedstocks include biomass species and municipal solid waste. In addition, plasma gasification can convert hazardous waste, hospital solid waste and contaminated materials, sewage sludge and low-level radioactive waste. Plasma conversion is an incomplete oxidation of hydrocarbon components of materials and generation of a combustible gas such as mixture of carbon monoxide and hydrogen (syngas) and other minor gases. Plasma conversion is also called "Plasma Gasification (Arena 2012)." If the syngas generation from plasma conversion is successful, it can be used for either direct power generation or generation of renewable hydrogen or other fuels where applicable as in gasification technologies discussed before. Plasma gasification also results in compaction and vitrification of solid wastes after gasification. This is achieved by the melting of inorganic material by high plasma temperatures eliminating voids and binding hazardous metals in a ceramic matrix (e.g., a silicate) with low leach rates.

Plasma gasification refers to the plasma technology that occurs in any gas in which at least part of the atoms or molecules are partly or fully ionized (Arena 2012). Thermal plasmas are generated by either an electric arc or by a radio-frequency induction discharge. In waste treatment, arc plasmas dominate because they are relatively insensitive to changes in process conditions. High-temperature treatment of waste material provides the following:

- Rapid heating and reaction start-up
- High heat and reactant transfer rates
- Smaller installation size for given waste throughput
- Melting of high-temperature materials.

A typical plasma system for treatment of solid wastes and biomass consists of a plasma reactor with collection of the metal and slag at the bottom and a power supply. Plasma gasification is a multistage process. Hydrocarbon materials are fed into the gasification chamber, and with plasma torch application, materials break down into gaseous compound where inorganic compounds melt into liquid slag which is removed and cooled. The generated gas goes through cleanup, and heat recovery is achieved by heat exchangers. In order to eliminate fugitive emissions, plasma gasification reactors should be operated under negative pressure. Plasma gasification temperatures may reach to 2000–30,000 °C (Guran et al. in press; Arena 2012; Morin et al. 2012; Murphy and Heberlein 2008; Dodge 2009).

2.3 Pyrolysis

Biomass pyrolysis is an emerging thermochemical technology that has the potential to serve as a viable conversion pathway to convert sustainable biomass into advanced fuels and chemicals to supplement fossil-based counterparts, bio-char to sequester carbon and sustainable management for biomass waste for overall energy security, mitigating climate change and achieving low-carbon economy. Viable feedstocks for biomass pyrolysis include purpose grown energy crops (i.e., switchgrass, hybrid poplar and hybrid willow), wood residues (mill residues, sawdust, urban wood and forest thinning) and agricultural and farm residues (i.e., corn stover, wheat straw, rice hulls, bagasse and low moisture animal waste) (Bond 2014; Agblevor et al. 1995; Wright 2010).

The pyrolysis process is a thermal degradation of materials in the absence of an oxidizing agent, causing irreversible rupture of polymer structures into smaller molecules leading to the formation of solid (char), liquid (bio-oils) and non-condensable gaseous products (i.e., CO, CO_2, H_2, CH_4, C_2H_6) (Babu and Chaurasia 2003; Bridgwater et al. 1999; Williams and Besler 1996; Bridgwater and Bridge 1991). Biomass pyrolysis reactions occur at lower temperatures of 400–700 °C; whereas, gasification reactions take place at higher temperatures such as 800–1100 °C. The pyrolysis reactor types and operating conditions such as reactor temperature, biomass feed rate and particle size, residence time, heating rate impact the yields of the various products. Depending on the heating rate, pyrolysis reactions can be categorized as slow or fast/flash pyrolysis with different yields. Slow heating rates and lower temperatures provide higher char yields because slow heating and longer residence times in a reactor result in slow decomposition; whereas in fast pyrolysis, the rapid heat transfer and short residence times coupled with medium and higher temperatures produce higher percentages of liquid products with decreased amount of bio-char yields. Both types of reaction conditions also generate non-condensable gaseous products such as C1–C4 hydrocarbons (Williams and Besler 1996; Bridgwater and Bridge 1991; Demirbas et al. 2004). Bio-char from pyrolysis can be used as activated carbon when its pore structure and surface area are appropriate. In addition, bio-char soil applications are emerging (Granatstein et al. 2009). Bio-oils can be upgraded by lowering the oxygen content by means of catalytic treatment and hydrogenation while non-condensable gases can be used to supply energy for the pyrolysis system (Demirbas et al. 2004; Heschel and Klose 1995; Hernandez et al. 2014; Shafizadeh 1985).

2.3.1 Fundamentals of Biomass Pyrolysis

Pyrolysis of biomass is a complex process and is influenced by many different reaction parameters. The fundamentals of pyrolytic decomposition reactions of biomass are still not completely understood because of the complex nature of biomass. A number of researches focused on decomposition of main structural components of biomass (lignin, cellulose and hemicellulose) to further understand the mechanisms of biomass pyrolysis (Wright 2010; Couhert et al. 2009b; Stefanidis et al. 2014; Liu et al. 2008; Burhenne et al. 2013; Kanaujia et al. 2014).

This approach was based on a theory that lignocellulosic biomass is mainly composed of structural components of cellulose, hemicellulose and lignin, and the aggregative decomposition behavior of these individual components would describe the decomposition behavior of any lignocellulosic feed (Williams and Besler 1996; Stefanidis et al. 2014). Thermogravimetric analysis (TGA) of these individual components has been studied. TGA measures the decrease in mass caused by the release of volatiles, or devolatilization, during thermal decomposition (White et al. 2011; Waters 1960). The TGA decomposition studies showed that cellulose decomposes over a narrow temperature range, between 280 and 360 °C with the highest decomposition rate being observed at 339 °C. Hemicellulose TGA decomposition resulted over a slightly wider range between 200 and 320 °C. The widest decomposition range was observed during the lignin pyrolysis which spans from 140 to 600 °C (Williams and Besler 1996; Stefanidis et al. 2014; Liu et al. 2008; Burhenne et al. 2013). Biomass pyrolysis products are a complex combination of products as a result of the individual pyrolysis processes for cellulose, hemicellulose and lignin, each of which has its own kinetic characteristics (Couhert et al. 2009b). Individual decomposition studies also reported that cellulose pyrolysis produces levoglucosan, levoglucosenone, furfural, substituted furans and small molecules including some aldehydes and ketones (Fig. 10), while lignin pyrolysis yielding methoxyphenols and other major phenolic compounds (Fig. 11) and hemicellulose thermal decomposition producing acetic and formic acid along with acetaldehyde and furans (Fig. 12) (Kanaujia et al. 2014). Although thermal analysis is a useful tool that may provide insight into the kinetics of heterogenous reactions, it is also debated that the kinetic data obtained from a single thermo-analytical technique used to investigate the decomposition of individual compounds may not provide sufficient evidence for the solid state decomposition of biomass (White et al. 2011). Research suggests that it is not possible to predict pyrolysis gas yields of any biomass from its cellulose, hemicellulose and lignin contents. Therefore, it is not clear that studying the thermal decomposition of a small number of model compounds such as cellulose, hemicellulose and lignin is sufficient to model the wide range of biomass species existing in nature and in waste biomass. In addition, the complex interactions between different organic and inorganic biomass components during pyrolysis have to be considered to understand the detailed decomposition pathways of biomass and wastes (Couhert et al. 2009a; b; White et al. 2011; Weerdhof 2010). It was shown that interactions occur both outside of the biomass particle in gas phase and inside of the particles since the minerals present in biomass influence these reactions (Couhert et al. 2009b). The inability to predict the kinetic behavior of various biomass species under various pyrolysis conditions has been puzzling and encouraging at the same time. A number of biomass pyrolysis studies have shown that the pyrolysis reaction may occur as follows (Guran et al. in press; Couhert et al. 2009b):

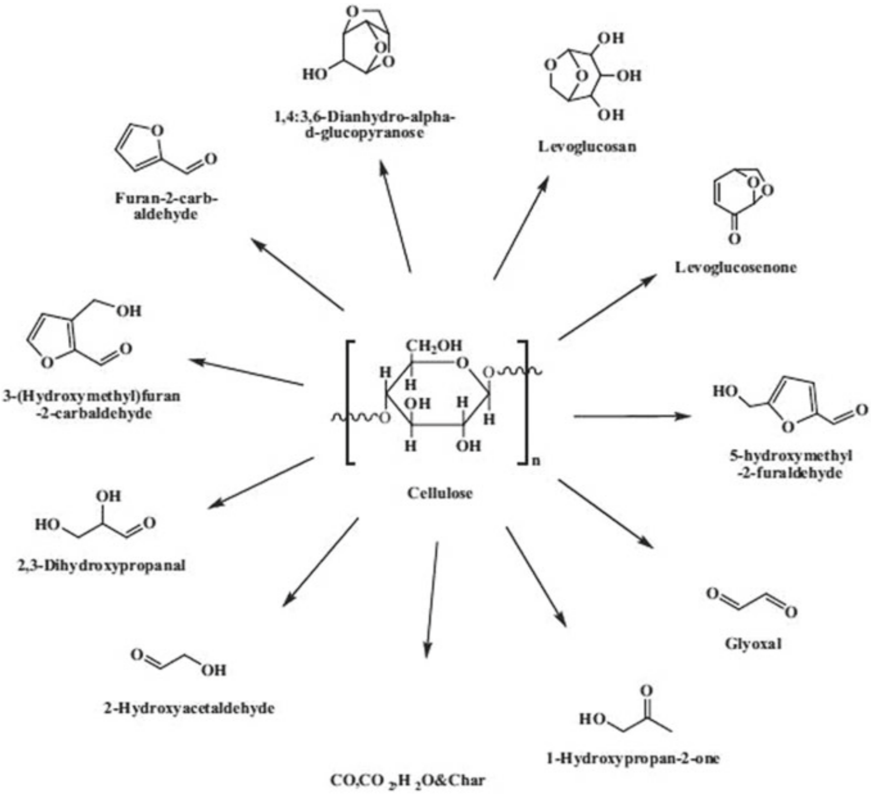
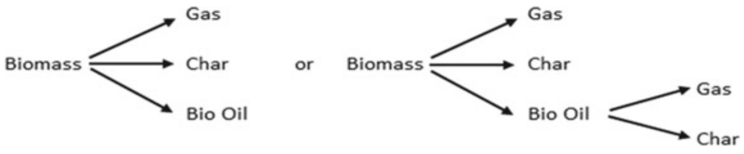


Fig. 10 Cellulose pyrolysis products (Kanaujia et al. 2014)



Detailed reviews on pyrolysis kinetic suggest that elucidation of reaction mechanisms for solid state thermal decomposition is not possible if kinetic modeling is not coupled with experimental trials by using analytical analysis tools such as Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC), high-performance liquid chromatography (HPLC), gas chromatography mass spectroscopy (GC-MS) and scanning electron microscopy (SEM) (White et al. 2011; Green and Feng 2006; Bonelli et al. 2003). Experimental research and modeling research confirm that increased heating rates reduce the char yield during biomass conversion. The distribution of products between bio-oil, char and gas on a mass basis for slow heating rates is approximately 30%, 35% and 35%, respectively; whereas, under fast/flash heating conditions the product distribution can be altered

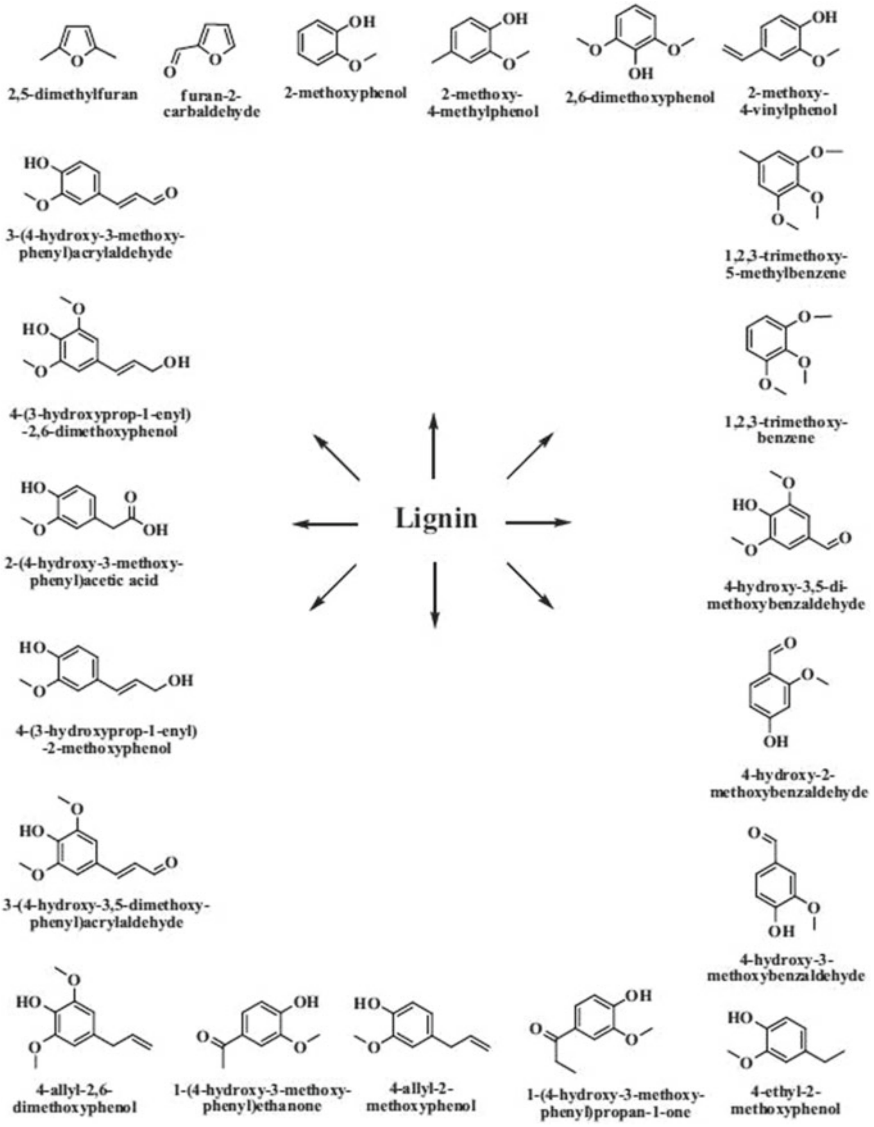


Fig. 11 Lignin pyrolysis products (Kanaujia et al. 2014)

dramatically. Under the fast/flash pyrolysis conditions, bio-oil, char and gas yields can reach up to 75%, 12% and 13%, respectively. Pyrolysis oils produced during the decomposition of biomass can decompose further through secondary reactions. In order to maximize the oil yield and reduce the char formation, the reactor design and optimization efforts should minimize the secondary reactions (Weerdhof 2010;

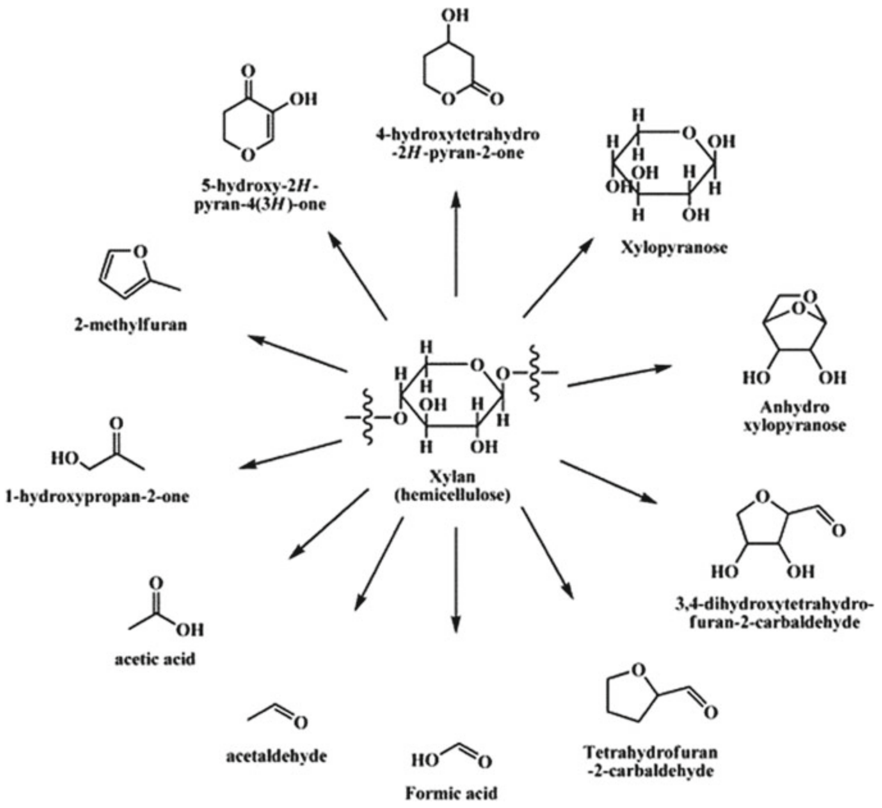


Fig. 12 Hemicellulose pyrolysis products (Kanaujia et al. 2014)

Thunman and Leckner 2002; Di Blasi 1996; Di Blasi et al. 1999; Broido and Nelson 1975; Bridgwater 2001; Agblevor et al. 1994).

2.3.2 Pyrolysis Reactor Types

Pyrolysis reactions are strongly influenced by the reactor design and operating parameters. The pyrolysis reactor can be categorized as follows (Wright 2010; Couhert et al. 2009b; Ringer et al. 2006; Lede 2013; Mohan et al. 2006):

- Slow Pyrolysis in Fixed-Bed Pyrolysis Reactors
- Fast/Flash Pyrolysis in:
  - Fluidized-beds Reactors (Bubbling-Bed and Circulating-Bed)
  - Vacuum
  - Transported beds

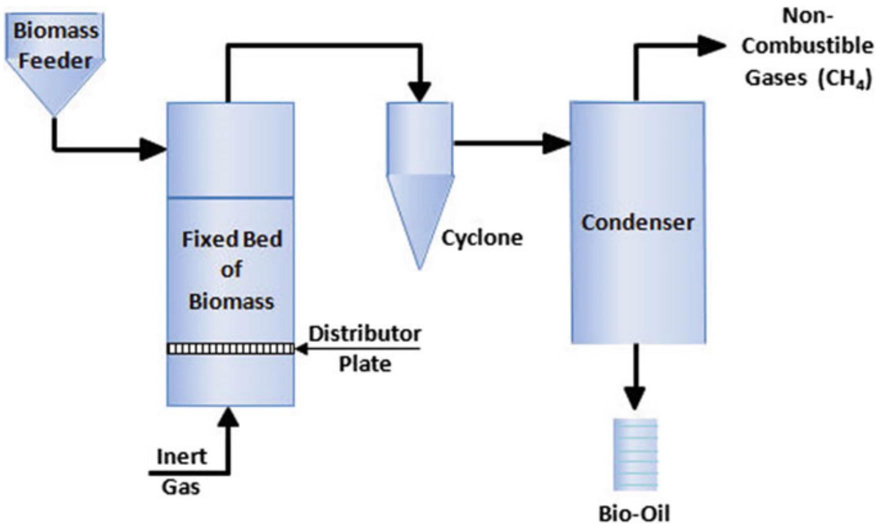


Fig. 13 Fixed-bed pyrolysis reactor

1. Slow Pyrolysis in Fixed-Bed Reactors

Slow pyrolysis reactions are generally performed in a fixed-bed reactor where the biomass is piled on a fixed support bed in the reactor as a batch operation (Fig. 13). The reactor is usually heated slowly to final temperatures below 500 °C. Slow heating rates coupled with longer solid and gas residence times maximize the yield of char via secondary coking and re-polymerization reactions (Guran et al. in press; Williams and Besler 1996; Lede 2013; Mohan et al. 2006). During the last few decades, slow pyrolysis reactors were mainly used for evaluation of operating parameters, such as temperature, heating rate and particle size; however, slow pyrolysis is receiving renewed attention due to carbon capture and storage benefits of bio-char to mitigate climate change (Verma et al. 2012). If a feedstock for slow pyrolysis is clean, untreated biomass, the char may also have soil remediation benefits (Granatstein et al. 2009).

2. Fast/Flash Pyrolysis

Fast pyrolysis conditions are critical in achieving maximized bio-oil yields through efficient heat and mass transfer during the pyrolytic thermal degradation of materials. Fast pyrolysis occurs during rapid heating (1000–10,000 °C/s) and at high temperatures (~650 °C) with very short residence time under inert conditions. Increased pyrolysis heating rates and increased surface area result in better heat transfer and increased mass transfer rates. Biomass rapidly depolymerizes to form vapors (a mixture of light hydrocarbons and oxygenates) which ultimately condense to form bio-oil (Bond 2014; Mohan et al. 2006).

Also, faster gas feeding rates will reduce vapor residence times in the hot pyrolysis zone, which will minimize secondary cracking and re-polymerization reactions and consequently increase the bio-oil yield while reducing the bio-char and non-condensable gaseous product yields. In order to achieve efficient conversion of biomass to liquid products, various types of fast/flash pyrolysis reactors have been developed, tested and scaled-up. In addition to pyrolysis reactor designs, biomass pre-treatment for moisture removal, size reduction and efficient continuous feeding into the pyrolysis zone are important parameters that can be optimized to achieve economically and technically feasible pyrolysis operations (Guran et al. in press).

– ***Fluidized-Bed Reactors***

Biomass conversion into higher oil yields requires smaller particle sizes, high heating rates, short vapor residence times and rapid cooling of the vapors. These characteristics can be achieved in fluidized-bed reactors (Aho et al. 2008). Initially, fluidized-bed reactors were developed for the petroleum and chemical process industries and have been in use for more than fifty years (Ringer et al. 2006). Fluidization technology is a process in which solids are made to behave like a fluid by feeding gas or liquid upward through the solid-filled reactor (Kunii and Levenspiel 1991). Fluidized-bed reactors are used for fast/flash pyrolysis to obtain efficient heat transfer rates from the heated bed material to biomass particles in order to achieve high heat transfer and efficient conversion before biomass particles become charred. The most commonly tested fluidized-bed reactors for biomass pyrolysis are bubbling and circulating-bed reactors. Silica sand is widely used as a fluidized-bed material (Knutsson et al. 2014). Literature has also shown in situ fractional fast pyrolysis with fluidized catalytic beds to influence heat transfer and secondary vapor reactions (Agblevor and Besler-Guran 2002; Guran et al. in press; Agblevor et al. 2010; French and Czernik 2010; Lappas et al. 2002).

Bubbling fluidized-bed—Pyrolysis occurs when the bed material is fluidized by a carrier inert gas fed from the bottom of the reactor to make the bed act as a fluid (Fig. 14). The important parameters are appropriate particle size for biomass and the bed fluidizing media. The inert carrier gas flow rate is important to ensure that the bed material gets fluidized properly but does not get carried away above the free board section of the reactor. Vapor residence times are controlled by the inert carrier gas flow rate. In order to avoid having the char catalyze the vapor cracking reactions, the residence time should be optimized, and char should be removed from the bed section as quickly as possible (Bond 2014). Bubbling fluidized-bed reactors have been reported to be easy to operate and are reliable.

Circulating fluidized-bed—Pyrolysis reactors provide more efficient heat transfer and shorter residence times (<1 s). These types of reactors are different from bubbling fluidized-beds. Following the pyrolysis chamber, there is a secondary reactor where the average particle residence time is 2–3 s to combust char and return the hot sands back into the first pyrolysis chamber (Fig. 15). These reactors require finer biomass particles (1–2 mm) since larger biomass particles may get combusted without pyrolyzed in the secondary reactor, potentially reducing bio-oil yields (Bond 2014; Ringer et al. 2006; Lede 2013).

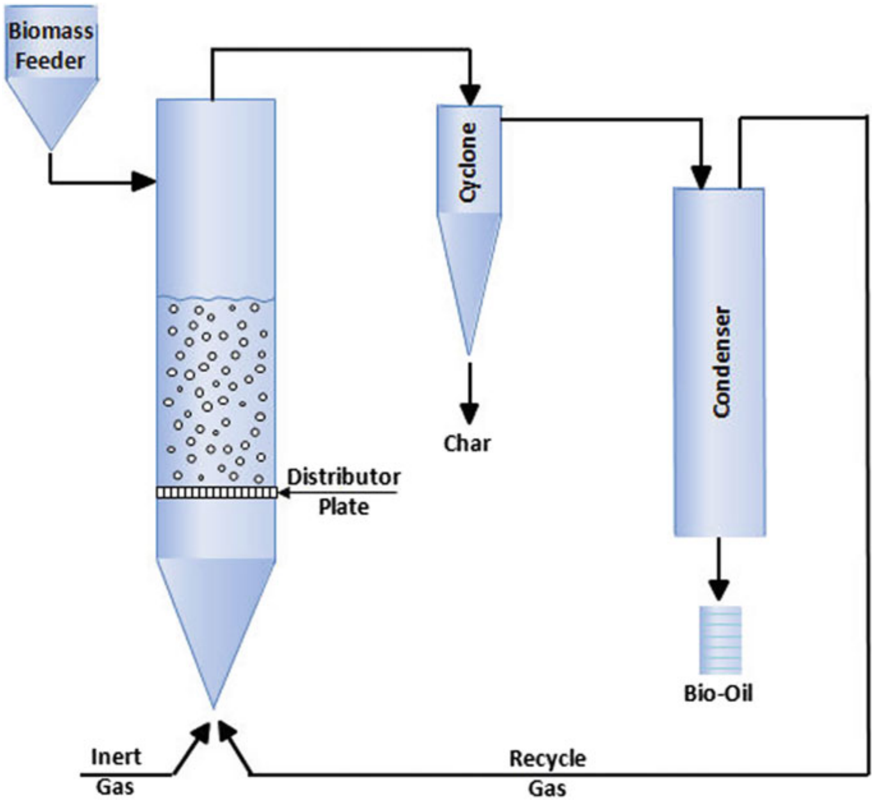


Fig. 14 Bubbling fluidized-bed reactor

– ***Ablative Pyrolysis Reactors***

Ablative (Vortex) pyrolysis reactors are designed to convert larger particle size (i.e., 2 cm) biomass into bio-oils. Heat transfer occurs when biomass particles are accelerated to very high velocities by a carrier gas in the tubular reactor. The particles are introduced into the reactor tangentially and contact with the hot (625 °C) surface of the reactor walls thermally decomposing them and generating vapors. Because of design issues such as particles entering into reactor may cause erosion and excessive wear and tear. These reactors have been evaluated on smaller scales, but scale-up to commercial sizes have been a major challenge for this technology (Ringer et al. 2006; Lede 2013).

– ***Vacuum Pyrolysis Reactors***

Vacuum pyrolysis reactors were developed to achieve a slow pyrolysis process with higher liquid yields by avoiding secondary cracking reactions. Vacuum pyrolysis

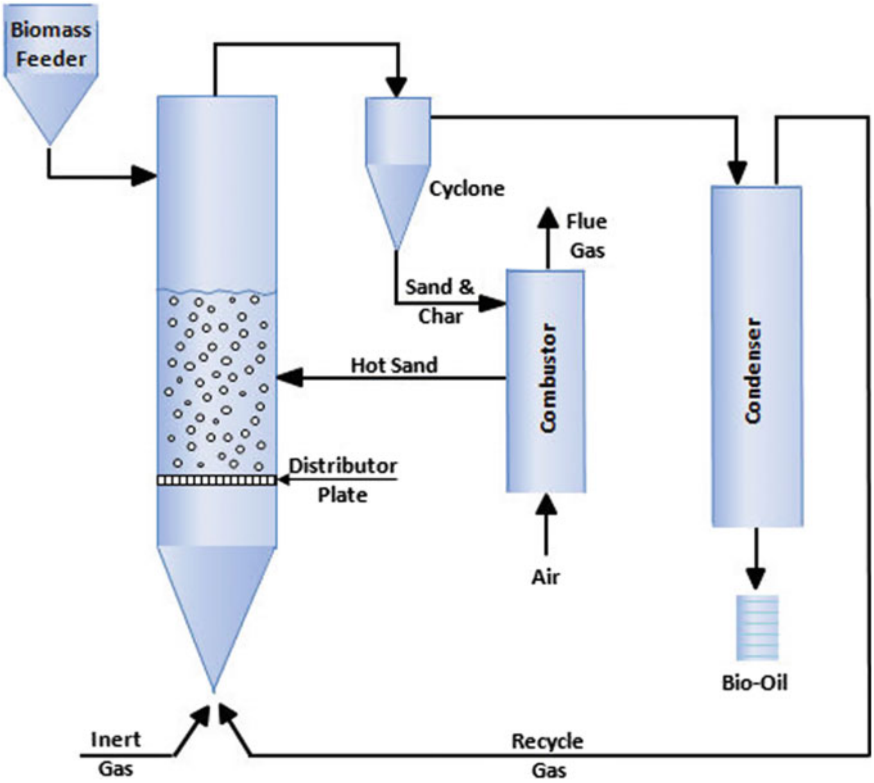


Fig. 15 Circulating fluidized-bed reactor

reactors oil yields were reported to be 35–40 wt% compared to 75–85% of fluidized-bed oil yields. These reactors never achieved the fluidized-bed reactors bio-oil yields and are relatively mechanically complicated (Bridgwater 2003; Ringer et al. 2006).

– ***Transported-Bed Reactors***

Transported-bed reactors do not require a carrier gas since biomass and sand are fed from the bottom of a cone reactor and spin upward to the top of the reactor. Literature reports scalability issues and mechanical problems with this type of pyrolysis reactors (Bridgwater 2003; Ringer et al. 2006).

2.3.3 Fractional Catalytic Pyrolysis

Biomass feedstocks are composed of structural (cellulose, hemicellulose and lignin) and non-structural (extractive) components which have distinct chemical properties (Agblevor and Besler-Guran 2002). The literature suggests that selectively converting biomass components to end products is possible through in situ fractional catalytic pyrolysis (Agblevor and Besler-Guran 2002; Bond 2014; Agblevor et al. 2010). Fractional pyrolysis is defined as a selective in situ conversion of biopolymers into desired fuels and chemicals without going through secondary separation and upgrading processes (Agblevor and Besler-Guran 2002). Fractional catalytic pyrolysis can be coupled with the pyrolysis types mentioned above. However, the best application results have been observed when coupling with fluidized-bed fast pyrolysis applications. Zeolite catalysts are widely tested catalysts for fractional pyrolysis to generate stable pyrolysis oils with minimal re-polymerization reactions and can potentially be processed in a conventional petroleum refinery (Agblevor and Besler-Guran 2002; Guran et al. in press; Bond 2014; Agblevor et al. 2010). Research suggests that a modified ZSM5 catalyst can be added to the fluidized-bed to convert pyrolysis vapors directly into aromatics and olefins. Also, aromatic yields were shown to be a function of zeolite pore size. Small pore zeolites (<5 A) produced negligible amounts aromatics and oxygenates, favoring instead the formation of CO, CO_2 and coke. Medium pore zeolites (5.2–5.9 A) gave the highest aromatic yields (10–35% on carbon basis), while large pore zeolites coked heavily with reduced amount of aromatics and small oxygenates. Also, catalytic pyrolysis can use the best lignin for the production of aromatics (Bond 2014).

2.3.4 Bio-Oil from Biomass Pyrolysis

Bio-oils can be produced from a variety of biomass feedstocks including forest and agricultural residues (i.e., bagasse, rice straw and hulls) and dedicated energy crops (i.e., switchgrass, aspen, poplar). The bio-oil yield, based on the feedstock and conversion technology, is in the range of 70–90% by weight. Feedstock with high lignin content, such as bark, may yield lower amounts of bio-oil in the range of 60–65%. Bio-oils have long been considered an alternative to petroleum-based fuels. However, since pyrolysis causes bond cleavage and produces small fragments of biomass polymers, most of the original oxygen in the biomass feedstock is retained as oxygenated compounds in the bio-oil (Bridgwater 2003; Mohan et al. 2006; Agblevor et al. 2010; French and Czernik 2010; Oasmaa and Czernik 1999). Bio-oil usually contains 45–50% weight oxygen depending on the moisture level of the feedstock. Also, most bio-oil analyses show that bio-oils appear to be acidic with a pH of 2.0–3.0 (Mohan et al. 2006; Piskorz et al. 1998; Demirbas 2004; Garcia-Perez et al. 2006). The chemistry of bio-oils can be tailored by changing thermal conditions and using catalytic treatments that influence characteristics of end products. High temperatures can increase the severity of cracking, which may result in lower molecular weight liquids and increased gas products. Higher temperatures also cause dehydrogenation/aromatization reactions to take place resulting in higher levels of polycyclic aromatic hydrocarbons (PAH). Fast pyrolysis appears to be a viable technology for producing olefins and aromatic monomers from carbohydrates if the reaction conditions are optimized (Bond 2014; Lede 2013; Garcia-Perez et al. 2006). The advantages include low production costs, high thermal efficiency and potential CO_2 reductions. Various researches on producing pyrolysis oils from agricultural wastes and residues and municipal solid wastes have shown that pyrolysis appears to be a promising technology, but requires further research and demonstration (Guran et al. in press; Putun et al. 2005; Reed and Williams 2004).

2.4 Hydrothermal Liquefaction (HTL)

The hydrothermal liquefaction (HTL) involves direct thermal liquefaction of biomass at high temperature and pressure in the presence of water into liquid oil and other products (Zhang 2010; Shuping et al. 2010). The advantage of this process is that it does not require feedstock drying and high-moisture feedstocks such as food processing waste, algae and manure which can be easily processed (Shuping et al. 2010; Vardon 2012). During HTL, water serves as the reaction medium; therefore, it is critical to understand the fundamentals of water chemistry when subjected to high temperature and pressure. At elevated temperature (200–350 °C) and pressure (5–15 MPa), water's chemical and physical properties change, and it becomes a good solvent for hydrocarbons to breakdown and reform biomass macromolecules into biofuel (Shuping et al. 2010).

2.4.1 Fundamentals of HTL

During the HTL conversion, water acts as reactant and catalyst, and biomass components first depolymerize followed by decomposition by cleavage, dehydration, decarboxylation and deamination. The final step is the recombination of reactive fragments (Toor et al. 2011). Influence of temperature on the yields of HTL is reported to be sequential (Akhtar and Amin 2011; El-Rub et al. 2004). Initially, increased temperatures trigger the bio-oil yield. Research showed that very high temperatures are not suitable for bio-oil production because high temperatures lead to formation of gases, and recombination of free radicals leads to the char formation. The HTL of main components of biomass such as cellulose, hemicellulose, lignin, lipids and proteins conversion has been studied, and it was found that during HTL cellulose and hemicellulose components undergo rapid hydrolysis to form glucose and other saccharides. Hemicelluloses and starches are hydrolyzed much faster than cellulose which has glucose units linked by glycosidic bonds. Cellulosic compounds in contrast to hemicelluloses have high degree of crystallinity which makes cellulose to hydrolyze more slowly (Toor et al. 2011; Bobleter 1994; Yu et al. 2008; Delmer and Amor 1995). Research showed that during the HTL of lignin various phenols and methoxy phenols are formed. Also lignin HTL is reported to result in significant amounts of solid residue. Therefore, research recommends that the amount of lignin in the substrate should be carefully balanced (Toor et al. 2011). The lipid components of biomass such as *glycerol* and *fatty acids* HTL resulted in 31% and 32% conversion, respectively (Toor et al. 2011; Buhler et al. 2002; Watanabe et al. 2006).

HTL still has relatively lower oil yields but fundamental advantages such as relatively stable oil product and an aqueous reaction environment which does not require moisture removal as in other thermal decomposition technologies. Therefore, HTL processes have the potential to convert especially high-moisture (wet) biomass and organic waste into bio-oil for fuel and other applications (Toor et al. 2011).

Glossary

Sustainable Biomass Biomass feedstocks that do not follow food to fuel pathways and do not result in forest conversion and/or land clearing for biomass production plantations.

Thermochemical Conversion Conversion technology that involves heat application to rupture the main structure of polymers. This can be applied with or without oxygen.

Combustion Combustion is an exothermic chemical reaction of a fuel with oxygen.

Gasification Gasification is a thermochemical conversion process in which carbonaceous substances are partially oxidized in the presence of a gasifying agent (air, steam and oxygen) converted into gaseous products.

Pyrolysis Thermal degradation of materials in the absence of an oxidizing agent, causing irreversible rupture of polymer structures into smaller molecules leading to the formation of solid (char), liquid (bio-oils) and non-condensable gaseous products (i.e., CO, CO_2, H_2, CH_4, C_2H_6).

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Microbial Fuel Cells: A Path to Green, Renewable Energy

Kausik S. Das

Abstract Microbial fuel cells (MFCs) are clean, renewable energy sources and they generate self-sustaining clean energy through cellular respiration. MFCs do not require any external energy to operate and do not emit any excess greenhouse gases. MFCs can also be used for bioremediation by removing toxic materials by respiring a variety of metals and other harmful elements including iron and uranium. In this article, we have discussed the principles and designs of biofuel cells.

Keywords Microbial fuel cell · Bioenergy · Bioremediation · Exo-electrogenic bacteria · Redox potential

1 Introduction

Microorganisms are ubiquitous in nature and play an important role in recycling organic compounds. Electron exchange properties of microorganisms are not only a fascinating and instructive area of bio-electrochemistry, but also have the potential to impact global bio-economy in a significant manner. Current domestic, industrial and animal wastewater together contains nearly 1.5×10^{11} kilowatt-hour (kWh) (~17 GW of power) of untapped bioenergy Logan and Rabaey (2012). Moreover, an estimated 1.44×10^{16} kWh of chemical energy stored in organic matters in marine sediment is ready to be harvested (Xie et al. 2013) in the face of current annual global power demand of ~17 TW (IEA). At present, the global energy consumption depends on extraction and oxidation of concentrated fossil fuels, such as oil (32%), coal (27%) and natural gas (21%) (IEA). Our demand for energy continues to increase while our present supply of energy resources is rapidly decreasing. Moreover, energy extraction from concentrated fossil fuel has its own shortcomings: Firstly, fossil fuel resources

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on earth are rapidly dwindling and secondly hydrocarbon combustion leaves significant carbon footprint and emission of greenhouse gasses behind. A rational approach to deal with this problem is to turn our attention to sustainable green and renewable energy where resources can be replenished in a human life span. Apart from solar, wind, tidal or geothermal energy, where fluctuating natural conditions may affect the output significantly, control parameters in bioenergy generation are much more flexible and turns out to be a potential candidate to harness sustainable green energy. Although there is an abundance of biomass on earth and without affecting food production modified agricultural practices could produce more than one billion tons of biomass, which is equivalent to 600 GW of energy, the challenge is to efficiently extract energy from much less concentrated biomass, (IEA 2012, 2013a, b). Energy recovery in low-density biomass is much lower than the concentrated fossil fuels so far. One way to overcome this challenge is to use microbe driven bio-battery or microbial fuel cell technology. In the USA, nearly 5% of the energy budget is used to treat waste water in treatment plants but instead of consuming energy these waste water treatment plants have the potential to generate energy using some special microbes capable of expelling electrons to external receptors outside their bodies.

A bio-battery is able to extract energy from organic compounds more like cells in a human body. When we consume food, cells breakdown energy reach food molecules such as glucose and pull off electrons in the process. The energy captured from electrons is stored in ATP, and the spent electrons are deposited to the terminal oxidants like oxygen. For example, in metabolism of carbohydrates living creatures extract energy in reactions similar to:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O. \tag{1}$$

In a living cell or a microbe, the process is more complex and involves many enzymes and progresses via a series of redox reactions involving NADH and other intermediates.

In a bio-battery, biomolecules such as enzymes or microbes catalyze oxidation of biomass to generate electrons. The goal of a bio-battery is to design an efficient way to harvest these electrons and channel them through an external circuit before they get oxidized at the cathode. There are different choices of cathodes and structures of a microbial fuel cell. Before going into the details of a bio-battery, let us first look at how an electrochemical battery works.

2 Electrochemistry of a Galvanic Cell

In a galvanic cell, energy is extracted through electrochemical reactions where oxidation-reduction takes place in two half-cells. Moreover, as oxidation occurs in one of the half-cells and reduction in the other, we can channel the electrons released in the process through an external circuit to do work. At the anode and cathode,

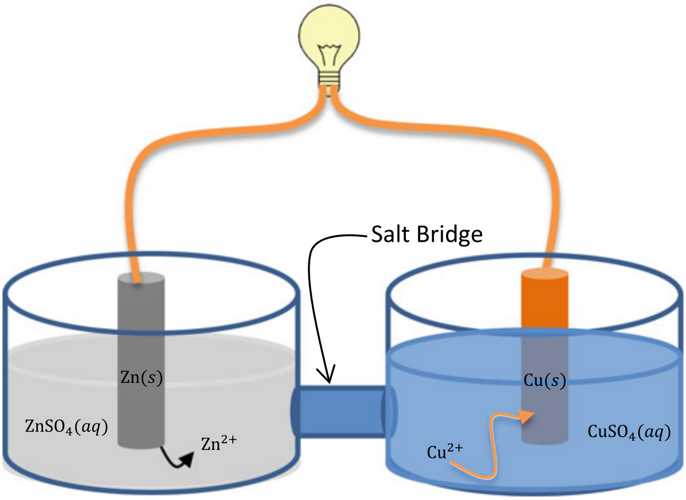

Fig. 1 A typical electrochemical cell with a salt bridge

chemical catalysts are neutralized using a salt bridge. A schematic of a standard Galvanic cell is shown in Fig. 1.

A typical cell might be constructed with two pieces of metal with different electronegativities one copper and one zinc say, each immersed in a solution containing dissolved salt of corresponding metal. It can be verified from the periodic table that copper (electronegativity 1.90) is more electronegative and has more electron affinity than zinc (electronegativity 1.65). When the copper and the zinc electrodes are connected through external circuit, zinc loses two electrons and gets oxidized to zinc cations, whereas copper ions gain these two electrons and get reduced to solid copper. These two half reactions can be written as

$$\mathrm{Zn(s)} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}$$
$$\mathrm{Cu}^{2+} + 2\mathrm{e} \rightarrow \mathrm{Cu(s)}$$

The rate of reaction can be precisely controlled by varying the external resistance connected to the electrodes. If an external source of electromotive force is connected to the circuit, the rate of reaction can be forced to proceed to non-spontaneous or even reverse direction. Current in the external circuit can be measured by an ammeter connected to the circuit. As current is a measure of amount of charge passing through the circuit, by measuring the current we can measure the amount of reactants or number of moles of reactants reduced in the process of cell reaction. For example, 1 A current flowing through a circuit means that there is 1 C of charge (1/96,467 mol of electron) flowing through the external circuit per second and determines the rate of reaction.

The electrochemical cell to operate not only needs an external electrical circuit, but the two electrolytes must be in contact with each other also. However, this type of redox reactions in two half-cells cannot continue forever. In the zinc half-cell, zinc dissolves continuously in the electrolyte to produce Zn^{2+} cations, whereas copper ions keep on receiving those excess electrons via external circuit and metallic copper is deposited on copper electrode. As a result, copper ions are neutralized and the half-cell becomes more and more negative (with sulfate anions), whereas zinc cations dissolved into aqueous solutions make the corresponding half-cell more and more positively charged. This certainly creates an imbalance and more and more work is to be needed to introduce additional Zn^{2+} ions into positively charged electrolyte or for electrons to flow into right compartment where they are needed to reduce the Cu^{2+} ions, eventually ceasing the electrons to flow from zinc to copper electrode. This type of back potential developed between the electrodes and the electrolytes is called *junction potential*. To prevent this charge separation from happening, the charge carried by the electrons through the external circuit must be compensated by some way of ion transport between the cells. This means that there should be a path for ions to cross from one cell to the other. It can be achieved by two ways: (a) two half-cells can be connected by a salt bridge, where the anions of the salt helps to neutralize the excess zinc cations and the cations of the salt helps neutralizing the sulfate anions in the aqueous solution of the copper half-cell to prevent the junction potential to develop and keep the battery running. Another way to keep the current flowing is to use a semi-permeable membrane instead of a salt bridge that prevents the electrolytes from rapid mixing, but allows ions to diffuse through.

3 Electron Transfer at an Electrode

Electron transfer during the oxidation or reduction process at an electrode may occur in a single step or as a succession of multiple steps. Electron transfer in an electrode takes place within a very thin solid-liquid interfacial region at the electrode surface where the electrode is in contact with the electrolyte. The structure of electrolyte within a nanometer of the metal electrode surface is known as electrical double layer. The molecular structure of the electrical double layer determines the nature of the interfacial electric field and in turn determines the reaction behavior in all electrochemical processes. Velasco-Velez et al. (2014) have explored the structure of the electrical double layer at a bare gold electrode and observed that with no applied potential and at positive potentials, the layer is highly structured (resembling ice) with few dangling hydrogen bonds. However, at negative potentials, the layer was more like bulk water, and half of the water molecules lie flat on the surface. The net oxidation or reduction process taking place at an electrode is normally referred to an *electrode reaction*. Electron transfer between electroactive species, i.e., the materials that receive or loose electrons, inside electrical double layers involves quantum mechanical tunneling. This process involves at least four steps: Firstly, hydrated cation enters electrical double layer from the bulk electrolyte solution.

Secondly, hydration sphere of cation is distorted by the electron gas at the metal surface. Thirdly, adsorbed cation gets dehydrated and ready to accept electrons and finally the water molecules break free from the former hydration shell.

4 Microbial Fuel Cell

Microbial fuel cells (MFCs) are bio-electrical devices that harness the natural metabolisms of microbes to produce electrical power, (Bennetto et al. 1985; Bennetto 1990; Allen and Bennetto 1993; Liu and Logan 2004a; Liu et al. 2004b; Logan and Regan 2006; Logan 2009; Logan and Rabaey 2012). Traditional fuel cells like hydrogen fuel cells require energy to generate hydrogen, whereas an MFC requires no external energy source, does not produce any additional greenhouse gasses, depends on the bio-degradability and is self-sustained. All these added advantages over traditional fuel cells make MFCs a potential candidate for sustainable green energy source. Within a MFC, microbes consume sugars and other nutrients in their surrounding environment and release a portion of the energy contained within that food in the form of electricity. Similar to a chemical fuel cells, MFCs offer an option to generate electricity from electron donors oxidized at the anode and electrons pass through an external load to a cathode where they combine with protons and a chemical catholyte such as O_2 is reduced. However, chemical catalysts in galvanic cells are replaced by exoelectrogens, a species of microorganisms that oxidize and transfer electrons to an electrode (Benneto et al. 1985; Chaudhuri and Lovley 2003; Logan et al. 2006). MFCs are typically designed as a two-chamber system with the bacteria in the anode chamber separated from the cathode chamber by a polymeric proton exchange membrane (PEM). Most MFCs use aqueous cathodes where water is bubbled with air to provide dissolved oxygen to electrode.

In the typical two-chamber MFC shown in Fig. 2 exo-electrogenic bacteria present in anode biofilm oxidizes fuel generating CO_2, electrons and protons. Electrons are transferred through an external circuit whereas protons travel from the anodic to cathode chamber through the PEM. At the cathode, protons recombine with electrons in the presence of oxygen to produce water.

It is observed that in a single chamber MFC in absence of PEM power density of generated electricity increases significantly (Liu and logan 2004a). Their construction the MFC consisted of an anode and cathode placed on opposite sides in a plastic (Plexiglas) cylindrical chamber 4 cm long by 3 cm in diameter (empty bed volume of 28 mL; anode surface area per volume of 25 m^2/m^3). The anode was made with carbon paper, and the cathode was manufactured by bonding a PEM directly with the carbon cloth cathode containing Pt catalyst. Using this architecture an order of magnitude higher power generation (146 mW/m^2) in comparison for other complex materials such as anaerobic sediments (16–28 mW/m^2), a high-starch content wastewater (19–20 mW/m^2), or domestic wastewaters (24 mW/m^2) with domestic wastewater can be achieved.

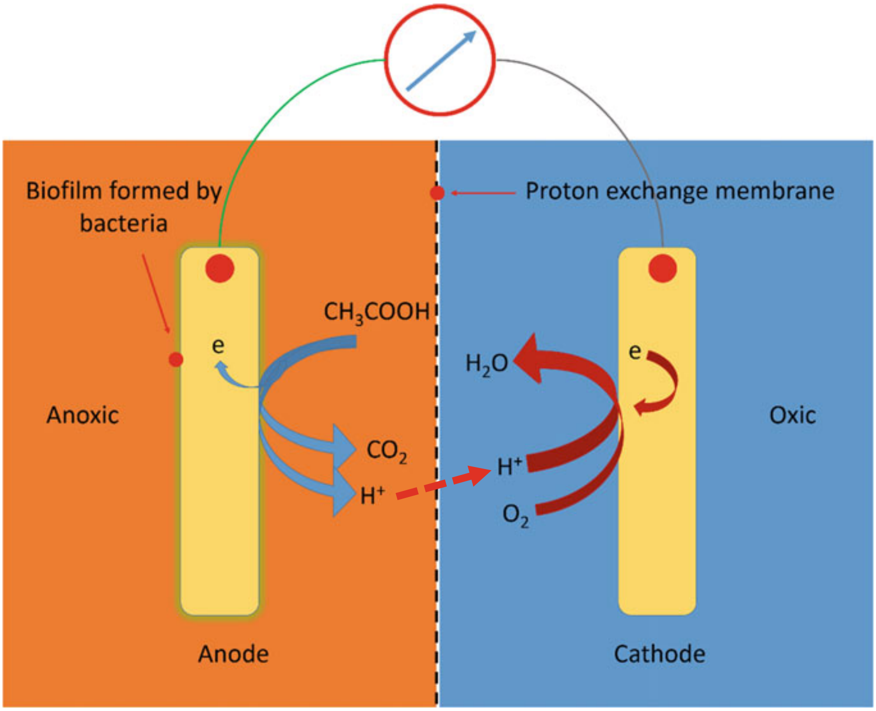

Fig. 2 A typical two-chamber microbial fuel cell with aqueous cathode

Voltage produced by a microbial fuel cell is primarily dependent on the two electrode environments (Rabaey and Verstraete 2005). The microbes form a community and grow on the surface of the anode of the MFCs. In the process of respiration, the biomolecules get reduced and decrease the overall potential of the anode, often steeling between −0.1 and −0.4 V versus a standard hydrogen electrode (SHE). On the other hand, the cathode is generally placed in a more oxygen-rich environment and the dissolved oxygen increases the electrical potential of the cathode, often ranging between 0.4 and 0.8 V versus SHE. The voltage of a MFC is thus the difference between the potential of the cathode and that of the anode and can reach the maximum theoretical limit of 1.2 V [0.8 V – (−0.4 V)]. Typical redox gradients with respect to SHE can be found in *Brock Biology of Microorganisms 13th edition* (Madigan et al. 2010).

5 Electron Transfer Mechanism at the Anode

At the anode when microbes form a colony they start to metabolize sugar and other nutrients, which act as fuel to the microorganisms. The process of metabolism generates highly reduced biomolecules with extra electrons attached to them. These extra electrons are then transferred to the anode generally in one of the following three ways (Fig. 3):

(1) Electrons can be transferred directly from the microbe's wall to the anode,
(2) Mediator assisted electron shuttling from the biomolecule to the anode and
(3) Electron transfer through microbial nanowires or conductive appendages grown by the microbes (Gorby et al. 2006). A schematic of networks of nanowires in microbes can be seen in Fig. 4.

Sometimes electrons are carried directly from the respiratory enzyme to the electrode when the microbe cells expose the redox active proteins on the surface of the electrode. Many strains of bacteria can release electrons from a terminal oxidase

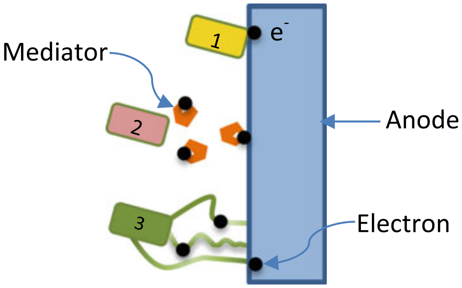

Fig. 3 Electron transfer mechanism from the microbes to the anode

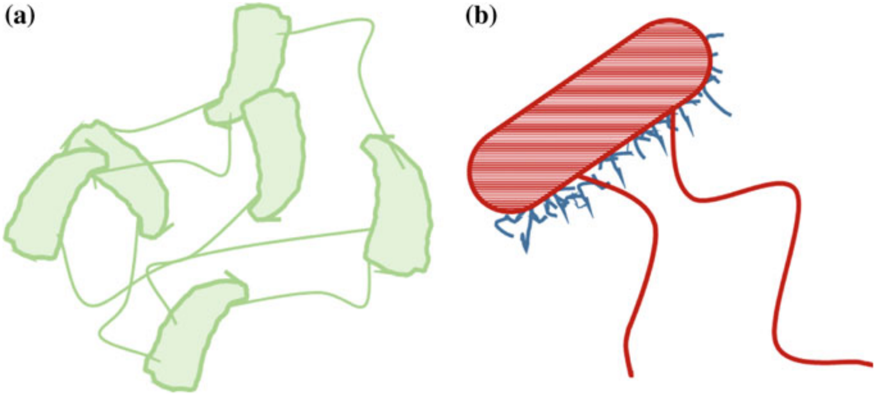

Fig. 4 **a** Electrically conductive nanowires extend many times the length of the bacteria *Shewanella oneidensis*. **b** *Geobacter* sp. with the pili

in the respiratory chain to Fe_{III} outside the cell, producing soluble Fe_{II}. Some electrochemically active bacteria such as *Aeromonas hydrophila* and *Shewanella putrefaciens* (Kim et al. 1999) can thus directly transfer electrons from the microbe to the electrode and these bacteria that can transfer electrons extracellularly, are called exoelectrogens.

Electron transfer through microbial nanowires was also observed when the fermentative bacterium *Pelotomaculum thermopropionicum* is linked to the methanogen *Methanothermobacter thermautotrophicus* by an electrically conductive appendage. This is a direct evidence for interspecies electron transfer (Gorby et al. 2006). However, recent studies have revealed that some of the bacterial nanowires were not made of pili, hair-like appendages that are common on single-celled organisms rather the wires are actually formed from the bacteria's outer membranes. For example *Shewanella oneidensis* soil bacteria extends its outer membrane in the shape of a long tube and its cell membranes have proteins embedded in them called cytochromes, which can pass electrons to one another (Pirbadian et al. 2014). The mechanism used by *Shewanella* spp. to transfer electrons outside the cell is still not clearly understood and most likely there is no single mechanism for the electron transfer. *Shewanella* spp. not only have outer membrane cytochromes for direct electron transfer by contact, but also they can extrude electrically conductive nanowires (Gorby et al. 2006).

Most of the microbial cells are electrochemically inactive. Between a microbe and electrodes, electron transfer is often facilitated by mediator chemicals. Commonly used mediators like neutral red, humic acid, thionine, methyl blue etc. are expensive and often toxic and thus detrimental to scale up the process (Delaney et al. 1984; Lithgow et al. 1986). *S. oneidensis* also produces flavins that can function as electron shuttles (Von Canstein et al. 2008).

6 Mud-Based MFC

A natural microbial fuel cell can be constructed using readily available soil. A mud-based microbial fuel cell adheres to the same basic principles of MFCs whereby mud acts as a source of exo-electrogenic bacteria, nutrient-rich anodic fuel and the proton exchange membrane. Microbes, including *Geobactor* and *Schewanela,* are ubiquitous in soil. Moreover, soil is naturally rich in complex sugars and other nutrients accumulated over millions of years of decayed plants, leaves and animal wastes. It also acts a natural proton exchange membrane as the oxygen consuming aerobic microbes present in the soil acts as an oxygen filter. Microbes present in the mud act as catalysts to break down sugars and complex nutrients thereby releasing a portion of their energy contained within those molecules in the form of electrical energy (Fig. 5).

For a mud-based fuel cell to function two electrodes— anode and cathode separated by a proton exchange membrane is needed. Similar to a galvanic cell discussed earlier, a proton exchange membrane (PEM) ensures that very small ions such as

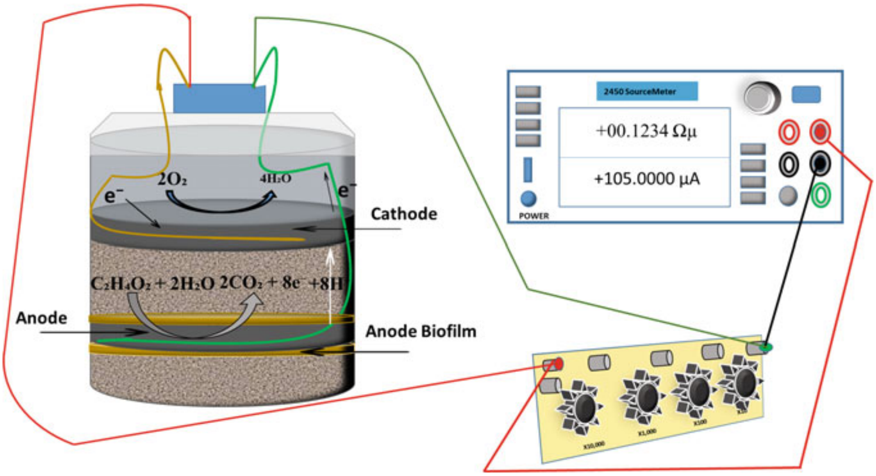

Fig. 5 Schematic of a mud-based MFC (MudWatt)

protons pass through although larger ions such as oxygen is blocked by this membrane. In a mud-based MFC, mud is not only a source of microbes and nutrients, but also it acts as an effective PEM. Inside a MudWatt, an **anode** is placed under the mud. In this anoxic environment, microbes metabolize sugars and other nutrients in the surrounding environment releasing electrons using **anaerobic respiration**. Bacteria multiply over time to cover the anode with a biofilm. Similar to a galvanic cell, the anode acts as the electron acceptor for **exo-electrogenic bacteria**, such as *Shewanella* and *Geobacter*. The other electrode, the cathode is normally placed in an oxic environment where electrons from the anode travel through an external circuit before reacting with oxygen and hydrogen to produce clean water. Thus, this set up not only generates electricity from microbes but also it can be used for bioremediation of waste water to regenerate clean water. Mud-based MFCs are also used to power sensors on the sea and river beds as microbes continue to generate electricity so long as there is a supply of nutrients and other conditions are fulfilled.

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Glossary

Aerobic Metabolism in presence of oxygen.

Anaerobic Metabolism in absence of oxygen.

Anode The electrode where electrons are collected (−).

Bioremediation Using microbes to breakdown environmental through natural biological processes.

Cathode The electrode at which electrons are released (+).

Cellular respiration The chemical process in which cells break down nutrients and sugars and release energy.

Electricity The net motion of charged particles (such as electrons) under a potential difference.

Electrogenic bacteria Organisms that can transfer electrons to extracellular electron acceptors outside their bodies (e.g., an anode).

Electrons Negatively charged fundamental particles.

Galvanic cell An electrochemical cell that uses spontaneous chemical reactions to generate electricity.

Redox Potential A measure of electron affinity or electronegativity of substances.

Redox reaction A reaction that involves electron transfer between two reacting substances.

Metabolism A process by which complex foods are broken down by chemical reactions to yield energy.

Microbe Short form of microorganism.

Microbial fuel cell A fuel cell that uses bacteria to produce electrons and a potential difference.

Review Questions

1. What is the difference between aerobic and anaerobic metabolism?
2. Electrogenic bacteria give off electrons when they respire. In an MFC, what are the transfer mechanisms of the electron from the microbe to the anode?
3. Globally, how much solar energy is captured by plants, algae and cyanobacteria through photosynthesis each year?
4. What is the net annual primary production of terrestrial plants?
5. What is the global sustainable bioenergy production potential? Is this figure significant in the current global energy demand?
6. What biomass materials are identified as bioenergy feedstocks?
7. What are biomass logistics? Name the typical operations of biomass logistics.
8. Explain the general logistics of switchgrass production for bioethanol.
9. What equipment is commonly used for collecting and densifying woody biomass in the field?
10. What techniques have been tested to pre-process lignocellulosic materials for bioethanol generation?

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Advancements in Thermochemical Modification of Wood for Bioenergy and Biomaterial Applications

David B. DeVallance, Xinfeng Xie, Tianmiao Wang and Jingxin Wang

Abstract This chapter explores recent work related to thermochemical modification of low-value woody biomass to produce high-value products for use in bioenergy and biofuel applications. Through thermochemical modification (i.e., pretreatment), woody biomass can be transformed into materials that have higher calorific values and improved electrical properties. In this chapter, advancements in research related to torrefaction and carbonization (i.e., pyrolysis) are discussed, along with the development of densified torrefied pellets and carbon materials. Torrefaction of woody biomass is a less severe thermochemical treatment that results in higher-value materials that can be used in energy applications as a substitute for coal and as a filler material for composites. To advance the use of torrefied woody biomass as a coal replacement fuel, densification technology is a key for improving storage and transportation. This chapter explores some key processing variables and their relationship to pellet quality. In addition, the relative carbon content of woody biomass is increased through pyrolysis. These carbonized materials can be used for fuel cells, energy storage, and as a filler and potential reinforcement in a variety of composite materials. During pyrolysis of wood, the porosity of the resulting material increases. In general, porous carbon materials are classified as microporous (<2 nm), mesoporous

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(2–50 nm), and macroporous (>50 nm) based on their pore diameters. This chapter focuses on research related to mesoporous carbon that has the ability to provide fast mass transport of molecules and large specific surface areas. These two properties are essential in many advanced energy storage and conversion applications.

Keywords Carbonization · Woody biomass · Thermochemical pretreatment · Carbonized wood · Biochar · Torrefaction · Densified biomass · Wood pellets

1 Overview of Wood Thermochemical Pretreatment

1.1 Torrefaction and Densification

1.1.1 Torrefaction

Torrefaction is a thermal pretreatment that is performed by heating biomass material at relatively low temperatures of 200–300 °C under atmospheric pressure and in the absence of oxygen (Prins et al. 2006). In torrefaction, the less thermally stabile hemicellulose, as well as a proportion of cellulose and lignin, decomposes in the temperature range of 225–325 °C (Prins et al. 2006). According to a research by Shang et al. (2012) on wheat straw, during torrefaction, hemicellulose is completely removed when treatment is performed at 300 °C for 2 h. Hemicellulose contains a large amount of hydroxyl groups, which cause biomass to be hydrophilic. Since hydroxyl groups are removed in torrefaction, the torrefied biomass would become less hydrophilic and maintain very low moisture content that commonly ranges from 1 to 6% (Li et al. 2012; Bergman 2005). This reduction in the hydrophilic nature should improve the storage properties of biomass pellets by making them more resistant to moisture uptake.

During the torrefaction process, portions of the woody biomass (mainly hemicellulose) are volatilized, removing more O_2 than C_2. The resulting biomass weight loss increases the energy density of the biomass. According to Bergman (2005), 30% of the biomass weight, and only 10% of the energy, was lost during torrefaction. These results indicate that 90% of the energy in biomass was retained in 70% of the biomass weight, which signifies that the energy density was increased 1.3 times by torrefaction. Furthermore, the weight loss of torrefied biomass becomes greater as the torrefied temperature increases. Specifically, over a two-hour period, the weight loss increases from 25% at the torrefied temperature of 250 °C to 53% at the torrefied temperature of 300 °C. In addition, the calorific value and energy density of torrefied biomass also increased with higher torrefaction temperature or longer residence time, which are key descriptors of the severity of torrefaction. Through torrefaction, the relative carbon content of biomass increases. The increase in carbon content through torrefaction is important as the resulting biomass calorific value becomes closer to that of coal. Li et al. (2012) reported that the lower heating value of biomass was increased from 18.0 to 20.5 MJ/kg.

1.1.2 Densification

Woody biomass properties are also improved by physical treatments such as densification where biomass is made to be denser and have a shape suitable for handling and transportation. Pelletizing is a common densification process in which biomass is compacted under high pressure and temperature into a solid cylindrical shape with varying dimensions (Kaliyan and Morey 2009). Woody biomass as a raw material for pellets is usually obtained from low-value sawdust, small diameter trees, and wood chips. Through pelletization, the bulk density of biomass can be increased dramatically from 40–200 to 600–800 kg/m^3 (Kaliyan and Morey 2009). The higher bulk and energy density lead to an increase in the calorific value and combustion efficiency of biomass. Biomass pellets can be burned with 78–85% of combustion efficiency in pellet stove (Wood and Pellet Heating, 2012). Telmo and Lousada (2011) reported the calorific value of softwood pellets as being from 19.7 to 20.4 MJ/kg, while the calorific value of hardwood pellets is between 17.6 and 20.8 MJ/kg. Pelleting also improves the transportation of woody biomass by reducing the amount of dust and small particles lost during transportation. Additionally, biomass pellets not only facilitate handling and use, but also save transportation and storage costs.

In the pelletizing process, final biomass pellet quality can be affected by different parameters such as pretreatment of biomass, as well as moisture content and particle size of raw materials. Furthermore, die temperature, die length to diameter ratio (L/D ratio), compaction pressure, and pelleting speed (rotations per minute, rpm) can influence pellet quality. Considering pretreatment, adding a torrefaction step into pellet production is a value-added process that combines the advantages of both torrefaction and pelletizing at one location to further improve biomass properties. Even though torrefied biomass pellets are not widely applied in industrial production at present, torrefied wood pellets still have the potential to compete with non-treated biomass pellets. Bergman (2005) reported that torrefied biomass pellets have a bulk density of 750–850 kg/m^3, a calorific value of 19–22 MJ/kg, and energy density of 15–18.5 GJ/m^3. In our research (Wang 2014), we found that red oak had a calorific value of 18.2 MJ/kg, and once torrefied and pelletized, the calorific value increased to 23.7–24.1 MJ/kg. However, there do exist some limitations when pelleting torrefied biomass. Specifically, torrefied biomass particles are more difficult to compact due to the change of chemical components in torrefaction. Additionally, torrefaction itself also consumes energy. Moreover, the pelletizing process requires more energy to compress torrefied biomass with increasing the severity of torrefaction (Stelte et al. 2013).

Compaction pressure is a key parameter in biomass pelleting and should be controlled to optimize efficiency and economic return. Although higher compaction pressure can increase pellet bulk density, Rhen et al. (2005) suggest that the pressure need not be over 50 MPa when using a single pellet die. Other parameters such as moisture content and particle size of raw materials can affect pellet quality. In most European standards, the moisture content is required to be below 10% for pellet production (García-Maraver et al. 2011). Mani et al. (2006) reported that pellet bulk density can be increased by decreasing moisture content (from 15 to 12%) and particle size (from 3.2 to 0.8 mm). Additionally, pellet strength can be improved by reducing moisture content (from 12.1 to 11.3%). However, reduced moisture content and decreased particle size appear to increase energy consumption during pelletizing because of increased friction between particles (Nielsen et al. 2009).

1.2 Carbonization

Carbonization is the process of increasing the carbon content of an organic polymer material by pyrolysis. As wood is carbonized, it undergoes thermal decomposition, which results in a reduction in mass and production of gases and vapor. A previous study (Beall and Eickner 1970) indicated that gases are produced as wood is pyrolyzed at different temperatures. At temperatures up to 170 °C, water vapor is the predominant product of wood decomposition. Between 170 and 300 °C, mass loss is due to torrefaction effects. During carbonization, wood undergoes a significant amount of mass loss between 300 and 350 °C as the cellulose rapidly degrades (Baileys and Blakenhorn 1982). Thermal decomposition of wood ends at about 800 °C beyond which there is no further significant mass loss of the material. The carbon content, however, of the carbonized material will increase when using higher temperatures, as the hydrogen and oxygen content are decreased (Setton et al. 2002).

A wood thermogram (graph showing the variation of mass as a function of temperature) is a combination of individual wood component (cellulose, lignin, and hemicellulose) thermograms (Beall 1971). The peaks due to decomposition of cellulose, lignin, and hemicellulose are distinguishable in the wood thermogram (Zeriouh and Belkbir 1995). Research performed by Beall (1969) points out that in terms of thermal stability, hemicellulose is the least stable component of wood, followed by lignin and cellulose, respectively. Cellulose is the only wood component that has a crystalline structure.

Tang and Bacon (1964) detailed the mechanisms involved when producing carbon from the modification of cellulose. They reported that four stages occur during carbonization of cellulose: (1) desorption of water below 150 °C; (2) removal of water from the cellulose structure between 150 and 240 °C; (3) polymer chain cutting and the breaking of C–O and C–C bonds at temperatures between 240 and 400 °C, and (4) forming of graphitic layers above 400 °C. Polycyclic aromatic hydrocarbon structures were formed during the pyrolysis of cellulose between 300 and 650 °C when the solid residual undergoes a chemical transformation and rearrangement.

1.2.1 Macro Structural Changes During Wood Carbonization

Wood carbonization used to manufacture conventional charcoal generally occurs at final temperature ranged from 400 to 600 °C. During the conventional processes, micro- and macro-sized cracks form in the charcoal as a result of stresses from shrinkage that occurs as the wood material decomposes in different rates at internal and external locations. McGinnes et al. (1971) found that the original cell wall microfibrillar orientation becomes destroyed during carbonization and is transformed into a smooth wall structure that appears more amorphous. They also reported the appearance of creases or folds parallel to and across the longitudinal axis that were a result of longitudinal and transverse shrinkage. These findings suggest that there would be a definite reduction in mechanical properties for wood that has been carbonized due to the inherent occurrence of defects and damage.

Kollmann and Sachs (1967) evaluated the effects of low processing temperature (190–240 °C) on the morphological change of hardwood cells through the use of an electron microscopy. They observed surface distortion of some vessel pits, but no major change in the pits or pit membranes in the treated specimen. These observations indicated that a heat treating process that occurs below 280 °C (before severe cellulose degradation) would most likely not produce any significant cracking or damage the wood material. There is, however, some observed distortion of vessel pits that result at this temperature that are most likely a result of volatiles or gases produced from hemicellulose or low molecular weight chemical decomposition at temperatures as low as 150 °C (Beall 1969). Another study by Blankenhorn et al. (1972) examined rate-controlled carbonization of hardwoods up to 900 °C in a nitrogen atmosphere. The hardwood was heat treated at 6 and 3 °C/min temperature rates. The resulting carbonized hardwoods appeared to have retained the majority of the morphology of the starting woody material at ultra-structure level.

1.2.2 Changes in Physical Properties During Wood Carbonization

Mass loss and the associated shrinkage are the most significant changes in the physical properties during wood carbonization. Most of the early studies have shown that mass loss takes place before volumetric shrinkage (Moore et al. 1974, Slocum et al. 1978). For example, during the carbonization of birch, the major mass loss occurred at about 300 °C, whereas major shrinkage took place at about 400 °C.

There also appears to be consistency in the amount of shrinkage along the longitudinal direction among different wood species (Byrne and Nagle 1997a). In other words, the axial shrinkage of carbonized wood was independent of wood species; however, the reasoning for this observation remains unclear. The dimensional shrinkage of carbonized wood is anisotropic and follows a similar pattern as that taking place during wood drying, where the tangential direction has the greatest shrinkage, and the longitudinal direction has the least shrinkage. Significant dimensional shrinkage continued until the carbonization temperature reaching 1000 °C (Byrne and Nagle 1997b).

Porosity evolution was another notable change in the physical properties during wood carbonization. There was a continuous increase in porosity when black cherry wood was heated in nitrogen from 100 to 600 °C. But the trend reversed as the temperature was further increased to 700 °C (Blankenhorn et al. 1978). More studies on different species and at higher carbonization temperatures are needed to further understand the porosity change during wood carbonization.

Carbonized wood changes from an electrical insulator to a conductor as the highest treatment temperature of the carbonization process is increased to 500 °C. Although the polycyclic structures form in carbonized wood at about 400 °C, the conductivity of carbonized wood has little improvement until the highest treatment temperature is increased to 500 °C. Further increase in the highest treatment temperature to 800 °C or higher makes carbonized wood an electrical conductor (Nishimiya et al. 1998, 2004).

1.2.3 Change of Mechanical Properties During Wood Carbonized

The studies on the changes in mechanical properties of carbonized wood were started with using it as filler for polymer composites (Blankenhorn et al. 1972). When the highest heat treatment temperature of carbonization was increased up to 900 °C, the dynamic mechanical properties of carbonized black cherry wood first decreased and then increased with the lowest modulus in the samples carbonized at 600 °C (Blankenhorn et al. 1972). Similar trend was found in the crushing and impact strengths of carbonized Acacia and eucalyptus wood samples which carbonized with the highest heat treatment temperature ranging from 200 to 1200 °C (Kumar et al. 1999).

A similar trend of change also was found in the tensile strength and modulus of carbonized cellulose fibers. The tensile strength and modulus decreased with increasing temperatures when the temperature is below 464 °C; while above this temperature, the mechanical properties increased linearly with increasing temperatures up to 1200 °C (Plaisantin et al. 2001; Shindo et al. 1969).

Comparison between the changes in the mechanical properties of wood and cellulose fiber showed that the carbonization of wood mirrors that of cellulose. Therefore, similarly to cellulose, greater strength would be expected in wood carbonized at a higher carbonization temperature. Byrne and Nagle (1997a) found that carbonized tulip poplar wood with the highest heat treatment of 1560 °C was 28% stronger in compression than the non-carbonized wood. Other studies (Bryne and Nagle 1997b) have shown that the 22% shrinkage in the longitudinal direction of wood was very close to the 24% shrinkage in the longitudinal direction of cellulose fibers (Tang and Bacon 1964).

Many anisotropic properties of wood are retained after carbonization; the axial or longitudinal direction has the highest performance in mechanical properties and other physical properties, while in the other two directions, radial and tangential directions, these properties are relatively weak (Byrne and Nagle 1997a, b; Greil et al. 1998). Regarding the relationship between the structure of carbonized cellulose fiber and that of raw fiber, the new carbon structure during carbonization may begin with the formation of carbon chains along the paths of the original cellulose chains (Bacon and Tang 1964).

2 Advancement in Wood Thermochemical Conversion: Torrefaction

2.1 Laboratory Scale Pelletization Methods

A specially designed, 6 mm diameter, single pellet die apparatus is used when making pellets for the purpose of studying pellet die temperature and pressure, compaction energy, torrefaction level, particle size, moisture content, and wood species (Fig. 1). This apparatus uses a piston rod to densify ground biomass at a prescribed rate using a universal test machine (UTM). To provide the necessary compaction force, the pellet die is placed into a MTS (MT Systems Corp. USA) universal test machine (UTM) (Fig. 2). This process does not precisely mimic that of a commercial pelleting operation, but does allow for finely controlled conditions when densifying biomass samples. The die itself is heated at a controlled temperature and wrapped with a high-temperature heating tape. To maximize heating, the die assembly is then covered by thermal insulation (to help maintain the temperature). In general, 0.7 g of biomass particles are added to the pellet die for producing pellets. The particles are compacted into pellets using a piston attached to the moving crosshead of a UTM at rates that can be varied. Generally, when using 0.7 g of woody material, the target length of pellets is approximately 25.4 mm (1-inch). Through this type of system, a variety of variables that influence pellet properties and manufacturing can be quickly investigated for further scale-up to larger pellet operations. Specifically, this research has been investigating the influence of woody biomass pretreatment (e.g., hot water extraction and torrefaction), wood species, particle size, moisture content (raw material and environmental storage conditions), pellet temperature and pressure, and compaction energy. Once the research is completed on the small scale,

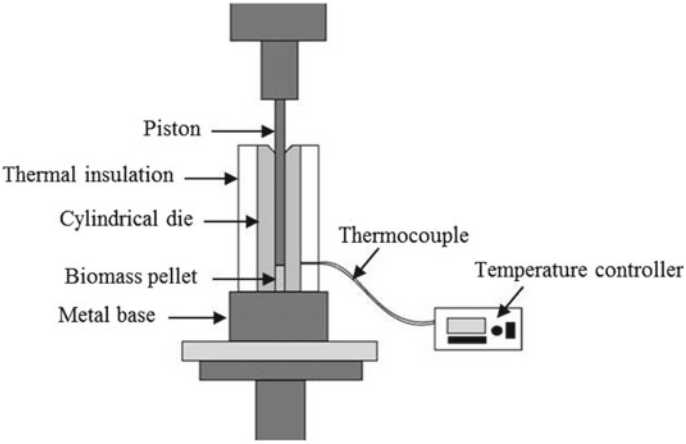


Fig. 1 Diagram of the single pellet die setup

single pellet die press, the work can then be scaled up to a larger pelleting mills, and in our research up to an Amandus Kahl (Reinbek, Germany) pellet press (Fig. 3).

Fig. 2 Single pellet die placed in the MTS UTM

Fig. 3 Full size laboratory Amandus Kahl pellet press

To date, a majority of the research has been focused on small-scale pelleting. Ongoing research is now being conducted on the larger pellet mill with the intention of developing correlations between the single pellet die and full-scale pelleting system. Future research is also being planned to develop correlations between the full size laboratory pellet mill and industrial-sized pellet press.

2.2 Compaction Energy

Compaction energy during pelleting operations can have a large influence on the energy required to push material through a pellet die and also on final pellet durability. Research has been focused on evaluating the compaction energy differences between raw (i.e., non-torrefied) and torrefied red oak (*Quercus rubra*). Specifically, the current research investigated the compaction energy of two levels of moisture content (1.5 and 5%) and particle size (0.5–0.7 mm and 0.7–1 mm) in both raw and torrefied red oak. While moisture content for raw red oak would typically be held higher during pelleting, in this particular research, the moisture content was set at a lower level to match what could be reasonably reached for the torrefied material. To determine the compaction energy needed to produce a given pellet, the area under the pelleting force versus displacement curve is calculated (Fig. 4).

The results of the research on compaction energy for raw and torrefied red oak showed a distinct difference in the amount of energy required. Specifically, the torrefied red oak, regardless of particle size and moisture content level, required a considerably higher amount of compaction energy (Fig. 5). Further analysis was performed to look at differences within both the torrefied and raw groups. Analysis of variance (ANOVA) testing indicated that there was a statistically significant difference in compaction energy in the raw red oak pellet groups (p-value < 0.0001, at $\alpha = 0.05$ significance level). Further analysis using the Tukey–Kramer comparison

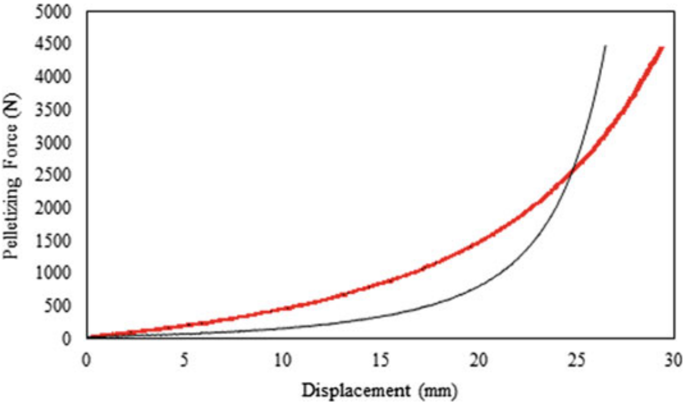


Fig. 4 Example pelletizing force versus displacement curve of raw and torrefied red oak

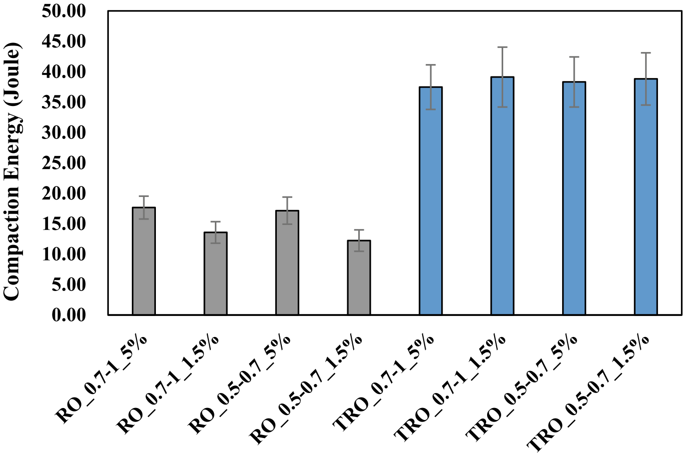


Fig. 5 Pellet compaction energy results for raw and torrefied red oak pellets at two moisture contents and two particle size levels

test indicated the raw wood materials pelleted at the higher moisture content (5%) required more compaction energy (p-value < 0.0001) in both particle size ranges. These results indicate that, in raw red oak, as moisture content decreases, the particles tend to flow and compact with less energy. In terms of particle size, when the moisture content was at 1.5%, the raw wood pellets with larger particle size of 0.7–1 mm required a higher average compaction energy (p-value < 0.0001) than pellets made from the smaller particles (0.5–0.7 mm). At a moisture content of 5%, however, the particle size did not influence the compaction energy (p-value = 0.7761). Based on these results, it appears that at a higher moisture content level, the particle size was less likely to influence compaction energy for red oak pellets. However, this research looked at a rather narrow range of particle sizes. From the parameters utilized in this particular research, the raw wood material with a moisture content of 1.5% and particle size of 0.5–0.7 mm consumed the least energy in pelletizing.

In the torrefied red oak pellets, however, the results of the research indicated that there was no statistically significant difference within the four groups (p-value = 0.2509). Specifically, there was no statistically significant difference in compaction energy between torrefied red oak pellets made from the two particle size ranges (0.5–0.7 mm and 0.7–1 mm) and at different moisture contents (1.5 and 5%). These results suggest that both particle size and moisture content may not impact the energy required to compact torrefied woody biomass (especially red oak) as much as they do in raw red oak.

2.3 Temperature and Pressure

In recent work, a limited study was initiated to determine the influence of pelleting temperature and pressure when torrefying woody biomass material using the single pellet die assembly shown in Fig. 1. Both red oak (*Quercus rubra*) and yellow-poplar (*Liriodendron tulipifera* L.) were torrefied at 250 °C for 30 min in a small laboratory scale setup. The resulting material was ground using a Wiley mill (Thomas Scientific, Swedesboro, NJ) fitted with a 1 mm sieve. The particles were then made into pellets at three different target temperatures (116, 178, and 195 °C) and two forces (4450 N and 6672 N). The results of this investigation found that an increase in temperature improved the diametric compression strength of both the torrefied red oak and torrefied yellow-poplar pellets (Fig. 6). For the temperature ranges investigated, the 195 °C target produced the strongest pellets for both species. With regard to compaction force, while only one temperature range was investigated, the increase in force resulted in a slight increase in pellet strength. The strength at a temperature of 195 °C and force of 4450 N resulted in the strongest pellets for both torrefied species and formed the basis for the torrefied woody biomass pelletization work presented in this chapter.

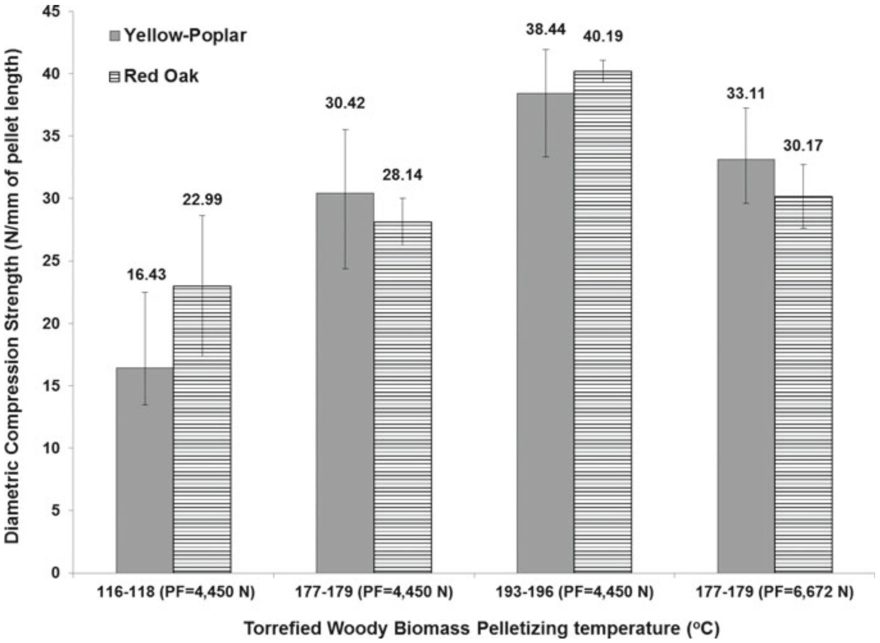


Fig. 6 Pellet compression strength of yellow-poplar and red oak as related to pelletization temperature and pressure.

2.4 Pellet Strength

Commercial-type pellets are typically evaluated for durability rather than strength, through the Pellet Fuel Institute Durability Testing procedure (PFI 2018). The durability test involves tumbling of approximately 1100 g of pellets. Results presented in this chapter for pellet strength, however, are based on a diametric compression test (Fig. 7). A diametric compression test was utilized as the research was focused on a small scale, individual production of pellets. Individually, studying the compression strength of the pellets allowed for a better understanding of the relationships between the different raw wood material input variables and measured values (e.g., required compaction energy and pellet strength). To test for pellet strength, the pellet was placed horizontally on a flat metal surface. Compression load was then applied to the pellet in a diametrical direction through the MTS UTM at a constant rate of 4 mm/min. As the loading increased, the pellet would begin to crack. Loading was continued until the compression load reached the maximum force and then decreased significantly as the pellet shatters or crumbled into pieces. Figure 8 shows the experimental setup along with a tested pellet that has cracked.

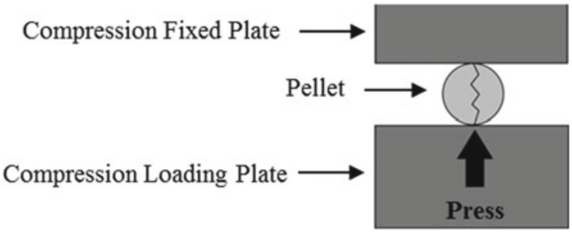


Fig. 7 Schematic of diametric compression test for pellet hardness

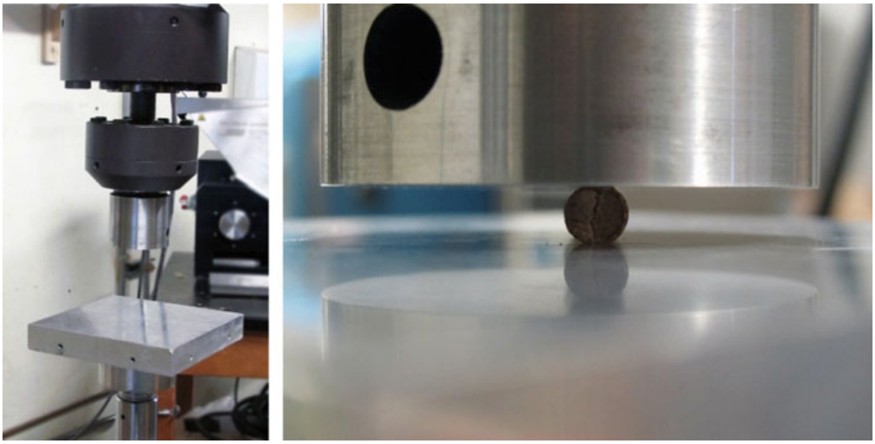


Fig. 8 Compression test for pellet hardness

To determine the final pellet strength, the individual pellet length needed to be considered, as the length of the pellet would impact the overall diametric compression strength. Specifically, in the research, the length of the produced pellets varied slightly, so the pellet strength was calculated by dividing the maximum compression force by pellet length (Eq. 1).

$$\text{Pellet Strength (N/mm)} = \frac{\text{Maximum force (N)}}{\text{Pellet length (mm)}} \tag{1}$$

To evaluate the effect of particle size and moisture content during pelleting of torrefied and raw red oak, twenty pellets were tested for each individual type of pellet produced at two levels of moisture content (1.5 and 5%) and particle size (0.5–0.7 mm and 0.7–1 mm). Overall, 160 pellets total pellets were tested. Figure 9 shows the hardness of both raw and torrefied red oak pellets.

Overall, the average strength of raw red oak pellets was approximately seven times larger than the torrefied pellets. In regard to the torrefied pellets, the particles appeared to be less compacted with large gaps between each other. The average density for the torrefied pellets (820 kg/m^3) was found to be significantly lower than the raw red oak pellets (1354 kg/m^3). These voids and lower density resulted in fracturing on the side surfaces at lower force and resulted in complete crushing at low force. These results indicate that the red oak as torrefied and pelleted in this research would most likely not make a durable pellet without the addition of binders or modification of the pelleting process. Stelte et al. (2013) and Li et al. (2012) also reported that as torrefaction temperature increased (i.e., higher the torrefaction level), torrefied biomass pellet strength and density both decreased. The raw red oak pellets, however, were able to achieve quite suitable strengths that would be expected in a commercially

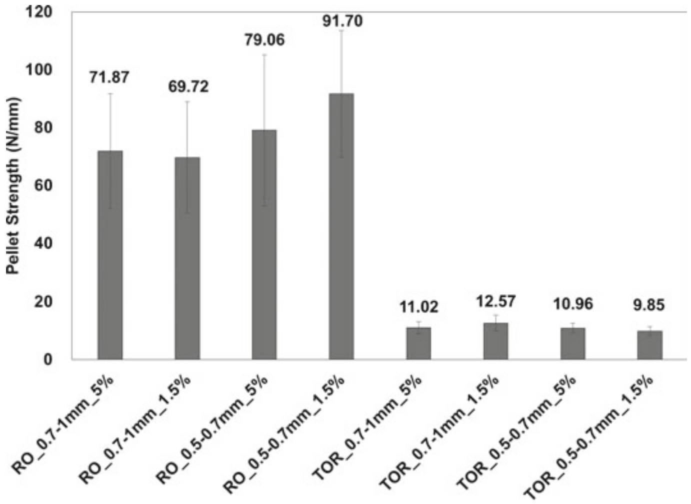


Fig. 9 Pellet strength (N/mm) of raw (RO) and torrefied (TRO) red oak pellets

available pellet. Further analysis of particle size and moisture content within the raw red oak group indicated that there was no statistically significant difference between the average strength of the pellet types, with the exception of the pellets made with the smaller particles at 1.5% MC (i.e., sample RO_0.5-0.7mm_1.5%). These pellets had a higher average pellet strength when compared to the pellets made from larger particle size (0.7 mm–1 mm) at both the 1.5 and 5% MC level. These results indicate that for the raw red oak, the smaller particles at a lower MC level were able to achieve the highest average strength. Interestingly, these particular pellets also required the least amount of compaction energy during pelleting (Fig. 5). In regard to the torrefied red oak pellets, the results of the analysis indicated that there was no statistically significant difference in the average pellet strength between the four types of pellets (p-value = 0.0742). This result indicates that for the production of torrefied pellets, moisture content and particle size were not important parameters in terms of pellet hardness. These results were similar to those found in relation to the required compaction energy, where particle size and moisture content differences in torrefied red oak did not appear to be significant factors. These results also appear to suggest that there may not be any benefits to raising the moisture content of torrefied woody biomass during the pelleting process.

2.5 Resistance to Moisture

To evaluate the resistance to moisture conditions found within typical storage and transportation environments, the pellets were subjected to various equilibrium moisture contents (EMC) based on normal wood EMC situations. Specifically, the raw and torrefied red oak pellets were subjected to the conditions in Table 1 in a CSZ environmental chamber (Cincinnati, OH). Additionally, to evaluate the effect of pelleting, representative raw and torrefied red oak wood chips were also subjected to the various EMC conditions. For each setting, the pellets were left in the environment until their weight stabilized.

Table 1 CSZ chamber settings for the target moisture content used in the experiment

Target moisture content (%)	Temperature (°C)	Relative humidity (%)
5	37.8	25
7.5	26.7	40
10	21.1	55
12.5	32.2	70
15	37.8	80
17.5	26.7	85
20	26.7	90

The results of environmental conditioning of the pellets are shown in Fig. 10. The results indicated that up to 12.5% EMC conditions, the pellets behaved similarly. However, above the 12.5% EMC condition, the raw red oak pellets began to take on considerably more moisture than the torrefied red oak pellets. Particle size and moisture content at the time of pelleting appeared to have little influence on final EMC for both the torrefied and raw pellets. However, it was evident that the pelletizing process resulted in better moisture resistance as compared to the raw and torrefied wood chips (Fig. 11).

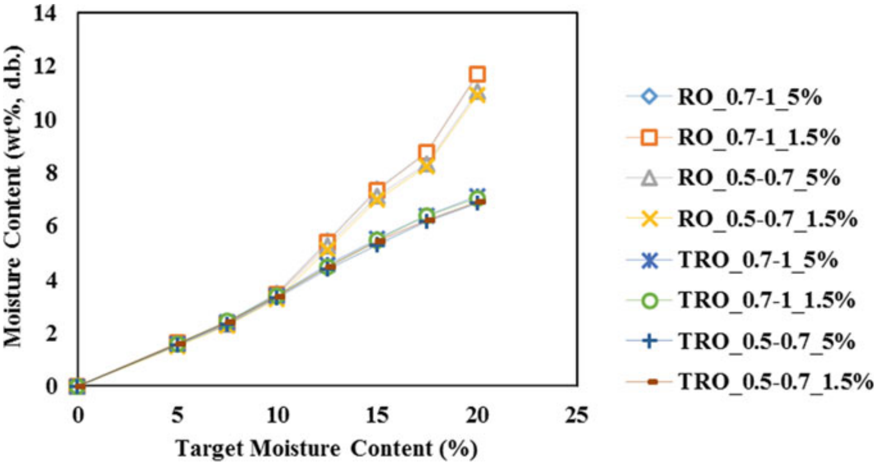


Fig. 10 Moisture content of raw and torrefied red oak pellets in chamber conditioning test

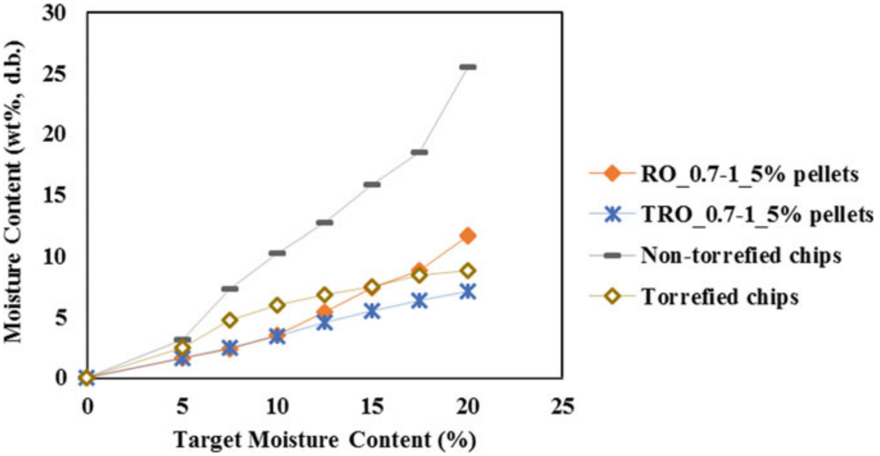


Fig. 11 Moisture resistance of raw and torrefied red oak chips and pellets

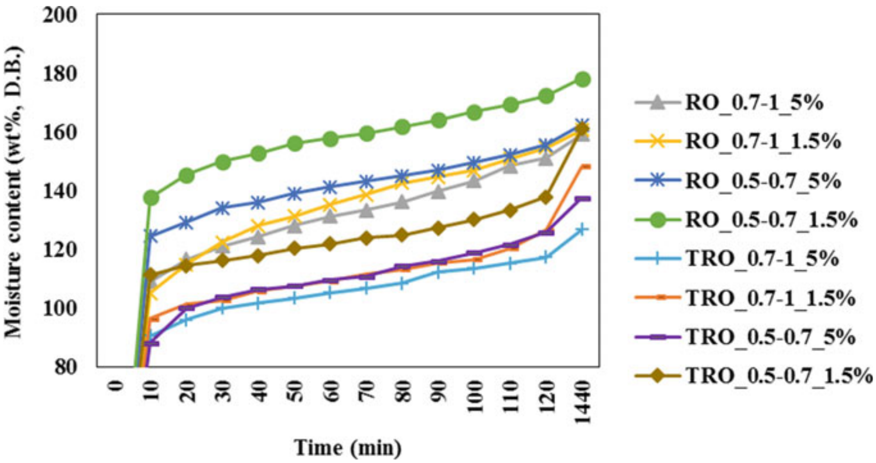


Fig. 12 Water absorption resistance of raw and torrefied red oak pellets

To evaluate the resistance to water submersion, the pellets were subjected to full immersion in distilled water for 24 h. Mass measurements were obtained in 10 min increments for the first two hours, and then one final measurement was taken at 24 h. Additionally, to evaluate the effect of pelleting, representative raw and torrefied red oak wood chips were also subjected to the water immersion tests. The results of the water immersion tests are shown in Fig. 12. The results indicate that each type of pellet absorbed a significant amount of water during the first 10 min period, with the raw pellets taking up a significantly larger amount of water. After the 10 min period, the pellets appeared to take water at a less rapid rate. The raw pellets took up a significantly higher amount of water than the torrefied pellets, with the exception at the 24 h finish time, where one torrefied pellet type (i.e., 0.5–0.7 mm particle size pellets made at 1.5% MC) took up a similar amount of water as three of the raw pellets. In contrast to the moisture content tests, however, the pellets took on more water during the absorption tests as compared to the chips (Fig. 13). This occurrence is likely due to the higher amount of surface area of the pellets when compared to chips.

In addition to the moisture and water absorption results, the visual appearance (i.e., physical breakdown) of the pellets under these conditions also showed that the raw pellets were not as durable as the torrefied pellets (Fig. 14). The raw pellets expanded considerably more in length and lost more particles than the torrefied pellets. The torrefied pellets' shape did not change significantly under high target moisture content conditions. Furthermore, the torrefied pellets retained their shape better as compared to the raw pellets that disaggregated during the 24 h of water immersion. Thus, the torrefied pellets presented better moisture resistance from an appearance standpoint.

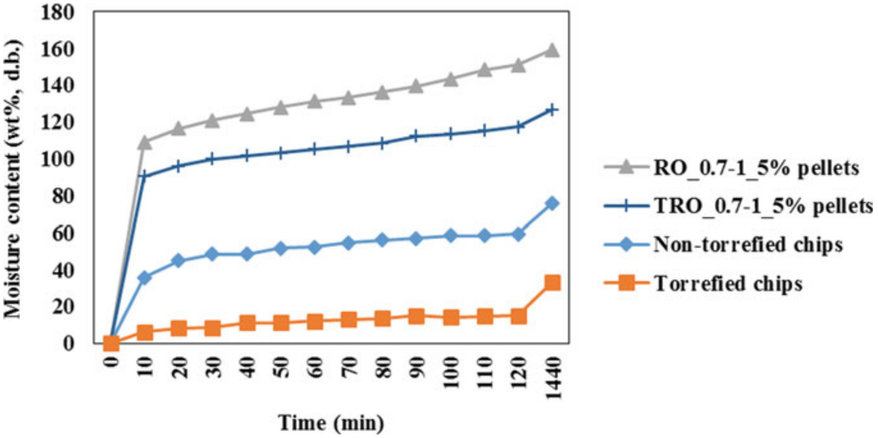
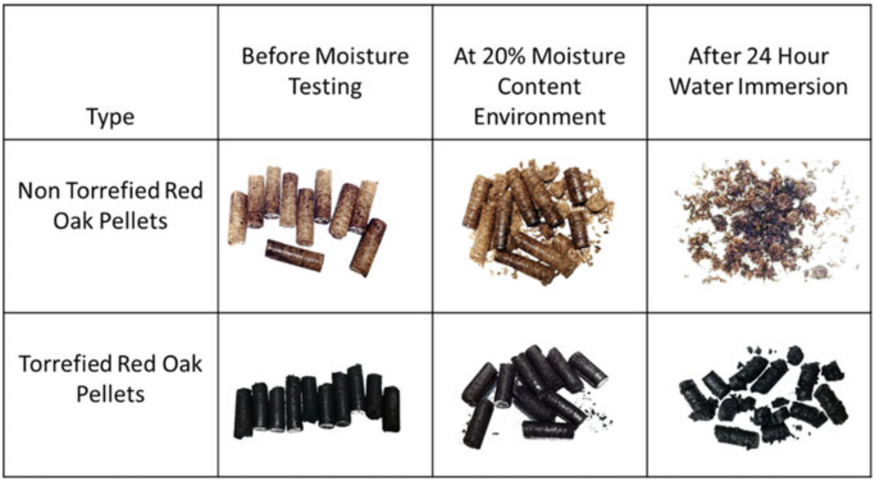


Fig. 13 Water absorption resistance of raw and torrefied red oak chips and pellets



Type	Before Moisture Testing	At 20% Moisture Content Environment	After 24 Hour Water Immersion
Non Torrefied Red Oak Pellets			
Torrefied Red Oak Pellets			

Fig. 14 Visual results from water absorption and environmental condition tests on non-torrefied and torrefied red oak pellets produced with particles at 5% MC and a 0.7–1 mm particle size

3 Advancement in Wood Thermochemical Conversion: Carbonization

3.1 Carbon Crystalline Evolution and Its Effects on Properties of Carbonized Wood

In this chapter, carbonized wood is referred to the char produced by pyrolysis of wood at temperatures ranging from 800 to 1300 °C. The lower limit of the temperature range is the temperature beyond which no significant mass loss due to the thermal decomposition of wood components was observed in previous studies. The higher limit of the temperature range is defined by the International Committee for Characterization and Terminology of Carbon (ICCTC). Carbonized wood consists of disordered carbon structures and graphite-like structures (Edwards 1989). The latter is also called a turbostratic (Kinoshita 1988) structure. Perfect graphite crystals consist of equidistant parallel graphene sheets (hexagonal carbon rings), and these graphene sheets are aligned perfectly in the direction normal to the sheets (Fig. 15). However, in carbonized wood, the graphene sheets rotate about the axis perpendicular to the graphene sheets, resulting in a turbostratic structure (Fig. 15) of two-dimensional order (Warren 1941).

Several studies have shown that the graphene sheets in the turbostratic crystallites formed during wood carbonization are preferentially oriented parallel to the axial or longitudinal direction of the wood cells (Byrne and Nagle 1997b; Paris and Zollfrank 2005; Greil et al. 1998). Recent study has provided insight into the orientation of the graphene sheets in the cross-sectional plane where wood cell profiles approximate ring shapes. It has been suggested that in the cross-sectional plane, the graphene sheets formed during the carbonization of wood are not arranged along the circumference of the wood cell walls.

The formation and growth of the turbostratic structure during wood carbonization are significantly influenced not only by the processing temperature but also

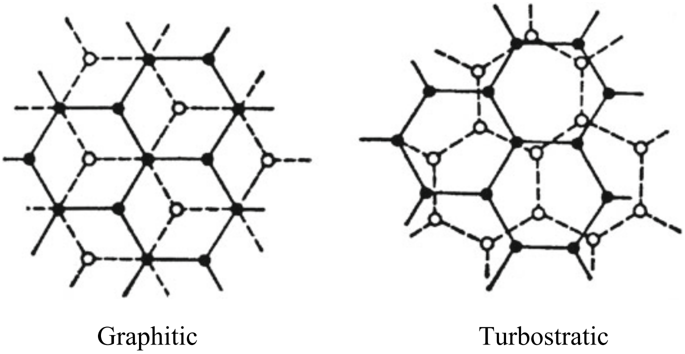


Fig. 15 Graphitic and turbostratic stacking of graphene layers (Inagaki 2000)

heating rate. Both higher processing temperature and slower heating rate can promote the growth of graphene sheets in the turbostratic structures. The structures formed at higher processing temperatures can be formed at relatively low processing temperatures if slow heating rates are adopted.

The electrical and mechanical properties of carbonized wood are related to its structure. Carbonized wood can be considered a two-phase system that includes disordered carbon and turbostratic crystallites with large size graphene, and with the latter being the electrically conducting phase of the material (Kercher and Nagle 2003). Both high temperature and slower heating rate can incorporate more carbon atoms into the turbostratic structures to form large graphene sheets, resulting in higher electrical conductivity.

The turbostratic structures have a significant influence on the mechanical properties of carbonized wood (Zeckler et al. 2006). Because the graphene sheets in the turbostratic crystallites were preferentially oriented parallel to the axial or longitudinal direction of wood cells, growth of these graphene sheets may increase the stiffness of the carbonized wood in the longitudinal direction. The preferred orientation of the turbostratic structure also explains the anisotropic properties of carbonized wood.

3.2 Highly Ordered Mesoporous Carbon Produced Using Wood Cell Nanostructure

Porous carbon materials are classified as microporous (<2 nm), mesoporous (2–50 nm), or macroporous (>50 nm) according to their pore diameters. The uniqueness of mesoporous carbon lies in its ability to provide fast mass transport of molecules and large specific surface areas as well. These two properties are required for many advanced energy storage and conversion applications of porous carbon involving liquid electrolytes. Highly ordered mesoporous carbon (HOMC) is a carbon material having well-defined nanostructures in the mesopore (2–50 nm) range. It has been an essential material in many high-performance electrochemical energy storage devices, such as supercapacitors of both high-energy and high-power densities (Simon and Gogotsi 2008; Li and Wei 2013).

Activated carbons produced from carbon-rich plant materials, such as coconut shells, fruit stones, and wood, have been the most widely used porous carbon materials in supercapacitors because of high specific surface area, low cost, and simple production processes. The carbons usually are prepared by carbonization of the precursors in an inert atmosphere with subsequent activation using carbon dioxide (CO_2), steam, or potassium hydroxide (KOH) to increase the specific surface area and pore volume. Conventional activated carbons have a specific surface area typically in the range from 1000 to 2000 m^2/g with a broad distribution of pore size. The presence of small bottleneck pores blocks access of electrolyte ions to the internal surface area of the pores, resulting in poor energy storage performance. Activation using higher burn-off rates is generally employed to increase the specific surface area and to introduce mesopores into the material for improved energy storage performance (Pintor et al. 2013; Iniesta et al. 2001). Previous studies have shown that the specific surface area of activated carbon is positively related to burn-off rate (Zondlo and Velez 2007). Therefore, the intrinsic non-selective burn-off can increase the energy storage density, but at the expense of significant reduction in overall yield of the final carbon product and additional cost to the products.

Most of the studies in developing new porous carbon directly from plant materials have focused on making use of the natural porous structure of the raw materials at plant cell and cell wall levels. Very few studies have investigated retaining the nanometer-scale architecture of plant cell walls, which consists of orderly arranged cellulose microfibrils embedded in a matrix of lignin and hemicellulose.

Recent studies (Xie et al. 2008a, b, 2009a) have demonstrated that wood can be used to produce unique porous carbon materials that contain orderly arranged nanochannels about 10 nm wide and 300–500 nm long surrounded with carbon walls about 8 nm thick (Fig. 16a). The process uses a stepwise oxidative carbonization process, in which wood was slowly heated in air to about 250 °C followed by oxidation of the treated material at 400 °C with limited oxygen supply. The orderly arranged nanostructure is totally different than the homogeneous morphology of conventional activated carbon at the nanometer level (Fig. 16b). Similar carbon nanostructure has been produced using special triblock copolymers and a more complicated nanocasting approach (Ramasamy et al. 2010; Jin et al. 2013).

It was proposed that those nano-channels were produced from selective ablation of the cellulose microfibrils, while the skeleton made of high-carbon yield lignin was retained, because the dimensions of the nano-channels fall into the size range of the original cellulose microfibrils in the wood cell wall (taking into account the

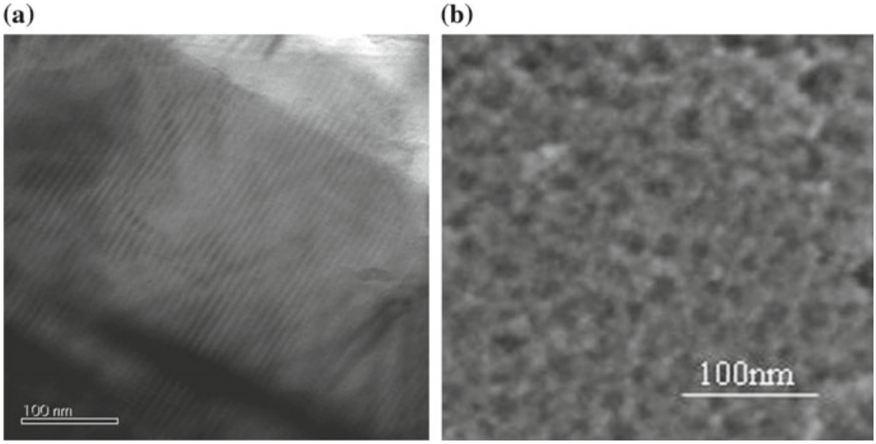


Fig. 16 **a** Ordered nano-channels in a carbonized wood cell wall using two-step oxidative carbonization (From: Xie et al. 2009a). **b** Conventional unordered activated carbon from lignocellulosic materials (From: Li et al. 2010)

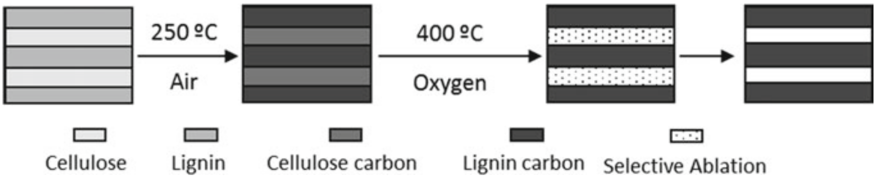


Fig. 17 Formation of nano-channels in wood cell walls during the stepwise carbonization process

shrinkage due to thermal degradation). In addition, the carbonization of pure cellulose or lignin using the same process did not produce nano-channels, indicating that the nanostructure of the original lignocellulosic cell wall is required for the production of the nano-channels.

When prepared under identical carbonization conditions at temperatures lower than 500 °C, the carbon from cellulose is more vulnerable to oxidation as compared to the carbon from lignin (Xie et al. 2009b). Higher carbonization temperatures reduce and eliminate this difference in stability to oxidation between the two types of carbons. This difference between the reactivity of cellulose and lignin carbons explains the selective removal of cellulose microfibrils at temperatures lower than 500 °C.

Slowly heating the woody material in air at temperatures lower than 250 °C is the key to stabilizing the nanostructure in the cell wall. The process could increase the glass transition temperature (T_g) of lignin (Braun et al. 2005), resulting in better thermostabilization of the materials. Cellulose is primarily undergoing dehydration in this temperature range, and the microfibril morphology could be retained. Hemicelluloses were removed during the process as they start to degrade at temperatures below 200 °C. Since hemicelluloses bridge cellulose and lignin in the cell wall structure, the removal of hemicelluloses could help separate the cellulose and lignin phases in subsequent processes.

The proposed mechanism involved in the formation of nano-channels in carbonized wood cell wall is demonstrated in Fig. 17.

The mismatch between the availability and the demand for mesoporous carbon materials is increasing progressively as we find more and more applications for these materials in renewable energy and manufacturing sectors. Conventional technologies for the production of porous carbon failed to produce well-defined nanostructures in the material, and existing methods to synthesize carbons with well-defined nanostructures using templates require high-energy input, toxic chemicals, and extremely limited types of raw materials. High cost is the biggest obstacle to wide range applications of such carbon materials. Taking advantage of the naturally well-arranged nanostructures in plant cell walls and producing well-defined carbon nanostructures may open up a new method for large-scale production of cost-effective mesoporous carbon materials.

Glossary

Bulk density "Mass per unit volume occupied by a large quantity of particulate material" (ASABE Standards 2011).

Carbonization "A process of formation of material with increasing carbon content from an organic material, usually by pyrolysis, ending up with almost pure carbon residue at temperature up to about 1600 K" (Marsh 1989).

Cellulose Linear long-chain polymer component, $(C_6H_{10}O_5)_n$, that is the primary material of the cell wall of wood and plant material.

Cellulose microfibril "A bundle of cellulose polymer chains and associated polysaccharides of other types that are united at some regions in highly ordered crystalline lattices known as crystallites and are less highly ordered in the zones between the crystallites (amorphous regions); it is the smallest natural unit of cell wall structure that can be distinguished with an electron microscope" (Panshin and deZeeuw 1964).

Compaction energy Energy required to compact wood particles or fibers to a specific final volume or density.

Densification "Process of increasing bulk density or energy content of biomass to improve handling, storage and transportation" (ASABE Standards 2011).

Hemicellulose Lower molecular weight, generally branched-chain polysaccharide component found in wood and plant material.

Higher heat value "The full energy content of a fuel. It is the amount of heat produced when a liquid fuel or oven dried solid fuel is fully combusted, all of the products of combustion are cooled to 25 °C (77 °F) and the water vapor formed during combustion is condensed into liquid water" (ASABE Standards 2011).

Highly ordered mesoporous carbon A porous carbon with very uniform pore size between 2 and 50 nm

Hot water extraction Process of using hot water (120–240 °C) or steam to extract hemicellulose in wood.

Lignin High molecular weight component based on phenylpropane units that is found in the cell wall and between cells in wood and plant material and acts primarily as a binding agent.

Lower heat value "Net heat released from the combustion of oven dry solid fuel after reducing the HHV by the heat of vaporization of the water generated by combustion of the hydrogen in the fuel. Each gram of hydrogen produces 9 grams of water" (ASABE Standards 2011).

Macroporous carbon A porous carbon material that has a major part of its porosity in pores of larger than 50 nm width.

Mesoporous carbon A porous carbon material that has a major part of its porosity in pores of width between 2 and 50 nm.

Pellet A densified or compacted product formed from particles or fibers.

Pellet durability A quality control measure that determines an index value of how well wood pellets hold up to feeding and handling.

Pellet hardness A quality control measure that determines the amount of force required to break a wood-type pellet.

Pyrolysis The chemical decomposition of a substance brought about by heat.

Thermochemical Heat-associated chemical and physical phenomena.

Torrefaction "A pretreatment method where biomass is subjected to moderate heating (200–300 °C) in a low oxygen environment" (ASABE Standards 2011).

Torrefied biomass Product resulting from the torrefaction of wood and other plant-type materials.

Woody biomass Any part of a tree and woody plants grown in forests and on other land that are generally classified as by-products from other harvesting operations.

Critical Thinking Questions

1. Pelleting and briquetting techniques have been used to densify woody biomass for many decades in the USA. Are there newer and less energy-intensive processes that may be adapted for densifying woody biomass?
2. Uses of torrefied woody biomass have primarily been limited to energy-related applications as a substitute for coal. Given the inherent properties of torrefied wood material, what other potential value-added applications could exist for torrefied biomass?
3. What role do wood pellets and carbonized materials play in the context of bioenergy and bioproduct development under a systems thinking approach?
4. Could woody biomass-derived carbon materials be made strong enough for structural applications?
5. What are the factors that affect the physical and chemical properties of the final products during thermochemical treatment of woody biomass?

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Chemistry of Bioproducts

Santanu Maitra and Kalyani Maitra

Abstract Bioproducts are bio-based products derived from sustainable resources or biomass. Energy, chemicals, and various materials obtained from such resources can be classified under the umbrella of bioproducts that provide an alternate to fossil fuel-derived products. Bioproducts offer the advantage of reducing greenhouse gas emission, arresting global warming, and preventing loss of fossil fuel resources. This document has attempted to review the three major classes of bioproducts, viz. bioenergy, biochemicals, and biomaterials from the viewpoint of a chemist. The emphasis has been primarily given to the understanding of chemical structures, formations, transformations, and reactions of various classified bioproducts. Chemistry is inevitable and omnipresent in the process of making bioproducts beginning with biomass through intermediates. The proper understanding, safe manipulation, and smart application of the chemistry involved in the generation of bioproducts are essential in the smooth transition from fossil fuel products to bioproducts with the ultimate goal of making the world a safer and cleaner place.

Keywords Bioproducts · Bioenergy · Biomass · Biomaterials · Biorefinery · Renewable energy · Sustainable energy · Fossil fuel · Green chemistry

1 Definition of Bioproducts

Bioproducts are simply characterized as products derived directly or indirectly from renewable biological resources (Singh et al. 2003; Bowyer and Ramaswamy 2005). Bioproducts are also called bio-based products that can be energy, chemicals, and materials as each of the three types of products could be derived from biomass. The primary difference between bioproducts and conventional petroleum-based products lies in the source or starting material used for the generation of the specific product. The non-bioproducts involve direct and indirect consumption of fossil fuel-based resources. The petroleum resources are not only non-renewable, but also lead to

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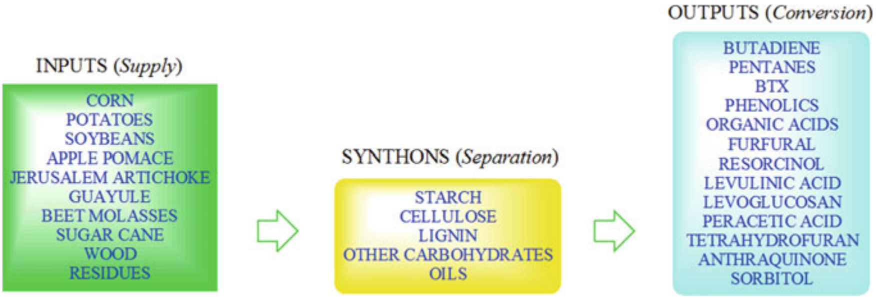


Fig. 1 Examples of bioproducts generated directly and indirectly from available biomass

the formation of hazardous by-products and pollution. Bioproducts, therefore, are produced from renewable biomass and generate no or significantly less hazardous materials as opposed to petroleum-based products. A few examples of bioproducts are organic chemicals, biofuels, organic solvents, synthetic building blocks, body lotions, bio plastics, etc. (Fig. 1).

Bioproducts offer tremendous hope for a safer and greener world for future generations, if adopted with an open mind. The hope and driving force are to replace petroleum-based products with bioproducts, as much as possible, and also to generate newer innovative bioproducts. The promise for a cleaner and safer world will become prominent as cutting-edge research leads mankind toward embracing the world of bioproducts with open arms. The pictorial depiction of the two pathways in Fig. 2 demonstrates the same general destination with the consumable products. The bioproducts may be a subset of the general products that humankind has been accustomed to or, the renewable resources that could also help produce a new item in the list of consumable products.

Bioproducts are often perceived as biochemicals and biomaterials exclusively (Nikolau et al. 2008). In reality, the vast category of bioproducts encompasses biochemicals, biomaterials, as well as bioenergy. Bioenergy is renewable energy that can also be derived from similar bioresources, viz. biomass that is commonly known to generate non-energy-based products.

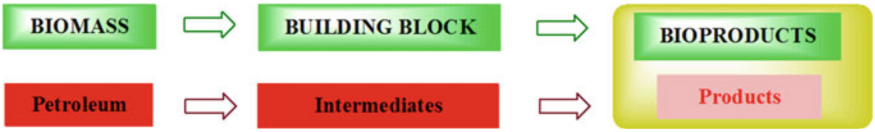


Fig. 2 Cartoon diagram of petroleum- and biomass-derived routes to yield products

2 Bioproducts and Bioeconomy

Bioeconomy is the economy derived from all bioproducts—their inception, research, development, and application (Hilgartner 2007). In reality, the term bioeconomy is often used by the biotechnology industries as biotechnology provides the know-how to generate bioproducts from biomass—renewable biological resources. Commercial chemicals, energy, agriculture, and health industries utilize and exploit the innovation, execution, and evolution of biotechnology advances and thus exercise a wide range of bioeconomic activity. Juan Enriguez and Rodrigo Martinez defined the term bioeconomy for the first time in 1997 at the American Association for the Advancement of Science (AAAS) meeting (Enríquez 1998). The authors later described how biodata flow can have a direct and indirect impact on the intellectual properties created from new discoveries and inventions made in the biotechnology field as more and more biotechnology ventures emerge (Martinez et al. 2003).

Bioeconomy can be considered as the economic parallel to the mainstream economy associated with the production process based on petroleum. Apart from the massive economy involved with all bioenergy, biochemical, and biomaterials production from biomass, bioeconomy can have another huge potential for the initial innovation aspects (Bhat 1999). The inevitable intellectual property involved with the production of new bioproducts and various new and novel methods or processes to generate bioproducts that contribute enormously to 'bioeconomy.' Examples of such bioproducts are electricity, heat, and biofuels under bioenergy, fine chemicals, chemicals, pesticides, and drugs under biochemical, and food and plastics under biomaterials.

3 Significance of Bioproducts

The incentive for bioproducts derived from biomass, unlike regular products from petroleum resources, is multi-fold. The continuous depletion of the petroleum resources from Earth is one of the primary incentives for discontinuing the production and use of petroleum-based products. The search for alternate resources was one of the major reasons for the development of bioproducts from renewable biomass. Since biomass is produced on Earth in the plant and animal kingdom, unlike fossil fuel resources stored inside Earth, it can be regenerated, and thus renewable.

Substitution of fossil fuel with biomass offers the promise to be less harmful to the 'carbon cycle.' Carbon cycle is the maintenance of carbon in its organic (biomass) and inorganic (CO_2) forms through a cyclic path generating CO_2 through photosynthesis. Dissipation of fossil fuel to generate consumable products disturbs this balance by producing an excess amount of CO_2 (Barbir et al. 1990; Goeppert et al. 2012). The route to bioproducts from biomass, on the other hand, offers to keep this natural balance of CO_2 undisturbed if planned, executed, and monitored properly (Withagen 1994).

The second remarkable benefit for the consideration of bioproducts is the ‘green’ advantage. The overall process to convert fossil resources into bioproducts harms Earth’s environment. All three components of Earth’s environment, viz. air, water, and land are directly and indirectly impacted by the constant production of a diverse array of products from fossil energy sources. Many of the pollutants used or generated during the conversion process are hazardous at various levels and toxic to humans and other living organisms. Often the ill health effects can be slow and silent, making the detection of pollutants challenging (Felix and Gheewala 2014).

Much of the air pollutants are generated during the energy-generating use of fossil fuels. Examples are carbon dioxide (CO_2), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOCs), etc. (Lyons et al. 2014; Liu et al. 2012). It is noteworthy to mention here that consumption of fossil fuels has led to the rapid generation of gases including a large amount of carbon dioxide, which retains heat in the Earth’s atmosphere. The process, in turn, has led to global warming—a term that has become quite common in the past several years. Global warming has been a continuous process with various adverse effects, viz. severe weather changes and subsequent after effects. Steady use of petroleum and petrochemicals has also caused atmospheric pollution. The generation of bioenergy from biomass is a *cleaner* process, despite being not yet completely free of pollution. Ongoing research holds more promise to further reduce the amount of pollution in the bioprocesses.

The pollution of land and water can be primarily blamed on the chemical processes used at different stages in the conversion of fossil resources into the plethora of chemicals, and materials for human use. Inorganic acids and bases, organic chemical building blocks, reagents for chemical transformations, chemical solvents, organic and organometallic catalysts, and metals are the primary culprits. The production or synthesis of bioproducts and biomaterials is not perfect; however, it offers cleaner paths through environmentally harmless or less intrusive processes. The phrase ‘Green Chemistry’ is often mentioned as a reasonable solution in the context of environmental pollution and hazardous chemical practices (Horvath and Anastas 2007; Anastas and Eghbali 2010). Green chemistry is sustainable chemistry with a careful of the chemical scheme aimed at preventing pollution at various levels and by various means. Although green chemistry is a separate field by itself, it often shares the principles valid for bioproducts. Green chemistry is more of a culture, mindset, and philosophy that lead to a set of principles, rules, and habits that help eliminate and reduce hazardous chemicals, procedures, and waste while alleviating safer practices. Despite bioproducts and biomaterial production begins with environmentally benign biomass, the chemical transformation process involving various intermediates and building blocks could pose similar challenges normally found in the petroleum-based procedures.

Thus, the development of safer methodologies and processes for bioproducts does not end at the use of biomass. The challenges can be overcome with innovation. Prevention of waste, safer chemicals and solvents, use of renewable feedstock, use of catalysts and biocatalysts, smarter synthetic schemes with fewer by-products, and biochemical pathways are techniques often used in the production of biochemicals

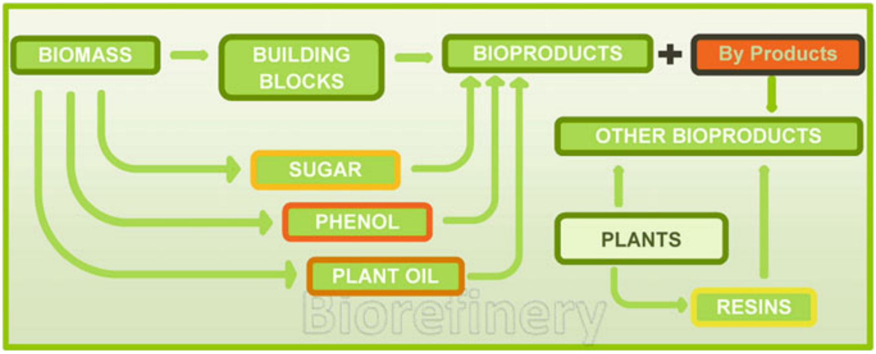


Fig. 3 A minimalist cartoon representation of a biorefinery

and biomaterials. Embracing the concept of bioproducts generation from biomass in a ‘biorefinery’ setup undoubtedly offers a better path to making the world a safer and greener place (Kamm 2014). A simple cartoon description of a biorefinery is shown in Fig. 3.

4 Classification of Bioproducts

The nature, kind, and properties of bioproducts can vary as shown in the following few examples of bioproducts and their uses.

i. Sorbitol: sweetener, laxative, healthcare, food, cosmetic, and rocket fuel.
ii. Glycerin: sweetener, humectant, laxative, soap, antifreeze, explosive, and polymer.
iii. Levulinic acid: precursor to pharmaceuticals, plasticizers, and additives.
iv. C3–C6 short-chain fatty acids (SCFA): preservative, anti-bacterial agent, textile, precursor to other products, condiment, medical use, and solvent.
v. Ethanol: solvent, chemical precursor, fuel, antiseptic, and beverage (food).
vi. Butadiene: synthetic rubber, polymer, and synthetic reagent.
vii. Eugenol: perfumeries, antiseptics, and anesthetics.
viii. Nylon: clothes, tires, and tents.
ix. Polyurethane: automotive, elastomers (footwear), and electronics.
x. Linoleic acid: paints, varnishes, surfactant, and pharmaceuticals.
xi. Biodiesel: fuel (automotive, rail, and aircraft), heating resource, and electricity generation using a generator.
xii. Arnica: medicinal use.
xiii. Menthol: medicinal use, pesticide, perfumery, chemical synthesis, etc.

Bioproducts can be broadly classified into three major categories: (a) bioenergy, (b) biochemicals, and (c) biomaterials.

(a) Bioenergy

Bioenergy is any form of energy derived from the renewable biomass source (Cornelissen et al. 2014). It is ironic that prior to the transformation and dependence on fossil fuels, biomass had been the source for all kinds of consumables, especially energy. That practice, however, was not as environmentally benign and a side-effect had been the rapid disappearance of forestry. The adverse effects of fossil feedstock use and depletion have forced us to revisit the source of all bioproducts and reconsider biomass instead of fossil resources. Bioenergy can further be classified into three segments based upon the sources, viz. from solid, liquid, or gas. The upcoming discussion of chemistry in bioenergy will follow this classification.

(b) Biochemicals

Biochemicals are chemicals that are extracted, derived, or synthesized from the green feedstock. The conversion of biomass to any biochemical could incorporate traditional chemistry, green chemistry, or a combination of both. It is imperative to clearly understand that despite the nature of the renewable feedstock and the final bioproducts, the nature of the conversion process and the intermediates could damage the otherwise ‘green and environmentally safe’ concept (Saidur et al. 2011). Biochemicals comprise a vast area of substances ranging from chemical solvents, chemical reagents, inactive pharmaceutical ingredients, and food additives to insect-repellents, surfactants, and rocket fuels. The discussion of biochemicals will be simplified based on the nature of their resources, viz. glucose, phenol, syngas, plant oils, and resins.

(c) Biomaterials

In the context of our current discussion, biomaterials are defined as material products derived from sustainable biomass. Biomaterials from biomass should not be confused with the material that necessarily mimics, replaces, or augments a specific biological system. The term ‘bio’ here is closely related to ‘biomass’ as opposed to ‘biological system.’ Despite biochemicals and biomaterials, generally are two distinct classes of bioproducts, biochemicals may serve as precursors to biomaterials. For example, a biopolymer or biocomposite is the final product for use unlike most biochemicals. Biopolymers are also bioproducts derived from polymeric materials made from renewable feedstock or biomass. Examples of biopolymers can be found almost everywhere, e.g., polylactic acid (PLA), polyisoprene, and poly-3-hydroxybutyrate leading to products such as polyester, bioplastics, cellophane, zein, and rubber. Production of biomaterials not only prevents depletion of fossil resources, but also keeps the environment cleaner. It is needless to mention that most biomaterials are biodegradable.

5 Sources and Chemistry of Biomass and Bioproducts

5.1 *Chemistry in Biomass*

Biomass, as already described earlier, is the biological and renewable feedstock present on Earth in diverse forms. Common examples of biomass are corn, potatoes, soybeans, beet molasses, sugarcane, wood, algae, various seeds, used fats and oils, and waste products. Used fats and oils, although originally resourced from the biological world, could provide a large opportunity to further derive bioproducts. Similarly, various bio-wastes—from animals, humans, agriculture, municipal, and other manufacturing processes can also act as second generation biomass for a wide range of bioproducts.

The primary chemical ingredients present in biomass are starch that contains:

(a) Polysaccharides

Polysaccharides are found in biomass such as corn, sugar cane, and soybeans. Polysaccharides are biological polymers of sugar monomers or monosaccharides composed of repeating units or a combination of monomers connected through glycoside bonds. Amylose is an abundant form of 'sugar' or polysaccharide in starch and is composed of repeating units of monosaccharides; glucose molecules connected through α(1 → 4) glycosidic bonds (Fig. 4). Amylopectin, a branched chain version of a polysaccharide, made out of the same glucose monomer is more rigid and harder to digest or hydrolyze (Fig. 5).

A disaccharide, sucrose, found in fruits is a product of glucose (a 6-membered ring structure) and fructose (a 5-membered ring structure) (Fig. 6). The figure also depicts the structure of another disaccharide, maltose which is composed of two monomeric units of α-D-glucose molecules coupled through a glycosidic bond.

Cellulose, another biological polymer found in the plant as well as animal kingdom, is closely related to the structure of amylose, but differs in the structure of the

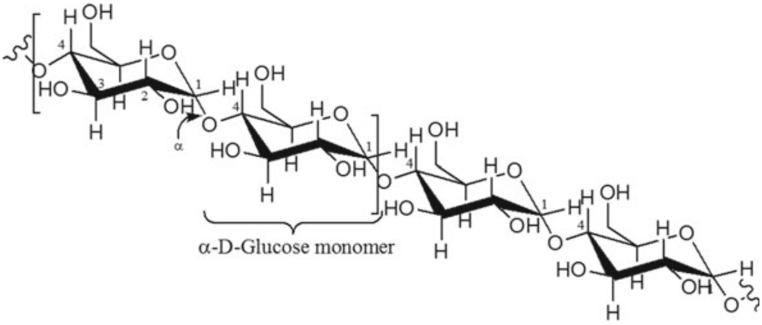


Fig. 4 Polysaccharide with a straight-chain structure, amylose in starch

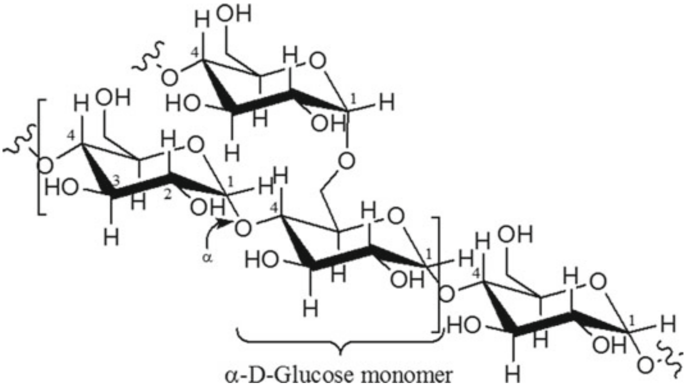


Fig. 5 Branched-chain amylopectin, made out of D-glucose

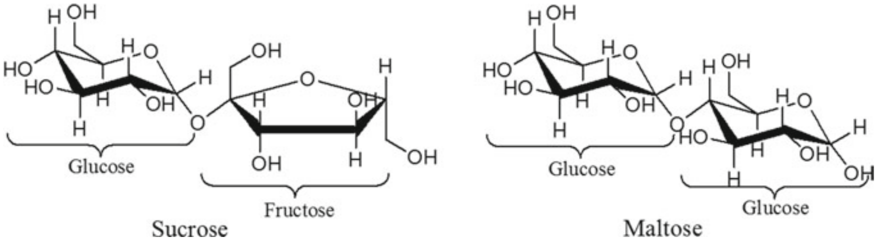


Fig. 6 Two different disaccharides: sucrose that exists in fruits and maltose that is found in barley as a breakdown product of amylose

bond in between monomeric glucose molecules. Figure 7 highlights the β(1 → 4) glycosidic bond connecting the β-D-glucose monomers together in the cellulose biopolymer.

Hemicellulose is a branched biopolymer constituted primarily from two monosaccharides, xylose and arabinose, along with some amount of glucose and mannose. Because hemicellulose is much more easily hydrolyzed than cellulose the production of monomeric sugar units is higher.

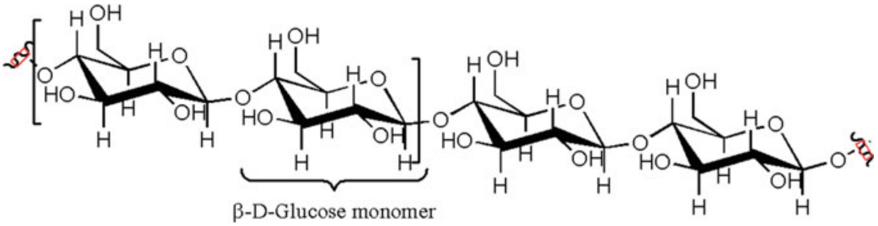


Fig. 7 Cellulose—another natural product constructed from D-glucose units

(b) Lignin

Lignin is a major constituent of the structure of wood and helps bind the cellulose-hemicellulose matrix. The molecular structure of lignin is highly disorganized and random, containing various aromatic units. Understanding the chemistry required to convert lignin into useful bioproducts or into building blocks (intermediates) is ongoing research, but offers much hope for the generation of useful bioproducts in the future. Although the structure of lignin, as depicted in Fig. 8, is the best predicted structure, it does shine some light in regard to the structural motifs. The structure is rich with aromatic (phenyl) rings, phenolic hydroxy groups, aliphatic alcohols, carbonyl moieties, and hydrocarbon linkers (Vanholme et al. 2010; Hatakeyama and Hatakeyama 2010).

(c) Oils

Most oils in biomass resources employed for the production of bioproducts possess a triglyceride structure as depicted in Fig. 9. Three identical or different fatty acids are connected with the three hydroxyl functional groups of one glycerol through three individual ester bonds. Figure 10 shows the chemical reaction between one molecule of glycerol (also called glycerin) and three molecules of fatty acids by an acid catalyzed Fischer esterification reaction to generate one molecule of triglyceride.

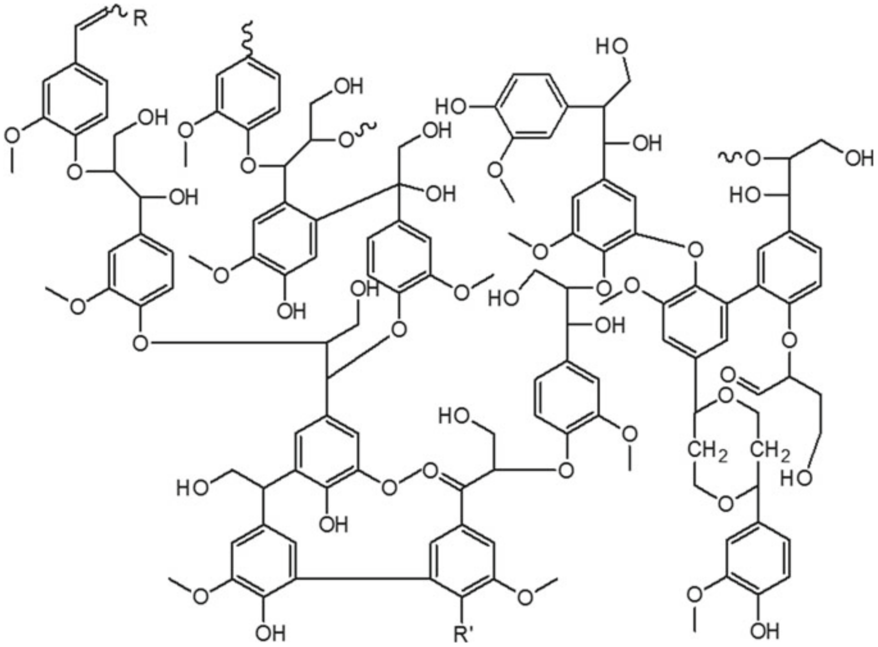


Fig. 8 Partial depiction of the structure of lignin

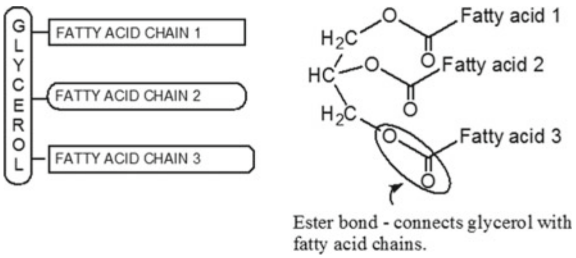


Fig. 9 Cartoon representation of vegetable oil

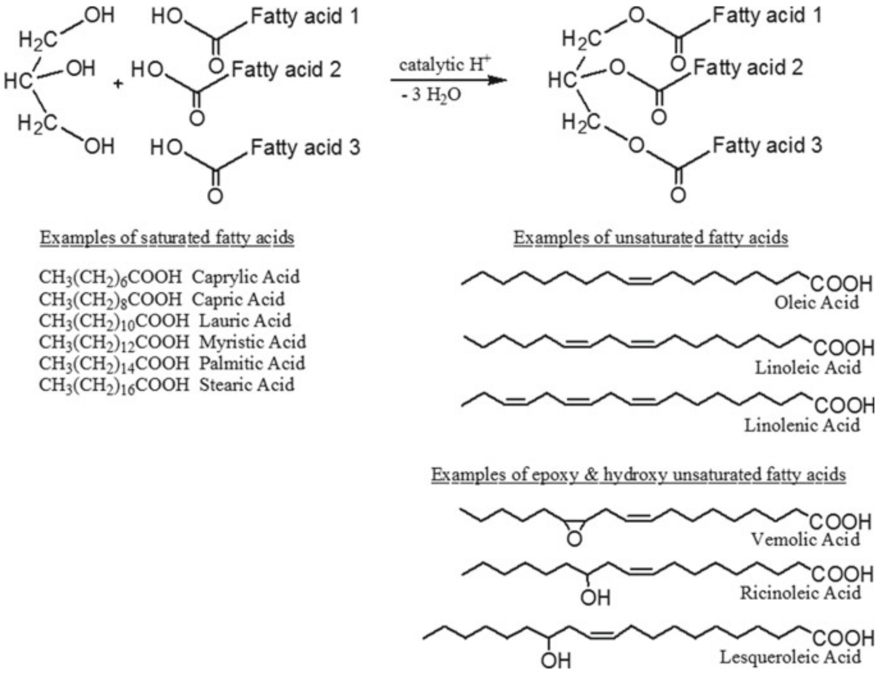


Fig. 10 Fisher esterification reaction to produce triglyceride from glycerol and fatty acids. Representative examples of saturated, unsaturated, and hydroxy unsaturated fatty acids

5.2 *Chemistry in Bioenergy*

Bioenergy can be generated in more than one ways and at various phases of the biomass process. Bioenergy also exists in more than one state of matter, viz. solid, liquid, and gas which had been exploited prior to the mass commercialization of fossil-based feedstock. Wood was one of the major, common, and universal energy resources, and dried animal waste is an example of cooking fuel in developing countries. Once again, biomass utilization does not necessarily guarantee 'green practice' and rapid deforestation was one of the downfalls as part of the aftermath. Petroleum-derived energy has clearly demonstrated the threats to the health of our planet and its residents; the responsibility to reverse these practices lies on us. It is almost unanimous that complementing or replacing fossil-based resources with renewable green resources offers a plausible solution toward building a cleaner, greener, and safer world. The three different categories of bioenergy will be discussed with an emphasis on chemistry.

5.2.1 Liquid Biofuel

Ethanol, biodiesel, other bioalcohols, green diesel, biofuel gasoline, vegetable oil, and bioethers are examples of liquid biofuel. Ethanol or ethyl alcohol is one of the most common forms of liquid fuels finding an increasing interest in certain parts of the world to complement petroleum resourced fuels. Brazil, notably, is aggressively pioneering the incorporation of bioethanol as an alternate fuel. Ethanol can be used as a supplement to regular gasoline adding to its popularity. Fermentation, a biological chemical transformation catalyzed by microorganisms and bacteria, converts polysaccharides into ethanol (Fig. 11).

Vegetable oil (see Fig. 9 for the triglyceride core structure) is also used as fuel, especially, with older or modified diesel internal combustion engines. A much more popular biofuel derived from plant oil by a chemical reaction is called transesterification. A molecule of triglyceride is converted into three molecules of new esters that serve as a biomass resource alternative or supplement to petroleum-produced diesel. Figure 12 describes the chemical transformation of a triglyceride molecule into biodiesel using methanol under anhydrous conditions.

Petrodiesel fuels are primarily composed of saturated hydrocarbons with the number of carbons ranging from 10 to 15. Branched alkanes and cycloalkanes also exist in the composition of petrodiesel; it contains aromatic compounds such as naphthalene and alkylbenzenes. From a chemist's perspective, biodiesel varies from petrodiesel by their inherent chemical composition. Biodiesel molecules contain a functional ester while petrodiesels do not. Examples of the composition of biodiesel from two different vegetable oils, soybean and sunflower oil, are shown in Fig. 13.

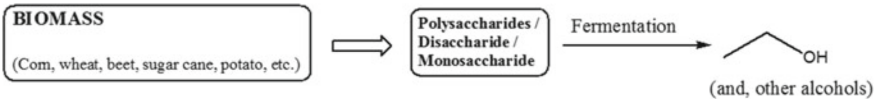


Fig. 11 Production of bioethanol from polysaccharide building blocks derived from renewable biomass

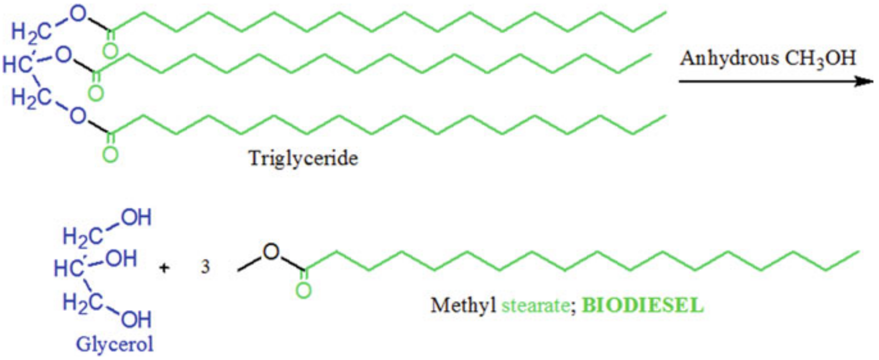


Fig. 12 Transesterification of vegetable oil into biodiesel in dry conditions

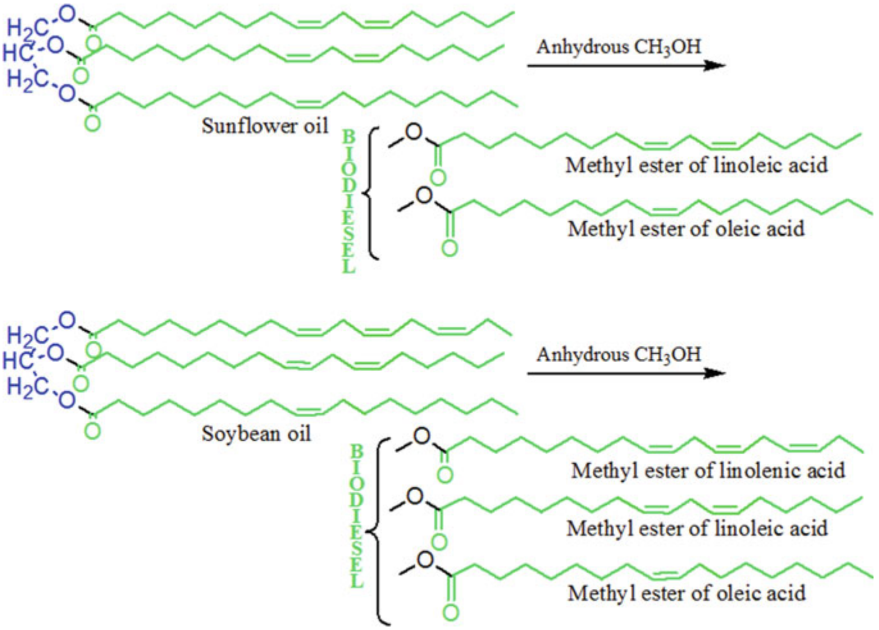


Fig. 13 Chemical composition of biodiesel produced from sunflower and soybean oil

5.2.2 Gaseous Biofuel

Biomass can also be converted into a combustible mixture of gases that can subsequently be used to produce power. Syngas and biogas are two such examples of gas mixtures that are produced by different techniques from renewable resources. Syngas is a ‘synthetic gas’ that can also be produced from coke—a non-renewable source of energy. Coke is a solid fuel source usually produced from petroleum fuel.

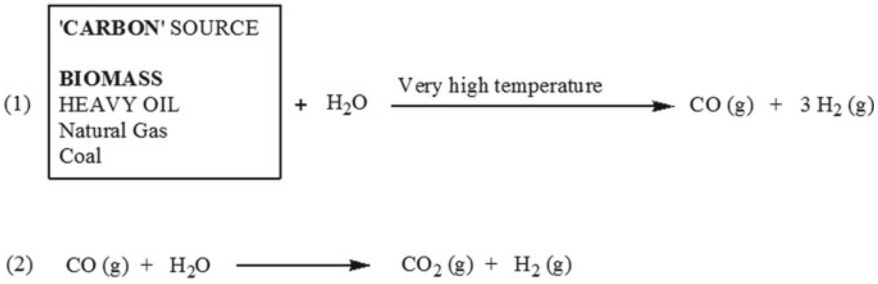


Fig. 14 Chemical reaction between biomass and steam to produce syngas

Syngas is a mixture of mostly carbon monoxide and hydrogen. A schematic diagram depicting the chemical reaction that generates synthetic gas is exhibited in Fig. 14.

The purified hydrogen gas is considered to be the fuel of the future. It is used as spacecraft rocket fuel for its high energy content per mass unit. Further development of the chemical reaction to produce syngas from biomass is of tremendous value as a solution to the energy crisis and the production of greener energy.

Syngas, also called producer gas, can be further converted into diesel, methane, and dimethyl ether by the Fischer–Tropsch process (Davis and Occelli 2006). Each of the products can either be used as fuel or as an additive to raise the octane value of a fuel.

The other gaseous biofuel mixture that biomass can generate is biogas. Unlike syngas, biogas is composed of methane and carbon dioxide. The chemical reaction to produce biogas from an organic matter, such as biomass, requires an anaerobic condition (Fig. 15).

Biogas formation can happen in nature in marshy lands, septic tanks, and in the digestive tracts of cattle. Since the disposal procedure for biological waste can be complex and expensive, utilization of the waste to produce biofuel is an excellent alternative. Biogas can be used in cooking, internal combustion engines, heating, and is easily stored in a compressed state.

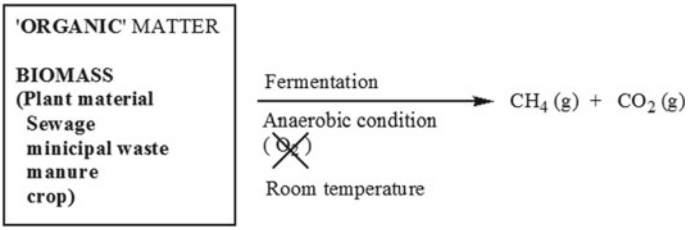


Fig. 15 Anaerobic digestion of biomass to biogas

5.2.3 Solid Biofuel

Solid biomass is the solid biofuel directly used to burn and produce energy. The chemical process is called ‘direct combustion.’ Recent technical developments have turned this antiquated process into a much more efficient and cleaner practice although there still is room for enhanced efficiency (Nussbaumer 2003). Combustion is defined as the exothermic chemical reaction between a fuel and an oxidant that produces energy and chemical by-products. The fuels exist in different shapes and forms, such as hydrocarbons, hydrogen gas, coke, coal, and other carbon and hydrogen-rich matter (Fig. 16). Biomass can also be burnt to generate steam which in turn produces heat and power by turning a turbine.

5.3 Chemistry in Biochemicals

Biochemicals are chemicals that are made from renewable feedstock in direct or indirect ways. A biochemical may be the final bioproduct or a useful building block for other bioproducts including biofuels and biomaterials. Biomass feedstock exists in many kinds and forms, and the chemical processes to convert them into bioproducts and/or building blocks are also diverse. A quick revisit to the conceptual biorefinery (Fig. 3) will help with the global view of biomass to bioproducts generation with an emphasis on the position and role of biochemicals. Figure 17 is another simplified representation of a biorefinery describing a few examples of biomass getting converted to bioenergy, biochemicals, and biomaterials. Despite some of the immediate products from biomass could be bioproducts, viz. syngas and oil, in most cases, the immediate derivatives of biomass are intermediates that further undergo chemical reaction to produce the ultimate bioproduct ranging anywhere from bioenergy to biomaterials.

Biomass can undergo fermentation—a microorganism-driven biological reaction to break down larger organic molecules to produce liquid and/or gaseous chemicals. Biomass, upon undergoing much harsher chemical reaction conditions, e.g., pyrolysis, gives rise to a completely different set of products also important for the generation of bioproducts. Chemical or biologically driven hydrolysis reactions lead

Fig. 16 Direct combustion to produce energy

$$\text{FUEL} + \text{OXIDANT} \longrightarrow \text{CHEMICAL BY PRODUCTS} + \textbf{ENERGY}$$

$$\boxed{\begin{array}{rcl} CH_4\,(g) + 2O_2\,(g) & \longrightarrow & CO_2\,(g) + 2H_2O \\ 2H_2\,(g) + 2O_2\,(g) & \longrightarrow & 2H_2O \\ C + 2O_2\,(g) & \longrightarrow & CO_2\,(g) \end{array}}$$

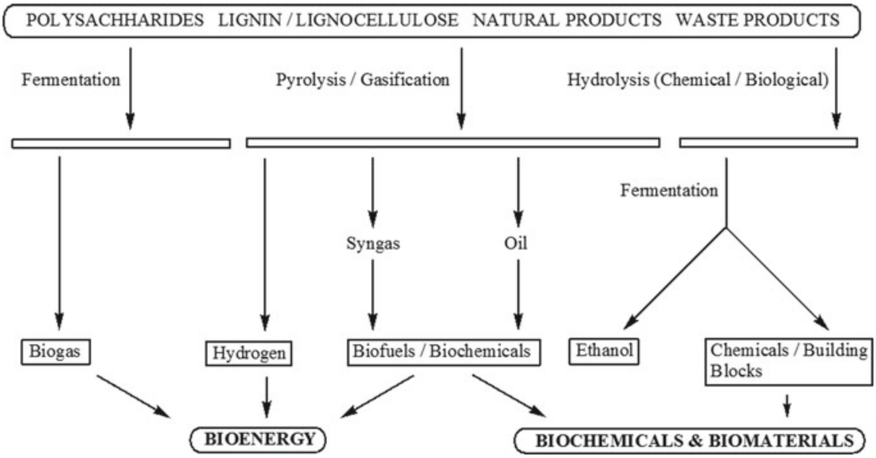
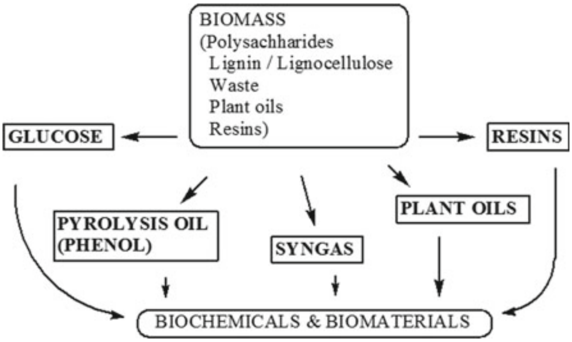


Fig. 17 Another representation of the biorefinery network depicting the interrelation between various stages of the process: resources, intermediates, and products including biochemicals

Fig. 18 Many building blocks to generate bioproducts



to a different set of biochemicals. Reduction of renewable starting materials with hydrogen, on the other hand, provides another platform of chemicals. An intermediate gas mixture, such as syngas, also plays a role in the production of biochemicals and biomaterials. Plant oils are also renewable feedstock for biochemicals, biofuels, and biomaterials. Plant oils vary in their source and nature and require a wide spectrum of efforts to yield the final bioproduct. Figure 18 captures the essence of various renewable precursors or building blocks, viz. glucose, pyrolysis oil, syngas, plant oils, and resins derived from biomass to generate biochemicals and biomaterials.

5.3.1 Biochemicals from Glucose

Glucose, a six carbon monosaccharide, is produced from the breakdown of polysaccharides in starch from a variety of biomass. Glucose undergoes a series of diverse chemical reactions to produce a large group of useful chemicals as direct bioproducts or as intermediates to bioproducts. Werpy and Peterson narrowed down the list of possible compounds to 12 synthons or building blocks sufficient to replace important building blocks obtained from fossil fuel resources (Werpy et al. 2004). Biochemicals produced from glucose have a wide range of applications. The following are examples of the use of some of the biochemicals shown in Fig. 19 and their general uses.

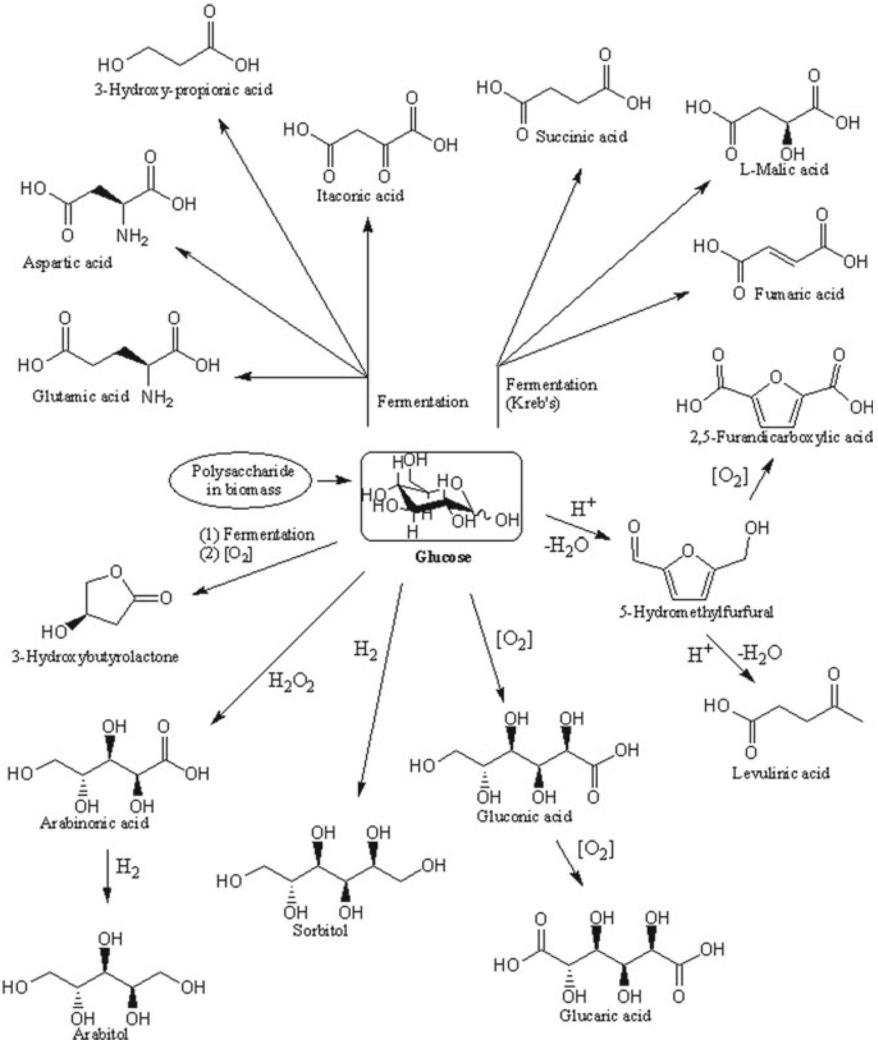


Fig. 19 Synthetic pathways to crucial building blocks from glucose

i. Succinic acid: surfactants, detergents, food, pharmaceuticals, precursor for antibiotics, amino acids, and vitamin.
ii. Itaconic acid: adhesives.
iii. Levulinic acid: fuel (to oxygenate), herbicide, solvent.
iv. Sorbitol: sweetener, laxative, health care, food, cosmetic, rocket fuel, and intermediate for fuel.
v. Gluconic acid: food additive and cleaner.
vi. Fumaric acid: food additive, acidity regulator, and medicine.

The reaction schemes in Fig. 20 expand upon the usefulness of some of the platform (intermediate) chemicals already shown in Fig. 19. The illustration in Fig. 20 validates the importance of 5-hydroxymethylfurfural (5-HMF). The next scheme, in Fig. 21, begins with the sorbitol intermediate and generates several very important chemicals highly sought in the biochemical and biomaterial world (Gallezot 2012).

Isosorbide has medicinal value since it is used as a diuretic and also for the treatment of glaucoma. The dinitrate ester of isosorbide is used in a combination of drug therapy for the treatment/reduction of coronary heart disease. Dimethyl isosorbide is used as a high boiling solvent for chemical reactions in the pharmaceutical and cosmetics industry and in media in the paint industry. The diesters of isosorbide are useful as plasticizers.

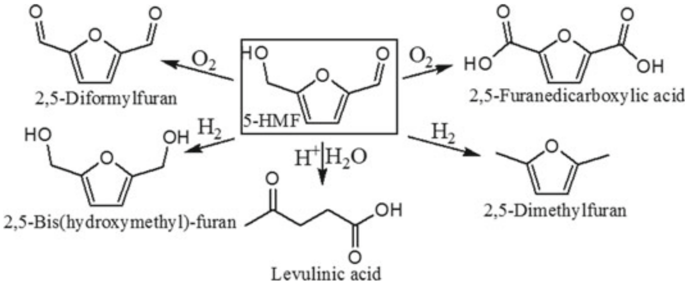


Fig. 20 Useful chemistry around 5-hydroxymethylfurfural

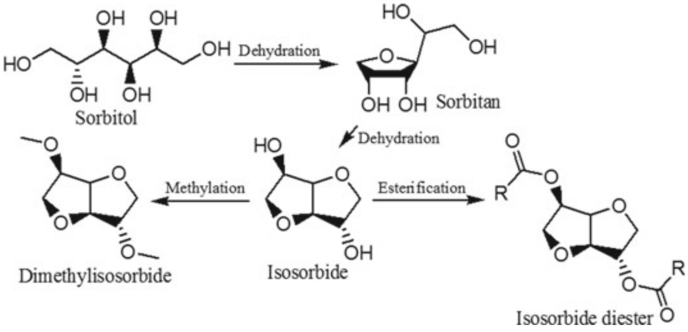


Fig. 21 Chemistry of sorbitol

5.3.2 Biochemicals from Phenols

Phenols are organic aromatic compounds with one or more free hydroxyl functional groups. Phenols represent a unique class of compounds, often nature-made, beneficial for many uses. Many such naturally occurring phenolic compounds are extracted, purified, and used directly or as a platform biochemical to synthesize other products.

Among the naturally occurring phenolic compounds, cresols, guaiacols, vanillin, eugenol, carvacrol, capsaicin, thymol, salicyclic acid, and cannabinoids are noteworthy. Many natural phenols are known to have antioxidant properties. Apart from the direct utility of natural phenolic compounds, synthetic molecules derived from bio-sourced phenols (platform phenols) are also popular. These molecules are used in the chemical industry in wood processing, pesticides, flavoring, and finally in the pharmaceutical industry. Figure 22 shows examples of phenolic compounds obtained from renewable bioresources. A selected set of examples highlights some of the exciting examples of phenolic molecules that come from lignin and other green resources. Isolation and structure elucidation of vanillin, ferulic acid, and coumeric acid derived from lignin assisted the scientific community with the better understanding of the complex structure of lignin. Each of the three building blocks of lignin has unique properties for direct use or as a platform toward another biochemical product.

Eugenol is oil extracted from cloves. Coumeric acid has antioxidant properties and is also thought to have anti-cancer properties (Cai et al. 2004). *Para*-coumeric acid is found in honey and might play a significant role in helping honeybees clear specific pesticides. Gallic acid is commonly found in nuts, tea leaves, oak bark, and other plants; it is used in the pharmaceutical industry as a platform compound. Quercetin belongs to the flavonoid family and is a ready-made bioproduct found in many plants including radish leaves, dill, cilantro, red onion, kale, cranberry, sweet potato, and tea. Quercetin has many therapeutic benefits, including anti-viral, anti-cancer, asthma-preventing, or anti-inflammatory activity. However, drug metabolism and pharmacokinetic (DMPK) studies and drug–drug interaction studies led to some concerns and it never received approval for human use from the Food and Drug Administration (FDA). Nevertheless, it offers an excellent platform for medicinal chemists to experiment in order to alter its chemical and pharmacokinetic properties while retaining the possible biological benefits in multiple therapeutic areas.

5.3.3 Biochemicals from Syngas

Synthetic gas or syngas is produced from biomass under the conditions of very high temperatures with water vapor. In addition to providing energy solutions, syngas generates a number of useful biochemicals with diverse utility. The specific reaction called the Fischer–Tropsch (F-T) process uses a fluid reactor (Mangold et al. 1982). Figure 23 depicts the various biochemical products generated from syngas and their general applications.

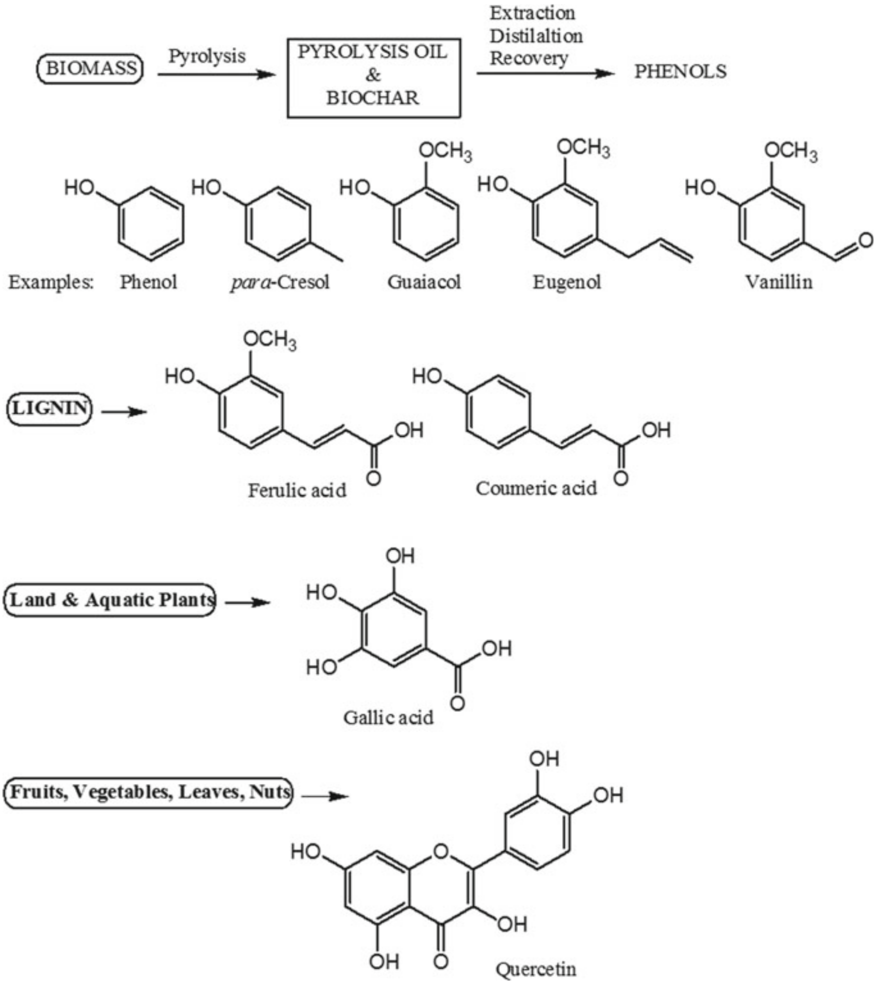


Fig. 22 Phenolic platform molecules from phenolic bioproducts

5.3.4 Biochemicals from Plant Oils

Plant oils constitute a vast variety of oils with unique structural features obtained from plant sources and are primarily classified into three categories. They are (i) vegetable fats and oils, (ii) macerated oils, and (iii) essential oils.

Vegetable oils can be further classified into three categories based upon the nature of the sources.

- Major oils that are extracted from coconut, palm, olive, corn, peanut, soybean, sunflower, etc.

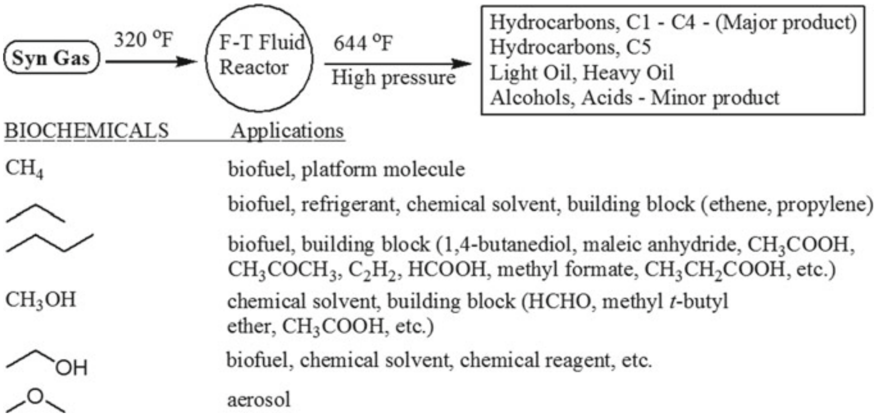


Fig. 23 Biochemical from syngas by Fischer–Tropsch process

- Nut oils from almond, hazelnut, cashew, pecan, etc.
- Citrus oils originating orange and lemon.

Plant oils have high application in the food industry as food supplements. Chemical reactions on plant oils produce biofuels, soaps, and surfactants. The basic chemistry involved in the break down or conversion of plant oils into useful bioproducts can be subtle and selectively lead to one class of products over the other. Figure 24 describes the saponification reaction of vegetable oil, where various triglycerides react with a base (sodium hydroxide, NaOH) to produce glycerol and three fatty acids, which then form 'micelle'-like charged-head, tadpole-like molecules. A surfactant's or a soap's primary job is to lower surface tension of a liquid and it accomplishes that by adsorbing itself at the interface of two media. Surfactants can have their head group positively charged, negatively charged, and in some cases, zwitterionic or even completely neutral. Depending upon their structural features, surfactants can adopt different shapes in addition to being spherical. Figure 25 shows two commonly used surfactants chemically obtained from biomass-derived building blocks.

Sodium dodecyl sulfate (SDS) has a wide range of applications such as household detergent, stain remover, floor cleaner, and experimental laboratory use. SDS is used in a technique called polyacrylamide gel electrophoresis (SDS-PAGE) to detect and identify proteins. Some other extreme properties of SDS include anti-viral effects and application in pesticide management (Krebs et al. 1999; Ghaemi et al. 2012). Monolaurin, another common surfactant, is used as an emulsifier in the food industry and as a surfactant in the cosmetics industry.

Macerated oils are extracted from plants with another natural additive—often an herb. Macerated oils have a widespread and traditional worldwide use based on its presumed therapeutic value. Elaborate scientific approaches and studies are needed to unravel the scientific mechanism of action responsible for the beneficial values of many herbs and plants. Examples of macerated oils include arnica, marigold, carrot, galangal, calendula, and seaweed oils. Therapeutic benefits range from massage

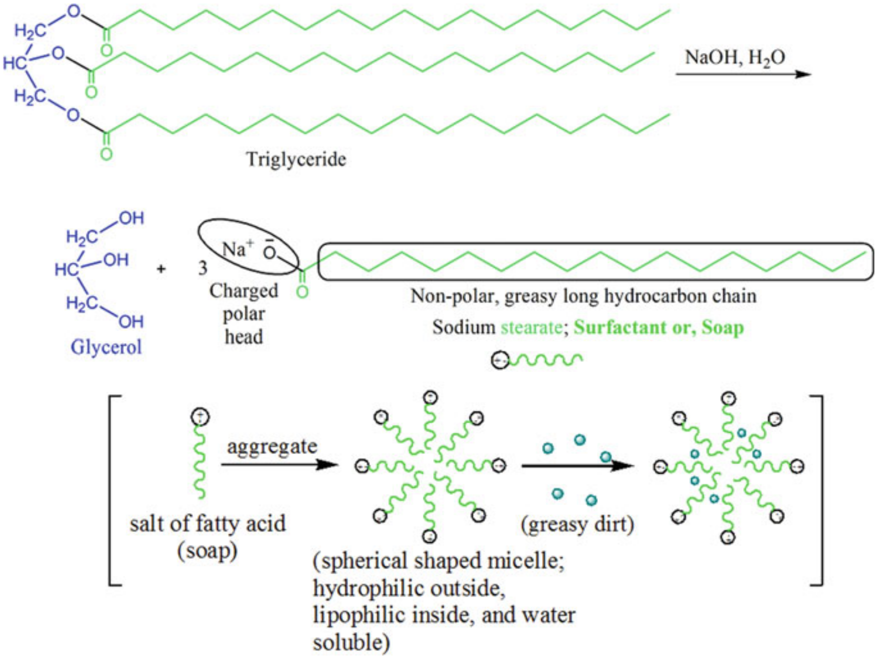


Fig. 24 Saponification of triglyceride into glycerol and soap

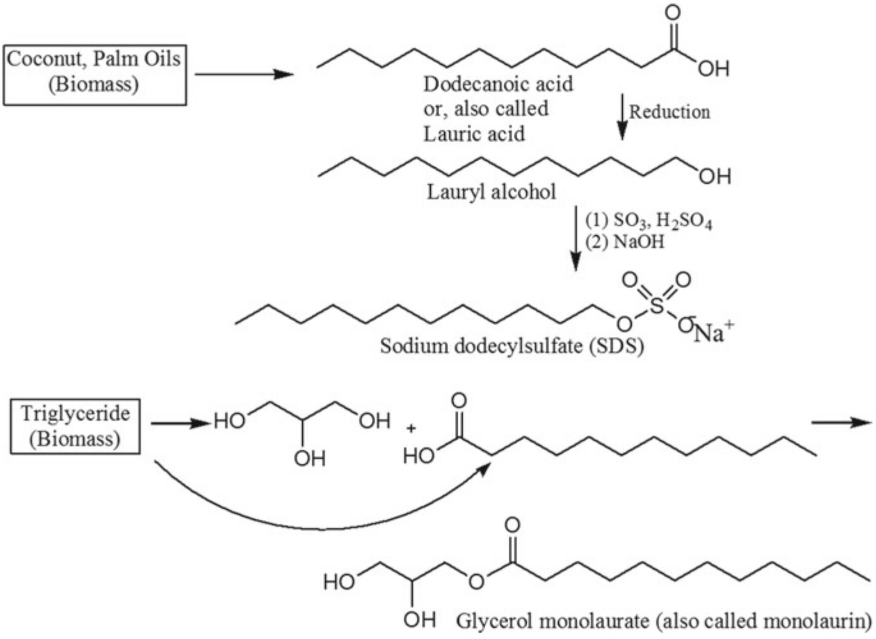
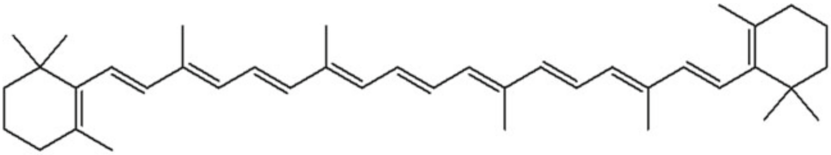
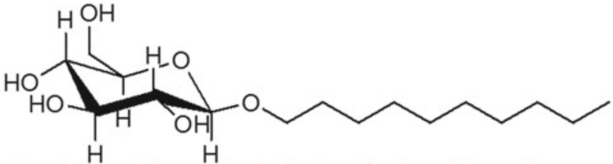


Fig. 25 Commonly used surfactants resourced from renewable biomass



β-Carotene, an orange oily non-polar compound and an active ingredient in carrot.



Decyl glucoside, a natural plant-made glucoside used as a surfactant.

Fig. 26 Chemical structures of carotene and a natural emulsifier (surfactant)

therapy, alleviating sprain, as anti-infective agent, coagulant, anti-bacterial agent to pest-repellency. The extraction of herbal ingredients is a sensible practice from the exclusive point of view of chemistry. Many of the isolated ‘bioproducts’ (in this context, natural products) are highly lipophilic in nature and therefore dissolution in edible oil significantly enhances the bioavailability. β-Carotene (Fig. 26) in carrot generally has a low rate of absorption. However, the absorption enhances multi-fold when a vegetable oil is applied as an edible medium for the application of the herbal material. β-Carotene catabolizes to vitamin A which is essential for the good health of the eyes. Often, some of the other natural bioproducts present in the macerated oil have amphiphilic properties that enable them to function as surfactants or emulsifiers (Fig. 26). Such ‘natural formulation’ of herbal agents accounts for the bioefficacy of the active bioingredient in the ‘natural’ form. Uncharged decyl glucoside earns its micelle-like properties by having a polar head (the sugar unit) and a non-polar tail. Polarity is garnered by the occupying four relatively polar hydroxy groups on the pyranose ring.

Essential oils are also direct plant products, but they do not need an oil base before application. Essential oils are pure biosynthesized molecules—essentially, nature’s gift of final bioproducts ready for use. These oils obviously are liquid biochemicals that are often aromatic and volatile in nature. Essential oils are sourced from seeds, berries, barks, wood, leaves, flowers, peel, roots, and resins. The usual chemical processes that are employed to extract and/or purify these oils are extraction, distillation, and steam distillation. Uses of these oils vary from alternate medicine to massage therapies. Figure 27 depicts the unique structures of some common essential oils.

Many of the essential oils belong to the terpenoid family of complex natural products produced primarily by plants. Many terpenes contain aromatic groups and are volatile. Terpenes are biosynthesized from units of isoprene, formally known as 2-methylbutadiene. It is thus possible to break down the complex structure of a terpene into isoprene units, joined head to tail. The stereoisomeric pairs of essential oils

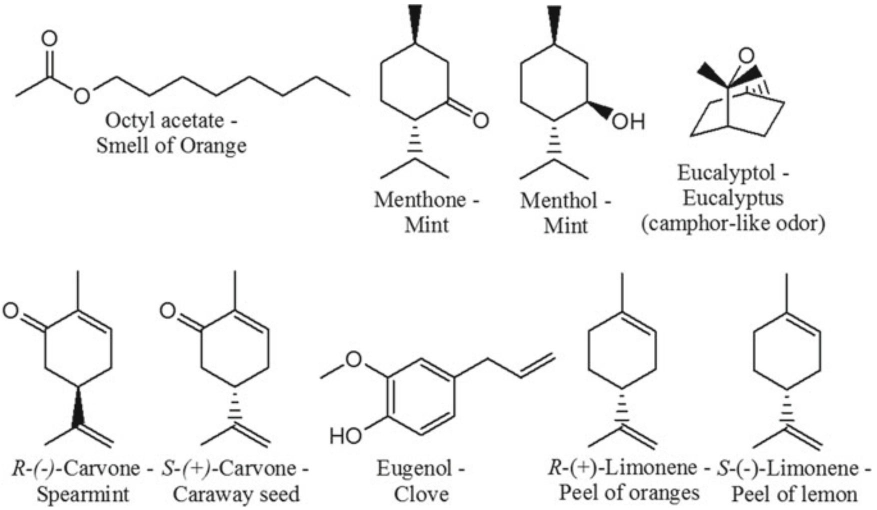


Fig. 27 Some essential oils in their bare-bond chemical forms

remind us once again of the power of handedness (one stereoisomer over the other) in various biological activities. In this context, the specific interaction of the molecule, depending upon its stereochemical disposition, varies from its mirror image with for example, the olfactory receptors. A real-life example of the importance of 'handedness' is ibuprofen, a synthetic nonsteroidal anti-inflammatory drug (NSAID) used as a pain reliever, fever reducer, and anti-inflammatory agent. The molecule—a phenyl-substituted propionic acid developed in the 1960s is chiral (has the 'handedness' property) by nature. It turns out that only one of the two stereoisomers, '*S*-(+)-' is actually responsible for the beneficial therapeutic properties.

5.4 Chemistry in Biomaterials

Biomaterials are often the final bioproducts needed in the society unlike many biochemicals that are essentially the intermediate platform or building blocks and not the final product. Often, biomaterials refer to the 'macro' matter state that is directly processed into the consumable item. Among all other items, various polymeric materials occupy a major area in this category. The context of the bioproducts discussion here will focus on the final bioproducts in the pipeline that are neither energy nor chemicals. The first category will focus on the use of appropriate biochemicals derived from renewable biomass to generate biomaterials, e.g., lubricants, plasticizers, and polymers. The other class of biomaterials is biocomposite made out of a matrix and fibrous material.

5.4.1 Biomaterials from Biochemicals Derived from Biomass

Three distinct classes, viz. lubricants, plasticizers, and biopolymers, make up the realm of biomaterials produced from biochemicals. The word ‘biopolymer’ here should not be confused with biological polymeric macromolecules. The ‘bio’-part originates from the renewable biomass, not biological molecules.

The philosophy and incentive behind the development of bio-based lubricants are nothing different than that of bioenergy and biochemicals: prevent fossil fuel loss, reduce pollution, and use renewable and green feedstock. Bio-based lubricants have advantages as well as disadvantages, and scientific efforts are ongoing to alleviate the benefits. Benefits include using renewable starting materials, being biodegradable, and having a low volatility, high flash point, and high viscosity index. On the other hand, stability issues, shorter life, and higher prices limit the use and expansion of these products (Bart et al. 2013). Nevertheless, biolubricants have made their way into various applications like hydraulic oils, cutting oils, grease, gear oil, and so on. Biolubricants can be specific triglyceride oils isolated from biomass in the simplest form. Specific needs led to the development of polyglycols and special synthetic lubricants sourced from biomass-derived biochemicals. Esters of unsaturated fatty acids can produce hydroxy ethers via two consecutive reactions to produce an epoxide, followed by alcoholysis in order to attain the desired properties as a biolubricant (Fig. 28).

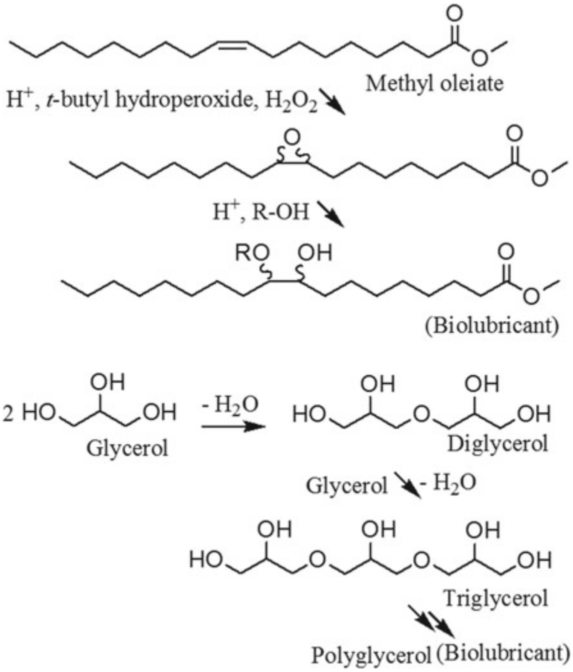


Fig. 28 Biolubricants from biochemicals

The traditional plasticizer normally used in polymers made from polyvinyl chloride is alkyl phthalate. Unfortunately, it has been linked with undesirable effects on human health and its use is restricted. This led to the development of harmless plasticizers preferably from renewable resources. Once again, triglycerides generated from biomass served as the initial platform. Epoxidation of unsaturated fatty acid chains in the parent triglyceride, which upon acetylation produced the acetoxy derivative of the oil used as a bioplasticizer (Fig. 29).

Apart from the development of bioplasticizers to contribute to the enhanced safety of polymers, a few biopolymers have also been developed. Some of these polymers are not only resourced from renewable resources, but are also biodegradable. Polylactides are one such popular polymer synthesized from lactic acid which in turn is made by the fermentation of polysaccharides. Lactic acid provides a regular biochemical synthesis platform leading to advanced intermediates for various uses. Its contribution to the high-volume generation of polylactides is phenomenal. Some interesting chemistry of lactic acid is captured in Fig. 30, including its polymerization.

Polyurethane is a polymer made out of amide bonds between the monomers. The polymer has innumerable applications that include different types of foams, coatings,

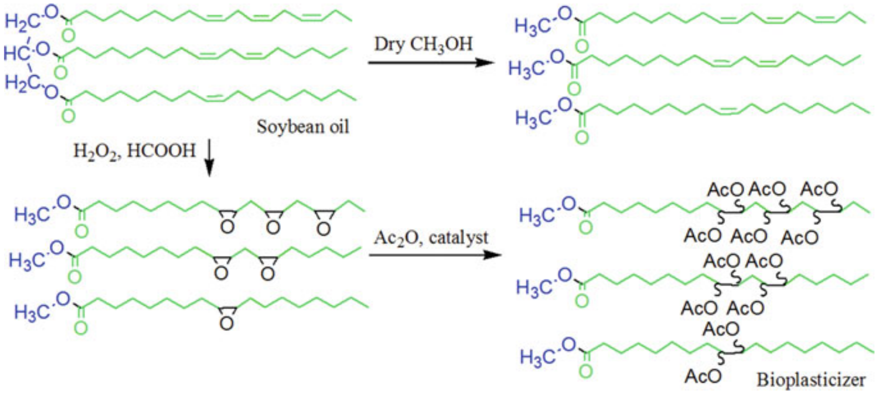


Fig. 29 Bioplasticizer from triglyceride derivatization

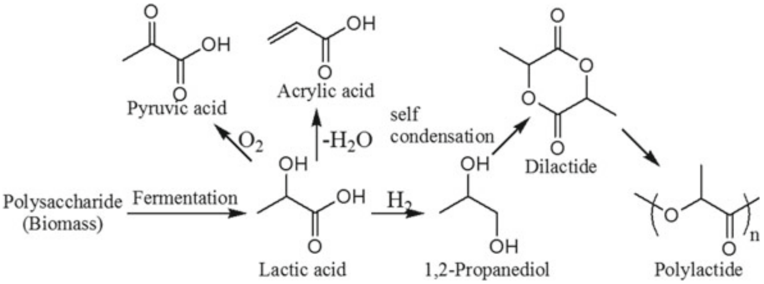


Fig. 30 Lactic acid chemistry and polylactide formation

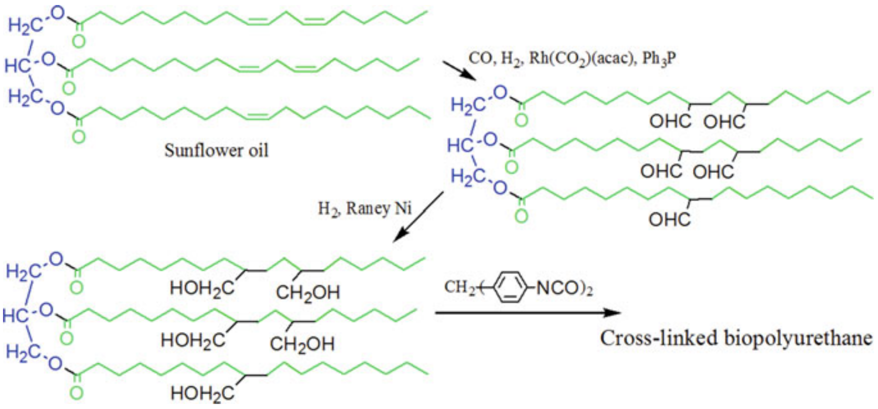


Fig. 31 Cross-linked polyurethane made from biotriglycerides and di-isocyanates

adhesives, and sealants. Biopolyurethanes are prepared by adding primary alcohol functionality around the unsaturation of appropriate triglycerides. The chemistry involved in this transformation is shown in Fig. 31.

5.4.2 Biomaterials from Biofibers

Composites are materials made out of more than one substance with different physical properties. The resulting material has properties different from each of its parent materials. These new properties of the composite are desired for specific reasons such as material strength, weight, or cost. The two media constitute a matrix and are often a bio-resourced resin and a natural fiber matrix for reinforcement. Utilization of renewable feedstock and the end product's biodegradability are the primary incentives behind the development of biocomposites. Floor coverings made from cork, jute, and flax are biocomposites as are textiles made from hemp, flax, and other plant fibers. Insulation materials can be biocomposites comprised of straw and protein glue (Anderson et al. 1997).

6 Conclusion

The journey from renewable biomass to bioproducts is not perfect. The concept and practice of switching to renewable raw materials is supposed to have therapeutic benefits for the ailing Earth. It is more of a philosophy and a mindset that will hopefully gradually become a habit and second nature to humans just like the acceptance of seat belts and recyclable bins. It is not surprising that there is still doubt in some minds about the validity and authenticity of global warming. The mass population is bound to be convinced about the threat from the constant and rapid usage of the fossil-based resources.

It should also be remembered that the ideas of biomass, bioenergy, biochemicals, and biomaterials can be rather convoluted at times and even confusing. A biopolymer may mean something other than biodegradable polymer or a synthetic polymer resourced from renewable resources. Similarly, natural products do not necessarily have to be bioproducts if they were not isolated or synthesized in environment-friendly ways. Likewise, a toxic natural product will be toxic—be it isolated in a green method from a renewable source or synthesized in a research laboratory. Irrational adoption of so-called green practices could also bring in devastating results. It was not too long ago when biofuels were primarily used in the absence of petroleum products and rapid deforestation became prominent and in no time turned into a threat.

Green chemistry can play a significant role in aiding the production of bioproducts from biomass in a ‘green’ way. Green chemistry is also a culture and mindset despite a number of basic rules of green chemistry. Chemistry—the science of matter helps with the journey from starting material to the final target molecule. Green chemistry is the same journey, but cleaner, safer, and economical. Proper utilization of biochemicals like enzymes, bacteria, and the knowledge of how to use these can also help with reaching the overall goal of attaining a safer, sustainable, hazard-free, and efficient practice.

The willingness to supplement and replace petroproducts with bioproducts and the adoption of greener practices from biomass to the end products will not only reduce the threat to the present human generation, but will also leave a better place for the generations to come.

Glossary

Acetylation Chemical or biochemical reaction by which an acetyl functionality is attached to a compound.

Alcoholysis A chemical reaction by which alcohol replaces the alcoholic part of an existing ester functionality to generate a new ester.

Aliphatic alcohols Alcohols comprising only aliphatic branches devoid of any aromatic groups.

Alkylbenzenes Alkyl substituted benzene-based aromatic compounds.

Amphiphilic The property by which compounds can possess solubility properties in both aqueous and non-polar solvents.

Amylopectin Amylopectin is a plant polysaccharide which in conjunction with amylose, constitute starch.

Amylose A polysaccharide containing α-D-glucose monomer.

Antioxidant Molecules that can prevent oxidation, often by being oxidized with their intrinsic reducing properties.

Arnica Herbaceous plant in the sunflower family.

Aromatic General: substances with 'aroma.' In organic chemistry terms, aromatic compounds are special cyclic molecules with alternating double bonds. These planar molecules have extra stability by virtue of their structure and electronic status.

Bioalcohols Alcohols derived from biological/renewable resources.

Bioavailability A pharmacokinetic property of drugs that defines the fraction of the drug reaching systemic circulation.

Bio-based 'Bio-base' is the type products specifically derived from biological/renewable resources.

Biocatalysts Chemical catalysts derived from the biological resources.

Biochemical pathways The mechanistic chemical pathways and directions for multi-step synthetic processes occurring in living organisms.

Biochemicals Chemicals of commercial value generated from biological/renewable resources.

Biocomposites A composite material made from natural fibers and does not contain petroleum-derived ingredients.

Biodegradability The biologically manifested breakdown of a material into smaller fragments.

Biodegradable The property of a substance or material that enables it to undergo biological degradation process.

Biodegradable polymer A polymer material that can breakdown into smaller subunits by natural processes biochemically motivated.

Biodiesel Diesel generated exclusively from biological/renewable resources.

Bioeconomic activity The complex economic network existing in the identification, isolation, and utilization of renewable resources to generate, distribute, and use of various bioproducts.

Bioeconomy Bioeconomy is the economy involved in the world of bioproducts: their production, distribution, usage, and waste management.

Bioefficacy The efficiency of a medicinal drug candidate to distribute itself into the systemic circulation.

Bioenergy Energy exclusively produced from biological or renewable resources.

Biofuel Fuel produced from biological resources or biomass.

Biogas The mixture of gases derived from renewable biological sources.

Biolubricant Biomass-derived lubricants.

Biomass Biomass is the renewable resource for commercial bioproducts. Biomass to bioproduct is equivalent to petroleum products to fossil fuel resources.

Biomaterials Commercial materials generated from biomass.

Bioplastics Plastics made from renewable sources.

Bioproducts Commercial products (chemicals, energy, and materials) derived from renewable raw materials and chemicals.

Biorefinery It is the whole process of using biomass to generate various bioproducts: biochemical, bioenergy, and biomaterial.

Biosynthesized Biochemical process of generating chemical products.

Biotechnology The technology developed by human to utilize biological resources in more than one way(s) to generate commercial products.

Cannabinoids Molecules that bind with cannabinoid receptors to reduce the production of natural neurotransmitter.

Carbon cycle It is the cyclic process by which carbon moves or exchanges through various parts of the biosphere.

Catabolize The natural biochemical pathway by which a molecule undergoes a structural alteration toward its expulsion from the living system.

Catalysts The process by which a natural or synthetic material can increase the rate of a chemical reaction.

Cellophane Cellophane, a bioproduct, is a transparent or translucent polymeric sheet made from regenerated cellulose (biomass).

Cellulose It is the most abundant biopolymer (biologically produced) with various commercial applications.

Combustion A chemical process by which an organic compound reacts with oxygen to break down into smaller fragments releasing energy. A common example of combustion is fire.

Composites Composite or composite materials are commercially produced from more than one materials with the final property different from that of the parent materials.

Disaccharide A carbohydrate consisting of two identical or different monosaccharide units. Sucrose, lactose, and maltose are examples of disaccharides.

Drug metabolism The biochemical process by which a medicinal molecule (drug) undergoes natural transformations in the living system, generally humans.

Drugs Natural, synthetic, or hybrid compounds developed for the management, treatment, or cure of an ailment.

Emulsifier A substance that stabilizes an emulsion.

Essential oils Essential oils are plant products that find a wide range of direct use ranging from alternative medicines to massage oils.

Eugenol An aromatic natural compound extracted from essential oils such as clove oil.

Fatty acids Naturally occurring long hydrocarbon chain carboxylic acids found in lipids, fats, and other complex natural products.

Fermentation The biochemical pathway for sugars to break down into smaller units such as acids, alcohols, and gases. Fermentation can occur without oxygen.

Fine chemicals Synthetic chemicals with substantial commercial value often produced through multi-step chemical syntheses. Their usage varies from being building blocks for other essential chemical products, intermediates in a multi-step process toward other target molecules, and active ingredients.

Fischer esterification The chemical transformation to convert a carboxylic acid and an alcohol into a carboxylic ester.

Fischer-Tropsch process A chemical process developed by Franz Fischer and Hans Tropsch to convert carbon monoxide and hydrogen gases into hydrocarbons.

Flavonoid A class of tricyclic aromatic plant biochemicals that contributes to the color of a plant's flower.

Fluid reactor A special chemical reactor where a gas or liquid flows through a solid at high speed.

Food additives Substances added to food in order to enhance its nutritional quality.

Food and Drug Administration (FDA) A federal agency under United States Department of Health and Human Services is a regulatory agency for various food and medicinal products, therapeutic agents, medical devices, cosmetics, animal foods, and veterinary products.

Food supplements Edible products that are supposed to provide with the nutrients that could otherwise be missed.

Fossil feedstock The non-renewable petroleum-based resources.

Fossil fuels Petroleum-based fuels.

Fumaric acid A 4 carbon-containing natural diacid that is used in the food and medicinal world.

Global warming The gradual and steady increase of the average temperature in Earth's climate.

Gluconic acid A natural poly-hydroxy carboxylic acid often used as a food additive to maintain pH.

Glucose The simplest sugar formed by plants during photosynthesis.

Glycerin, Glycerol A trihydroxy small organic molecule that is the backbone of several natural triglycerides (fat). It has multipurpose uses spanning from the food, chemical, and medicinal industry.

Green chemistry Green chemistry is the environmentally safe chemical method of producing commercially viable products employing safer and less harmful reactants, reagents, solvents, methodology, and producing less hazardous waste materials.

Green diesel Diesel produced from biomass in a less hazardous process.

Green practice The overall practice giving maximum priority to environmentally safe procedures.

Guaiacols Naturally occurring phenolic compounds that use in food and medical industry.

Hemicellulose Non-crystalline, amorphous mix of polysaccharides.

Hydrolysis Water-mediated degradation of organic compounds containing primarily ester and amide bonds.

Insect-repellants Natural and synthetic compounds that repel insects.

Intellectual property Intellectual property (IP) is the technical know-how of an invention pertaining to the individual(s) responsible for the particular invention. IP is often legally protected in the form of patents, trademarks, and copyrights on behalf of the inventor(s).

Isoprene 2-Methyl butadiene, a small 4-carbon chain alkene, emitted by the green vegetation. Isoprene is often found to be the building blocks for many natural chemical products.

Isosorbide A bicyclic alcohol derived from glucose and used as a diuretic.

Itaconic acid A naturally occurring dicarboxylic acid produced from glucose fermentation.

Lactic acid Nature-made small organic acid produced during metabolism and exercise.

Levulinic acid An organic keto acid (contains a ketone functionality) produced from cellulose.

Lignin A highly complex biopolymer often obtained from tree barks. It has great potential to be used as biomass to generate bioproducts.

Linoleic acid A natural polyunsaturated omega-6 fatty acid.

Lipophilic The property of non-polar molecule to be soluble in hydrocarbon-rich, non-polar, lipid and lipid-like compounds.

Lubricants A material developed to enhance the mobility of two moving surfaces that are in mutual contact, reduce friction, and heat in order to prevent wear and tear of the moving parts.

Macerated oils Macerated oils are extracted directly from plants and ready for use with an oil base.

Maltose A disaccharide made from two glucose units.

Menthol A cyclic organic alcohol isolated from mint plants and has various medical applications.

Micelle A spherical assembly of amphiphilic compounds with a polar head and non-polar tails organized with the polar tips around the exposed surface.

Monolaurin A monoglyceride meaning a glycerol molecule with one of its three hydroxy groups forming an ester bond with a long chain fatty acid.

Monosaccharides The smallest sugars containing one cyclic group, viz. glucose, fructose, and galactose.

Naphthalene A bicyclic, crystalline, volatile aromatic compound often used as an insect repellant.

Nylon A commercially viable synthetic polymer containing an amide bond attaching the monomers together.

Octane value A measure of the performance of a liquid fuel relevant to the type of the engine it is being used for.

Organic catalysts Organic molecules capable of catalyzing a chemical reaction by increasing the rate of the reaction.

Organometallic catalysts Organometallic catalysts differ from organic catalysts by having one or more metal elements.

Oxidant A compound capable of reacting with another compound by either providing with oxygen or removing hydrogens. An oxidant removes electron(s) from the other compound.

Pesticides Synthetic or natural compounds that eliminate pests.

Petrochemicals Commercially useful chemicals derived from fossil fuels.

Petrodiesel Diesel derived from fossil fuels.

Petroproducts Commercial products made from fossil fuel-resourced ingredients.

Pharmacokinetic (PK) Pharmacokinetic (PK) properties describe the properties of a medicinal agent moving through a living system.

Phenol An acidic aromatic alcohol originally isolated from coal tar. It is widely used in polymer and medicinal industries.

Photosynthesis The natural process by which plants use chlorophyll as a biocatalyst to convert light energy into storable chemical energy in carbohydrate molecules.

Plant oils Oily natural compounds extracted from plants ready for human use with or without other substances.

Plasticizers Additives to increase plasticity of materials.

Polyester Synthetic polymer containing repetitive ester bonds in between the monomeric units.

Polyglycols Polymers containing repeating monomeric units of glycols (1,2,3-trihydroxy propane).

Polylactides Polymers containing repeating monomeric lactic acid units.

Polysaccharides Natural polymeric compounds made of repeating monomeric units of monosaccharides connected together with a glycosidic bond.

Polyurethane Synthetic polymer containing urea bonds between the repeating monomeric units.

Producer gas Commercial gases or mixture of gases, viz. town gas and syngas.

Pyrolysis oil Renewable biomass-derived synthetic fuel and a possible alternative to fossil fuel.

Quercetin Naturally occurring flavonol (tricyclic polyphenolic compound) used in supplements and foods.

Renewable biomass The natural feedstock alternative to fossil fuel-derived substances for the generation of commercial products.

Renewable feedstocks See renewable biomass.

Resins Thick, often sticky liquid secretions from specific plants and trees that have commercial use.

Salicylic acid A nature-made aromatic phenolic carboxylic acid. It is widely used in variety of organic synthesis and contributes significantly to the structure of aspirin.

Saponification Base-catalyzed hydrolysis of an ester moiety (functionality/bond) into an alcohol and carboxylate salts of the free carboxylic acid.

Short-chain fatty acids (SCFA) Natural carboxylic acids with the aliphatic hydrocarbon chain not exceeding six carbons.

Sodium dodecyl sulfate (SDS) It is the sodium salt of dodecyl sulfate—an amphiphilic molecule that has widespread usage as a surfactant.

Sorbitol A straight-chain poly-alcohol derived from glucose and used as a sweetener.

Starch It is a natural polysaccharide and a plant product stitched together from glucose units. It is one of the most common carbohydrate sources for humans.

Succinic acid A natural diacid containing four carbons used in food and polymer industries.

Sugar The natural, water-soluble carbohydrates can be mono- or disaccharides with a sweetening property.

Surfactants Generally long hydrocarbon chain containing molecules with polar heads. They possess the amphiphilic property of liking both aqueous and non-polar media, thus can form micelles and act as surfactants.

Sustainable biomass Biological feedstock or starting materials for the generation of various commercial end products that can be regenerated. The production, isolation, use, and waste management of sustainable biomass are expected to be environment friendly and less hazardous.

Sustainable chemistry Energy produced from sustainable biomass and not fossil fuel-related resources.

Syngas Synthetic gas that is a mixture of hydrogen and carbon monoxide primarily.

Synthetic building blocks Unnatural smaller chemical fragments that can be used as segments or blocks in the synthesis of a larger target molecule.

Synthetic schemes The multi-step chemical process starting from commercially accessible starting materials to produce the final target molecule is generally known as the synthetic scheme. A plan or strategy could constitute a 'chemical scheme' as well.

Synthons Synthetic building blocks or pieces that are joined together carefully in a multi-step chemical process to yield the final target product.

Terpenoid Large natural organic molecules where repeating monomeric isoprene units can be found as building blocks.

Thymol A natural monoterpene phenolic compound responsible for the distinctive smell of thyme.

***Trans*-esterification** Conversion of an existing ester molecule to a different ester by an exchange reaction with an alcohol catalyzed by a base or an acid.

Triglyceride (TG) A naturally occurring fat or lipid containing one unit of glycerol and three units of identical or different fatty acids bonded together through three ester bonds.

Vanillin A natural monocyclic, aromatic, phenolic aldehyde often used as a flavoring agent.

Vegetable fats A triglyceride fat found or extracted from a plant.

Vegetable oil See vegetable fat.

Zein It is a natural protein found in corn.

Questions

1. How are bioproducts different from other products derived from petroleum resources?
2. Define biomass.
3. What is the traditional equivalent of biomass?
4. What are the three major classifications of bioproducts?
5. Do you think the modern society and governments should heavily invest in developing bioproducts? Justify your answer laying out the pros and cons supporting your arguments.
6. Are bioproducts always derived directly from biomass? Please explain.
7. Give a few examples of bioproducts that are directly obtained from nature.
8. Give a few examples of bioproducts that involve one or more steps between biomass and the final product.

9. Are all soaps bioproducts? Justify your answer.
10. Is it possible to produce soap from any plant or algae that produces triglyceride? Please justify your answer.
11. What is biodiesel? Please explain its structure and the precursor it is made from.
12. What are the two major components of a triglyceride?
13. Are all fatty acids identical?
14. What is the fundamental difference between saturated fat and unsaturated fat?
15. Should the nature of the starting fat (triglyceride) affect the nature of the biodiesel as a product?
16. What is the three-dimensional shape of soap in water?

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Heating in the Northeastern USA with a Biomass Pellet Stove: Lessons Learned in a Rural Residential Setting

Corinne J. Rutzke and Michael A. Rutzke

Abstract The chapter provides an overview of the carbon-neutral biomass-based alternatives for residential heating in rural areas. As with all alternatives, there are trade-offs. For example, biomass pellet stoves and gasifiers provide heat at a lower cost compared to fuel oil, but using a pellet stove or gasifier requires the installation of new equipment and often daily filling and cleaning that is not required by oil or natural gas furnaces/boilers. An overview of existing technologies for the conversion of biomass to heat and methods for preparing the biomass are discussed. The impacts to air quality differ greatly with each technology. More research is necessary to determine how to best prepare the biomass, which equipment is most efficient for burning biomass, and which combination of biomass and equipment is best at reducing negative impacts to air quality.

Keywords Biomass · Heating · Pellet stove · Bioenergy · Corn stove

1 Authors' Note to the Reader

Prior to moving into an old farmhouse in 2002, the authors did not think much about keeping warm in winter until we had to flip on the furnace switch that first cold day of autumn when baking something was no longer sufficient to warm the house. We learned that many rural households begin preparing for winter by harvesting and stacking wood in May, giving the wood time to age and dry out by the winter heating season. This change in perspective (of when to start thinking about winter

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heating) was the first of many lessons learned in moving to the farm. Today, we find ourselves thinking about heating year-round. The first two heating seasons in the old (circa 1801) drafty oil furnace-heated farmhouse convinced us to look for less expensive heating options. Our first motivation in seeking an alternative heating system was economic, but in exploring the options and thinking long-term, we quickly became convinced that we needed an alternative that was also sustainable for our land/environment, our lifestyle, and our physical abilities. We explored many heating technologies, and these are the focus of this chapter. We also became familiarized with local and federal environmental laws relating to residential heating technologies and air pollution. The regulations have changed in the last decade with the increase in the use of biomass-based heating technologies. As with any decision, there are always trade-offs, and the best choice for each situation will depend upon the unique conditions at each site. We settled on a multi-fuel pellet stove and recorded fuel-usage data for one year prior and two years post-installation of the pellet stove. In our setting, the pellet stove paid for itself in the very first year of use (based on savings of displaced #2 heating oil). We are able to heat our home each winter in central New York on less than two acres of field corn. We recommend considering residential pellet stove installation for cost savings in homes heating with #2 fuel oil. In addition to providing heat, we also recommend placement in a location conducive to good ambiance for the family ‘gathering around the fire.’ We find our children compete for the ‘best spot’ on cold mornings. We have experimented with a variety of biomass feedstocks and prefer a homemade mixture of corn, cherry pits, grass, and wood pellets. Based on fuel use prior to installation of the pellet stove and prior to house renovations that improved insulation, we estimate the biomass heat we are using displaces approximately 10 tons of fossil fuel each winter. Due to newer, more efficient heating technology (compared to our oil furnace), we use about six tons of a combination of corn, cherry pits, grass, or wood pellets. At this writing, we are exploring biomass-based heat sources for extending the growing season in our farm’s high-tunnel vegetable operation.

2 Introduction

According to a recent analysis by the USA Energy Information Administration (EIA), Americans are spending less of their total energy budget on heating our homes today than 20 years ago (Energy Information Administration 2013). It is believed this is due to the increased energy efficiency of homes and newer heating systems. Currently, there are approximately 116 million households in the USA. An estimated 97% of these households provide some form of heat to the residence for at least part of the year (Energy Information Administration 2014a). Nearly half (49%) of the households in the USA are heated with natural gas. Electricity follows natural gas as a primary residential heating source, with 34% of US homes heated by electricity. Homes located in areas that do not have access to natural gas pipelines often use truck-delivered heating oil (6%) or propane (5%) as the primary residential heat source. Wood is the primary heating fuel source in an estimated 1–2% of US homes, representing a 39% increase in this fuel type since 2004 (MacIntyre 2013). Nearly 2.5 million households (2%) used wood as their primary residential space heating fuel in 2012, which represents a 39% increase in wood use since 2004 (MacIntyre 2013; Energy Information Administration 2014b). The primary heat source varies by region of the country. Natural gas is the principal heating source for the majority of homes in the northeast, midwest, and western USA, while electricity is the primary heating source for the majority of homes in the southeast and central southern USA. Heating oil is primarily used in the northeastern USA, which accounts for 87% of the USA home heating oil market (Energy Information Administration 2014a, b).

This chapter discusses the technologies available currently and technologies under development for displacing fossil fuel sources of residential heat with less carbon-intensive biomass sources of heat.

3 Methods of Making Heat from Biomass Materials

Biomass (primarily plant-based sources of carbon) can be converted to heat for residential heating in three ways: combustion, gasification, and pyrolysis (Liu 2011). From a chemical conversion standpoint, the primary difference in the three methods is the availability of oxygen in the conversion reaction and the resulting end products. All three methods begin with a source of carbon-containing material such as biomass. In general, combustion is a chemical reaction of hydrocarbons in the presence of oxygen that produces carbon dioxide (CO_2), water (H_2O), energy (heat and light), and ash. Gasification also is a chemical reaction of hydrocarbons, but they are heated in the presence of low levels of oxygen producing a mixture of simple gaseous compounds such as carbon monoxide (CO), CO_2, hydrogen gas (H_2), and other flammable hydrocarbon gases such as methane. Other compounds produced from gasification are char and ash. The hydrocarbon gas (syngas) is then burned in a secondary combustion chamber where heat and light are again end products. Pyrolysis is a conversion method that involves heating a hydrocarbon source in the absence of oxygen to produce a black liquor liquid. The liquid can be refined and combusted in a turbine as well, for the production of heat and electricity (http://energy.gov/eere/energybasics/articles/biopower-basics).

In the archeological record

The original type of biomass heat combustion—the wood fire—has been providing heat to humans for over one hundred thousand years. This controlled, direct combustion of biomass for heating is a technology that appears in the archeological record during Paleolithic times, at least 125,000 years ago, when Homo sapiens left evidence of controlling fire (James 1989).

Current technologies increase efficiency and reduce pollution

Today's biomass combustion technologies allow for more complete combustion, as well as better capture and retention of heat from combustion than an open campfire; however, the fundamental thermochemical process is the same. Burning biomass for heat displaces the fossil fuels that we typically burn to provide heat, namely petroleum, natural gas, and propane. The idea of using biomass such as wood for heat is not a new concept. However, there are new technologies on the horizon that improve the efficiency and the environmental safety of using biomass for heat. Each has advantages and disadvantages for the user (Ciolkosz 2012; Foran 2014).

Fireplace technologies

The use of a residential fireplace helps capture more heat than an open outdoor fire, but fireplace combustion remains among the least efficient methods of producing heat from biomass. This low efficiency is due to two factors. First, much of the heat produced escapes along with smoke through the chimney. The upward draft that removes the burning wood's particulate matter from the house relies on convection and the upward movement of heated air. Second, fireplace combustion normally utilizes ambient air within the room, and the resulting fire burns at a lower temperature than in higher-efficiency combustion where the flow of oxygen to the flame is controlled, allowing more of the biomass to be completely combusted. In the process of direct combustion, dried biomass (often wood) is ignited by a spark or flame. The wood biomass contains hydrocarbons and carbohydrates which react with oxygen to produce heat, water, carbon dioxide, and light. If there is not sufficient oxygen present, the combustion process will leave behind residues and particulate matter. Over the centuries, attempts have been made to improve fireplace design for better retention of heat within the room. For example, the Rumford fireplace designed by Count Rumford of Massachusetts in the late 1700s provided a taller, narrower fireplace box that heated more fireplace bricks as the heat rose and radiated the additional heat back into the room (Brown 1969). An alteration in the shape of the exit path of the smoke into the chimney also reduced the amount of smoke in the room. Today, Rumford fireplace kits can be purchased for installation; however, the wood logs must be placed lengthwise to fit within the tall narrow fireplace box. The efficiency of fireplaces also can be increased by designs providing a longer exit-pathway through the chimney, collection of heat in chimney radiators with fans to blow chimney heat back into the room, and addition of oxygen inlet ports that bring outdoor air into the firebox with small fans for more complete combustion of the biomass. Biomass fireplaces require constant monitoring and feeding as the wood within the firebox is depleted and cannot be rapidly 'turned-off' if the fire tender needs to leave the house. Most fireplace systems remain excellent for ambiance and charm and for temporarily heating a single room, but low efficiency and high-maintenance reduce its usefulness in serving as a primary heat source in residential settings.

Outdoor wood boiler technologies

Outdoor wood boilers are another way to use biomass to deliver heat of combustion to a residential setting. As with fireplaces, the fuel source for an outdoor wood boiler is wood logs, though boiler burn chambers are in general larger than fireplace boxes, so the wood logs also can be a larger size. The boiler is located outdoors, so the biomass combustion takes place outside the home with this technology.

Large logs are placed into the outdoor wood boiler firebox, usually twice each day. The firebox of the boiler is surrounded by a metal enclosure. The firebox access door often includes a temperature-controlled fan to provide oxygen to the fire as needed. The metal enclosure is in turn surrounded by a water-reservoir jacket surrounding the metal box. The burning wood heats the water jacket that is in a closed loop, continuously being heated by the wood burner and cooled as water passes through each distribution point (radiators in the house). At the point of adding heat to the closed loop of water, a 'water jacket' surrounding the outdoor wood burner's burn chamber is heated to a target temperature of about 150 °F. When the water reaches the target temperature, a sensor turns on a pump that transfers the heated water through pipes into the building being warmed. Cooler water moves into the 'water jacket' around the burner, and the process repeats. Heat is transferred to the building either through hot water radiators or a heat exchanger to provide domestic hot water for the building's occupants. In general, outdoor wood burners are not very efficient for burning biomass, and due to the incomplete combustion of the biomass fuel, these boilers tend to produce a large amount of smoke and particulate matter during operation (Foran 2014).

A study from New York State found that outdoor wood boiler brands vary in efficiency and completeness of combustion and can also produce noxious pollutants that are harmful to human health. (Spitzer 2005) In recent years (since 2007), installation of new outdoor boilers requires the new units to meet US Environmental Protection Agency (EPA) regulations for heating efficiency and air pollution reduction. However, because outdoor wood burners are very convenient and provide a low-cost heating option, especially in rural settings where waste wood from nearby forest plots could be used, this stove has been a popular heat source for many farms in the northeastern USA. The wood logs need little pre-processing before use in an outdoor wood burner, and the boilers require very little maintenance. Nevertheless, the smoke produced is an irritant, and some of the pollutants in the smoke can cause negative cardio-respiratory effects (Foran 2014; Spitzer 2005). For these reasons, this type of heating system is generally considered undesirable and is now even illegal in many towns and cities where the population density is higher than in rural settings (Foran 2014; EPA's Air Rules for New Residential Wood Heaters 2015).

Indoor wood-burning stoves

Indoor wood-burning stoves provide heat by burning wood logs inside a chamber that is vented to the outdoors. The surrounding metal (and sometimes ceramic) stove parts heat up and radiate heat to the surrounding room air. Indoor wood-burning stoves must be re-filled several times each day, and during the filling, some smoke may escape into the room, while the stove door is opened. In general, the efficiency of heat capture from indoor wood-burning stoves is better than fireplaces but lower than biomass pellet or grain-burning stoves.

Benjamin Franklin invented a wood-burning stove that used a baffle behind the firebox. The baffle increased the length of the path smoke and waste heat traveled before exiting the house, and thus, more heat could be transferred to the room. The ‘Franklin Stove’ is one of several design attempts to improve the efficiency of burning wood for heat (Franklin 1786).

Efficiency of wood-burning stoves can be increased by increasing the length of the exhaust pipe between the stove and the exterior wall or ceiling, allowing some of the heat that enters the stove chimney to be recaptured by the room before being expelled outdoors. Wood fuel must be cut to lengths that will fit within the indoor stove chamber (usually 16–18 inches long). Indoor wood stoves, like fireplaces, provide localized room heating but at slightly higher heat-transfer efficiency than a fireplace.

Indoor Biomass pellet stoves/grain stoves

High-efficiency grain-burning and pellet-burning stoves address several of the concerns raised in utilizing other combustion technologies for heat production (Crema et al. 2011). The indoor version of pellet/grain stoves is similar in size to an indoor wood-burning stove but is filled through a hopper rather than by opening the burn chamber door. The hopper is an external bin that serves as a reservoir so that grain or pellets can be automatically fed into the burn chamber as needed, eliminating the problem of smoke escaping through the stove door into the room. This feature makes pellet stoves cleaner to operate indoors than the log-burning stoves. The pellet/grain stoves include a fan that provides oxygen and keeps combustion efficiency high and smoke and particulate matter low in comparison with the log-burning stove technologies (Cherney 2010). The burn chamber is surrounded by a metal housing designed with multiple layers and folds to capture as much heat as possible. High-efficiency pellet stoves capture so much heat of combustion that the chimney pipe is often cool to the touch with most heat being removed before the waste gases reach the chimney. Indoor biomass pellet/grain stoves require filling the hopper approximately twice a day (using approximately 40–80 lb of biomass at each filling) and cleaning every one to two days for the best operation. Heat from the burning biomass warms the stove jacket (usually a metal or ceramic block) and is distributed by a small fan that moves warmed air into the surrounding room.

Outdoor (or basement/garage-stored) biomass pellet or wood chip boilers

The biomass heat industry is expanding today through more efficient, more clean-burning stoves available for use in homes, and through an emerging biomass pelletizing industry. Outdoor pellet-burning boilers work in much the same way as outdoor wood boilers, by heating water that is transferred into the residence. However, less smoke/particulate matter is produced than with an outdoor wood boiler unit because the main burn chamber is not opened to the outdoors to feed additional fuel and because the consistent pellet size or wood chip size allows setting the correct oxygen flow for more complete combustion (EPA’s Air Rules for New Residential Wood Heaters 2015). Outdoor pellet/wood chip boilers either have larger hoppers or can be automatically fed from a larger storage bin through an auger/pellet-feeding mechanism that reaches from the boiler into a large outdoor storage container of pellets. In these systems, pellets can be delivered in bulk (by the ton) into the storage units. The outdoor pellet boiler heats water, and the hot water is circulated within the residence to provide heat through interior radiators or domestic hot water through a heat exchanger. In some settings, this type of boiler may be housed within a small building or basement with easy access for feedstock supply and ash removal.

Biomass gasifiers

Gasifiers are another type of biomass heat technology/equipment that converts wood chips, logs, pellets, and even bio-based oils to heat through 'gasification' under conditions that provide control over the air–fuel mixture in the gasification chamber (Pahl 2004). In the gasification process, biomass is heated in the presence of low amounts of oxygen so that combustion does not occur and instead flammable gases are produced. The gases contain flammable hydrocarbons that can be collected and burned. Thus, gasifiers contain a secondary burn chamber for combustion of the gases. The gasification process is as follows: Wood chips, logs, or other biomass (including bio-based oil) is fed into the gasifier. The biomass is slowly converted to gas (syngas), and the gas is then burned in a secondary chamber to produce heat. The heat is collected through a series of exhaust pipes that wind through a water bath. The water is heated and then pumped into the residence where heat can be distributed either through a heat exchanger that can heat the building's hot water or to a series of room radiators that heat the air. While the external plumbing aspects are very similar to an outdoor wood-burning boiler system, the gasifier provides a much cleaner burn, through more complete combustion. This significantly reduces particulates and other pollutants and ash compared to the outdoor wood boiler.

Biodiesel replacement of fossil-fuel heating oil

Heating oil furnaces are used for heating homes and businesses in many areas of the country. The traditional fuel utilized is referred to as '#2 heating oil' or 'HHO' (home heating oil) (Pahl 2004). This heating oil is very similar in composition to diesel fuel. In industry, a red dye is added to #2 heating oil to prevent its sale as a motor fuel (which is taxed differently than heating oil). The home heating oil is usually delivered to the home or business by truck as opposed to pipelines utilized by natural gas home heating furnaces.

Biodiesel can be burned in oil furnaces with a specialized furnace motor that prevents biodiesel from clogging the lines. Biodiesel will gel or solidify at low temperatures, so the storage tank also needs to be kept warm for winter use. This can be accomplished through indoor storage of the biodiesel storage tank and any lines going from the tank to the furnace. Biodiesel can be made from waste cooking oils or plant seed oils; however, waste cooking oils tend to be high in particulate matter, and additional filtration may be needed to prevent clogging the furnace fuel lines. Another approach to prevent fuel-line clogging is to use a percentage of biodiesel mixed with #2 heating oil; for example, B20 is a mix of 20% biodiesel with 80% heating oil (petroleum-based).

4 Methods of Preparing Biomass to Serve as a Heating Fuel

Biomass for outdoor wood boilers and indoor wood stoves

Wood logs are collected and processed by sawing, chopping, or splitting into sizes that will conveniently fit inside the burn chamber. From the time of cutting, the split logs should be air dried and aged (seasoned) prior to use. Seasoned wood can be purchased (pre-dried), or greenwood can be purchased or collected in spring and then seasoned prior to use in the fall, depending on conditions. Drying the wood reduces pollutant emissions during combustion. In areas that permit wood burning for heat, the use of only seasoned wood (no greenwood) is recommended by stove manufacturers and also usually is required through local burning ordinances. Certain species of wood and climates that have high humidity much of the year may require longer time periods (up to two years) to season the wood.

Biomass for pellet stoves and pellet boilers

The production of biomass pellets begins with the harvest or collection of the biomass feedstock. The biomass can be baled, chipped, or bagged for transport. Currently, most biomass used for pellet production is transported by truck from fields, forest, or mill waste sites to a pelletizing plant http://www.biomasscenter.org/images/stories/grasspelle-trpt_0111.pdf. At the plant, the process begins with grinding of the biomass feedstock into a coarse powder. The grinding or size-reduction process may require several steps through a series of chippers, choppers, hammer mills, and grinders to obtain the right-sized biomass particles for pelletization. The coarsely ground biomass powder is compressed and heated as it is passed through an extruder, which shapes the pellets. Typically, the heating process in the extruder melts some of the natural plant lignin, providing a natural glue that holds each pellet together as it cools. The cooled pellets are bagged and stacked on a pallet for shipment or storage. Kept cool and dry, the pellets remain stable for a long time in storage but will quickly return to the powder stage if wetted or crushed in handling http://www.biomasscenter.org/images/stories/grasspelle-trpt_0111.pdf.

Corn or other grains can be used in specialized pellet stoves designed to handle multiple fuel types (pellets, grains, or cherry pits). Most stove manufacturers recommend corn or other grains should be dried to approximately 8% moisture content for the best combustion, compared to seasoned wood logs, which are recommended to be dried to 20% moisture content or less at the center of the log.

The Rutzke Biofuel Mix: Anecdote from experience: Through trial and error experimentation, we found that a combination of fuels works best in pellet/grain stoves. The ideal combination for heat production and completeness of combustion is mixes that contain a small amount of oil (such as corn) and a material that serves as kindling to overcome variations in moisture content often found in grains (such as wood pellets, grass pellets, or cherry pits). When the fuel mix was 100% corn grain, variations in ambient humidity could reduce the completeness of combustion, resulting in less heat produced and large 'clinkers' (stone-like residue formed from un-combusted corn residue) left behind on the stove burn pot or auger. Clinker formation also increased the frequency of cleaning required for pellet stove operation. On the other hand, when the fuel mix was 100% wood pellets or grass pellets or cherry pits, these very dry fuel sources burned easily and rapidly but required more frequent filling of the stove hopper. Burning grass pellets alone also left large amounts of dry, fluffy ash. However, using a combination of corn and one of the drier feedstocks (wood pellet, grass pellet, or cherry pits) provided a number of advantages. Using a mixture that was approximately (by volume) one-third corn and two-thirds of either wood pellet or grass pellet or cherry pits (or any combination of the three) provided a steady burn rate, with high heat output and low-to-no clinker formation. This combination of fuels reduced the number of times we needed to refill the stove, reduced the number of times we needed to clean the stoves, and provided more heat at a more uniform rate of output. We hypothesize that the drier fuels (wood, grass, and cherry pits) may be serving as hot burning fire kindling to overcome any moisture carried in the corn grain. When burned at the higher temperatures provided by the drier fuels, the corn grain provides a small amount of corn oil which may explain the overall increase in heat output and uniformity. We observed a benefit in mixing biomass fuel types for pellet stove heating purposes. Controlled studies are needed to examine these hypotheses and to optimize pellet and grain fuel mixtures for residential heating.

Biomass for gasifiers

Depending on the type of residential gasifier, some may require a uniform wood chip size, log size, or pellet size to function properly. Newer biomass gasifiers are being marketed as ‘fuel agnostic’ and can also burn combinations of dried biomass and bio-based oils. Gasifier exhaust tubes serve as heat exchangers in many systems and require frequent cleaning due to creosote buildup. In general, all of these technologies will perform more efficiently with dry biomass because less energy is consumed removing water.

5 Heat Value of Fuel Sources and Trade-Offs

The amount of heat that can be produced by a given quantity of fuel is called its ‘heating value.’ The heating value can be measured in a few different ways. A bomb calorimeter is one commonly used method. It can be difficult to compare heating values in the literature because they might be expressed in different units, such as the energy/unit mass of the fuel, energy/unit volume of the fuel, or energy/mole of the fuel. Heating values found in literature also vary based on the amount of moisture in the biomass feedstock, the type of biomass tested, and the efficiency of the particular burner utilized to convert the biomass to heat. Different biomass sources—and even different species of wood—have different heating values. The differences are based on the chemical composition of the biomass material. Some plant species contain more oils or more lignin than other species, and there can be differences between varieties within a species. The moisture content of the fuel also impacts a fuel's heating value. Another important factor influencing heating values found in literature is the percent efficiency of the biomass burner utilized.

The following list provides some standard heating values for both bio-based and fossil fuels for comparison (http://www.fpl.fs.fed.us/documnts/techline/fuel-value-calculator.pdf; Bartok 2004).

Fuel source	Standard heating value
Seasoned firewood	15.4 million Btu/cord
Premium wood pellets	13.6 million Btu/ton
Corn cobs	16 million Btu/ton
Propane	92,500 Btu/gal
Oven-dried switchgrass	14.4 million Btu/ton
Fuel oil #2 (heating)	115,000 Btu/gal
Natural gas	100,000 Btu/100 ft3 (1 therm = 100 ft3)

Heating values found in literature can vary based on % moisture, type of biomass, and percent efficiency of the boiler/burner used

BTU British Thermal Unit is the amount of energy required to increase the temperature of one pound of water by one degree Fahrenheit

Data sources Data (http://www.fpl.fs.fed.us/documnts/techline/fuel-value-calculator.pdf) and http://www.hrt.msu.edu/energy/pdf/heatingvalueofcommonfuels.pdf, developed by John Bartok, Jr., University of Connecticut, 2004

Trade-offs

As with all alternatives, there are trade-offs. Biomass pellet stoves and gasifiers provide heat at a lower cost compared to fuel oil, but using a pellet stove or gasifier requires the installation of new equipment and often daily filling and cleaning that is not required by oil or natural gas furnaces/boilers. Outdoor wood boilers are less expensive, but labor-intensive, making this technology more difficult to maintain for an aging rural population. Furthermore, the impacts to air quality differ greatly. Natural gas burns cleaner than #2 fuel oil (residential heating oil), and #2 fuel oil burns cleaner than heavier fuel oils or many biomass heat sources. More research is necessary to determine how to best prepare the biomass, which equipment is most efficient for burning biomass, and which combination of biomass and equipment is best at reducing negative impacts to air quality (Winebrake et al. 2012; http://www.biomasscenter.org/images/stories/grasspelle-trpt_0111.pdf). Another consideration in selecting a residential heating technology is fire safety. All heating methods carry some degree of risk to life and property. The nature of the fire risk changes with each particular heating method.

6 Environmental Laws Relating to Residential Heating Technologies

The US Environmental Protection Agency (EPA) oversees regulation of biomass heating technologies that impact air quality. The Clean Air Act, section 111, is amended, and new regulations created that evolve with new biomass heating technologies manufactured after 1988 (EPA's Air Rules for New Residential Wood Heaters 2015). On January 3, 2014, EPA proposed revisions to the residential wood heater new source performance standards (NSPS), and in 2015, new NSPS standards were published and are available in full through the EPA website (EPA's Air Rules for New Residential Wood Heaters 2015). These standards govern the manufacture of new wood stoves, and certain fireplace inserts and impose certain minimum standards for the reduction of air pollution. Wood-burning units made today must meet these standards and must provide the buyer with a tag confirming that the stove has been tested and certified to meet the air emission requirement standards. In order to allow time for manufacturers to ease into the new standards, the EPA is launching the compliance process in two steps: Step 1—requires the first level of air emissions (particulate matter maximum of 4.5 g/h of operation) beginning December 2015, and Step 2 requires that manufacturers meet the Step 2 air emissions (particulate matter maximum emissions of 2.0 g/h of operation) standards by 2020 (EPA's Air Rules for New Residential Wood Heaters 2015).

7 Capital Cost Comparisons

An important factor in the selection of a biomass heating system is the capital costs required to purchase a unit. The following provides price ranges from industry in autumn of 2015 for comparison. In general, the newer technologies (residential gasification units) are the most expensive.

Residential technology	Approximate capital cost range (US dollars) (2015)
Rumford fireplace	\$4000–\$10,000
Outdoor wood boilers	\$3000–\$10,000
Indoor wood-burning stoves	\$500–\$3000
Indoor biomass pellet stoves	\$1000–\$4000
Outdoor pellet or woodchip boilers	\$6000–\$18,000
Biomass gasifiers	\$6000–\$20,000
Biomass CHP systems	Not yet available for residential settings in USA

Cost is influenced by the size of the stove required to heat the space. In determining the size of the heating unit, a good rule of thumb for the average residential setting is to select a unit that will provide approximately 35 BTU per square foot of space to be heated (Albright 2006).

8 On the Technology Horizon

Newer high-efficiency burners have been developed and are used in Europe. Some of these technologies and equipment are also being developed by several companies for both industrial and residential markets in the USA. These new technologies are including options for systems that provide a combination of heat and power in the form of electricity (combined heat and power or CHP). A company in Europe has created a residential-scale CHP unit using a pellet-burning stove and a Stirling engine. Companies are responding to consumers' requests for more efficient, lower-pollution heating technologies that can utilize carbon-neutral biomass.

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Glossary of Terms

B20 A mixture of 20% biodiesel and 80% conventional diesel.

Biodiesel A biodegradable transportation fuel for use in diesel engines or heating fuel for use in specially-converted furnaces. Biodiesel, a fatty acid methyl ester, is produced through the transesterfication of organically-derived oils.

Bioenergy Refers to biomass based production of heat, transportation fuel, or electricity to displace fossil petroleum sources.

Biofuels Biomass converted to liquid fuels such as ethanol and biodiesel.

Biomass Any biologically-derived organic matter. Biomass available for energy on a sustainable basis includes herbaceous and woody energy crops, agricultural food and feed crops, agricultural crop residues, wood residues.

Biomass Pellet A biomass pellet is a cylindrical, extruded form of ground and heated biomass (usually made from wood or perennial grasses). Biomass pellets are approximately 10 times more dense than un-pelletized biomass. The pelletization of biomass improves efficiency of transportation, storage and improves fluidity of biomass feedstock in automatic feeding systems for heating units.

Carbon Dioxide (CO_2) A colorless, odorless gas produced by respiration and combustion of carbon-containing fuels. Plants use it as a food in the photosynthesis process.

Carbon Monoxide (CO) A colorless, odorless, poisonous gas produced by incomplete combustion.

Combined Heat and Power (CHP)/Co-Generation The technology of producing electric energy and another form of useful energy (usually thermal) for industrial, commercial, or domestic heating or cooling purposes through the sequential use of the energy source.

Combustion A chemical reaction of hydrocarbons in the presence of oxygen that produces carbon dioxide (CO_2), water (H_2O), energy (heat and light), and ash.

Feedstock Raw materials that may be treated or converted to create fuels. Biomass feedstocks may include forestry products, crop residues, municipal waste streams, manure and food processing waste.

Gasification of biomass A chemical reaction of hydrocarbons, but they are heated in the presence of low levels of oxygen producing a mixture of simple gaseous compounds such as carbon monoxide (CO), CO_2, hydrogen gas (H_2), and other flammable hydrocarbon gases such as methane. Other compounds produced from gasification are char and ash.

Gasifier A device that converts solid feedstocks to gas and then burns the gas in a secondary burn-chamber. Heat can be captured and redistributed by a variety passive and active methods. Generally refers to a heating technology using thermochemical processes.

Heating oil/home heating oil/#2 heating oil Fossil-fuel based #2 distillate from crude oil processing. Heating oil is chemically identical to diesel fuel but is dyed pink to differentiate between taxable transportation fuels and heating fuel.

Heating Value The maximum potential energy released during complete oxidation of a unit of fuel. Includes the thermal energy recaptured by condensing and cooling all products of combustion.

New Source Performance Standards (NSPS) Standards developed by the U.S. Environmental Protection Agency that govern the manufacture of new wood/biomass stoves and impose certain minimum standards for reduction of air pollution from biomass stoves.

Outdoor wood boiler A biomass (wood-based) heating technology that captures heat of combustion of logs in a water-jacket and redistributes the heat through a radiator system.

Indoor wood-burning stoves A biomass (wood-based) heating technology that captures heat of combustion of logs in metal or ceramic casing of the stove and passively redistributes heat to the surrounding airspace. Some stoves may contain a small fan that speeds distribution of heat to the surrounding space.

Particulate Matter Fine liquid or solid particles such as dust, smoke, mist, fumes, or smog, found in air or emissions. It is usually separated into PM10 and PM2.5, which are particles of diameter equal to or less than 10 and 2.5 micrometers (μm), respectively.

Pellet See biomass pellet.

Pellet stove A heating device used in residential settings that utilizes biomass pellets or grains as the heating fuel source. Biomass pellets are combusted and heat is captured and distributed to the room space.

Pyrolysis The breaking apart of complex molecules by heating in the absence of oxygen, producing solid, liquid, and gaseous fuels. a conversion method that involves heating a hydrocarbon source in the absence of oxygen to produce a black liquor liquid. The liquid can be refined and combusted in a turbine as well, for the production of heat and electricity.

Rutzke (rut-skee) Biofuel Mix A biomass heating fuel mixture for use in pellet/grain stoves that contains a mixture of corn grain, wood or grass pellets and cherry pits.

Seasoned wood Wood that is aged and dried over time (6 months to 2 years, depending on wood type and environmental conditions) through exposure to wind, rain, sun and natural drying conditions to remove moisture from newly harvested (green) wood. Seasoned wood produces less creosote and burns more cleanly than green wood.

Syngas Syngas, short for synthesis gas, is a mixture of carbon monoxide (CO) hydrogen (H_2) and methane. It is the product of high temperature gasification of organic material such as biomass. Following clean-up to remove any impurities such as tars, syngas can be converted to liquid biofuels such as synthetic diesel (via Fischer–Tropsch synthesis).

Thermochemical Gasification A process operated at elevated temperature that converts a solid feedstock into a gaseous fuel, while maximizing the chemical energy content of the product gas.

Questions for Critical Thinking

(1) What is the most cost efficient method of heating residential space in the Northeastern United States today?
(2) Which heating technology and fuel combination is responsible for the most air pollution in the United States today? Which is the cleanest burning?
(3) With use of wood-based heat on the rise in the United States since 2004, what number of households could be sustainably heated by wood-heat?
(4) How many acres of woods could we sustainably utilize annually to supply heat? What factors influence tree-replenishment rates?
(5) If a 1500 square foot home could meet all winter heating needs using 2 acres of field corn, how many acres of corn would be required to provide the nation's winter heating needs? Is this sustainable?

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