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Introduction to Thermochemical Processing of Biomass into Fuels, Chemicals, and Power

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Abstract
Thermochemical processing of biomass uses heat and catalysts to transform plant polymers into fuels, chemicals, or electric power. Thermochemical conversion can be categorized as combustion, gasification, pyrolysis, and solvent liquefaction. The key operating parameters governing these routes are degree of oxidation, temperature, heating rate, and residence time. Among the thermochemical technologies, combustion is the most widely deployed in commercial practice. The commercialization of second-generation biofuels is widely limited by their high cost of production, which can be as much as two to three times higher than for fossil fuels. Biofuels produced from sustainably grown biomass have several environmental benefits compared to petroleum-derived gasoline and diesel. Among the most important of these is net reductions in life-cycle GHG emissions, which arise from the fact that the carbon in biofuels is taken up from the atmosphere through photosynthesis of growing biomass. This introduction also presents an overview of the key concepts covered in this book.

Disciplines
Bioresource and Agricultural Engineering | Catalysis and Reaction Engineering | Energy Systems | Polymer and Organic Materials

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Introduction to Thermochemical Processing of Biomass into Fuels, Chemicals, and Power

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1.1 Introduction

Thermochemical processing of biomass uses heat and catalysts to transform plant polymers into fuels, chemicals, or electric power. This contrasts with biochemical processing of biomass, which uses enzymes and microorganisms for the same purpose. In fact, both thermochemical and biochemical methods have been employed by humankind for millennia. Fire for warmth, cooking, and production of charcoal were the first thermal transformations of biomass controlled by humans, while fermentation of fruits, honey, grains, and vegetables was practiced before recorded time. Despite their long records of development, neither has realized full industrialization in processing lignocellulosic biomass. While petroleum and petrochemical industries have transformed modern civilization through thermochemical processing of hydrocarbons, the more complicated chemistries of plant molecules have not been fully developed.

Ironically, the dominance of thermochemical processing of fossil resources into fuels, chemicals, and power for well over a century may explain why it is sometimes overlooked as a viable approach to bio-based products. Smokestacks belching pollutants from thermochemical processing of fossil fuels is an indelible icon from the twentieth century that no one wishes to replicate with biomass. However, as described in a report released by the US Department of Energy in 2008 [1], thermal and catalytic sciences also offer opportunities for dramatic advances in biomass processing. Actually, thermochemical processing has several advantages relative to biochemical processing as detailed in Table 1.1. These include the ability to produce a diversity of oxygenated and hydrocarbon fuels, reaction times that are several orders of magnitude shorter than biological processing, lower cost of catalysts, the ability to recycle catalysts, and the fact that thermal systems do not require the sterilization procedures demanded for biological processing. The data in Table 1.1 also suggest that thermochemical processing can be done with much smaller plants than is possible for biological processing of cellulosic biomass. Although this may be true for some thermochemical options (such as fast pyrolysis), other thermochemical options (such as gasification-to-fuels) are likely to be built at larger scales than biologically based cellulosic ethanol plants when the plants are optimized for minimum fuel production cost [2].

Table 1.1 *Comparison of biochemical and thermochemical processing. Adapted from Reference [1].*

	Biochemical processing	Thermochemical processing
Products	Primarily alcohols	Range of fuels and chemicals
Reaction conditions	Less than 70 °C, 1 atm	100–1200 °C, 1–250 atm
Residence time	2–5 days	0.2 s–1 h
Selectivity	Can be made very selective	Depends upon reaction
Catalyst/biocatalyst cost	$0.50/gallon ethanol	$0.01/gallon gasoline
Sterilization	Sterilize all feeds	No sterilization needed
Recyclability	Difficult	Possible with solid catalysts
Size of plant (biomass input)	2000–8000 tons/day	5–200 tons/day (fast pyrolysis)

The first-generation biofuels industry, launched in the late 1970s, was based on biochemically processing sugar or starch crops (mostly sugar cane and maize, respectively) into ethanol fuel and oil seed crops into biodiesel. These industries grew tremendously in the first 15 years of the twenty-first century, with worldwide annual production reaching almost 26 billion gallons of ethanol [3] and 5.3 billion gallons of biodiesel in 2016 [4]. The development of first-generation biofuels has not been achieved without controversy, including criticism of crop and biofuel subsidies, concerns about using food crops for fuel production, and debate over the environmental impact of biofuels agriculture, including uncertainties about the role of biofuels in reducing greenhouse gas emissions [5]. Many of these concerns would be mitigated by developing second generation biofuels that utilize high-yielding nonfood crops that can be grown on marginal or waste lands. These alternative crops are of two types: lipids from alternative crops and lignocellulosic biomass.

Lipids are a large group of hydrophobic, fat-soluble compounds produced by plants and animals. They are attractive as fuel for their high energy content. The most common of these are triglycerides, esters consisting of three fatty acids attached to a backbone of glycerol. They can be converted into transportation fuels in one of two ways. Biodiesel is produced by transesterification of the triglycerides to methyl ester, which is blended with petroleum-derived diesel. Renewable diesel is produced by hydrotreating triglycerides to yield liquid alkanes and co-product propane gas (see Figure 1.1). Biodiesel has dominated most lipid-based fuel production because of the relative simplicity of the process, which can be done at small scales. Biodiesel is not fully compatible with petroleum-derived diesel, an advantage of renewable diesel. However, hydrotreating requires higher capital investment, with economics favoring larger facilities that may be incompatible with the distributed nature of lipid feedstocks [6].

Soybeans were originally thought an attractive feedstock for biodiesel production, reducing GHG emissions by 41% compared to conventional diesel and producing 93% more energy output compared to corn ethanol [7,8]. However, use of soybeans and other edible oils for fuel has been criticized as competing with its use as food [8,9]. Soybeans are also an expensive energy source, representing 85% of the cost of producing biodiesel [8]. For this reason, most first-generation biodiesel and renewable diesel have been produced from low-cost waste fats and oils.

Wider use of biodiesel and renewable diesel will require alternatives to traditional seed crops, which only yield 50 - 130 gal/acre [10]. Suggestions have included jatropha (200 - 400 gal/acre) [11] and palm oil (up to 600 gal/acre) [12], but the most promising alternative is microalgae, which are highly productive in natural ecosystems with oil

yields as high as 2,000 gal/acre in field trials and 15,000 gal/acre in laboratory trials [13]. Lipids from algae also have the advantage of not competing with food supplies. However, the process is currently challenged by high cost associated with harvesting and drying algae and practical difficulties of cultivating algae with high lipid content. [14] Considerable engineering development are required to reduce capital costs, which are as high as $1 million per acre, and production costs, which exceed $10/gal. The challenge of lipid-based biofuels is producing large quantities of inexpensive lipids rather than upgrading them to fuels.
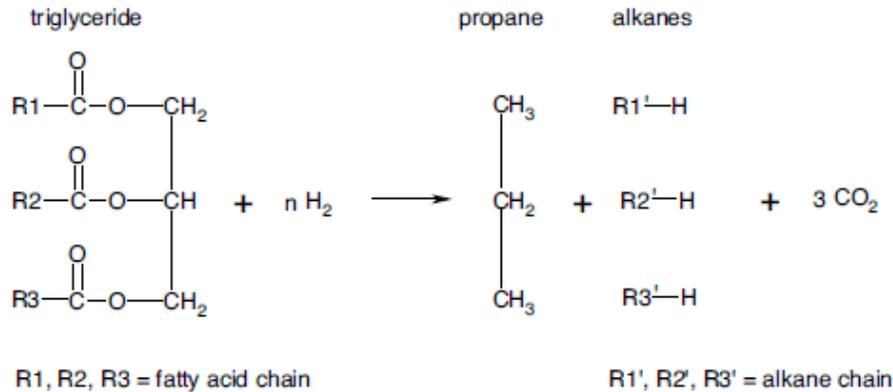

Figure 1.1 Simplified representation of hydrogenation of triglyceride during hydrotreating

Lignocellulosic biomass is a biopolymer of cellulose, hemicellulose, and lignin (Figure 1.2) [15]. Lignocellulosic biomass dominates most terrestrial ecosystems and is widely managed for applications ranging from animal forage to lumber. Cellulose is a structural polysaccharide consisting of a long chain of glucose molecules linked by glycosidic bonds. Glycosidic bonds also play a vital role in linking pentose, hexose, and sugar acids contained in hemicellulose. Breaking these bonds releases monosaccharides, allowing lignocellulosic biomass to be used for food and fuel production. Biochemical processing of lignocellulosic biomass employs a variety of microorganisms that secrete enzymes that catalyze the hydrolysis of glycosidic bonds in either cellulose or hemicellulose. Many animals, like cattle and other ruminants, have developed symbiotic relationships with these microorganisms to allow them to digest cellulose. Thermal energy and catalysts can also break glycosidic bonds although usually less selectively although more inexpensively than enzymes.

Lignin, a complex cross-linked phenolic polymers, is indigestible by most animals and microorganisms. In fact, it protects the carbohydrate against biological attack. Thus, even ruminant animals that have evolved on diets of lignocellulosic biomass, such as grasses and forbs, can only extract 50–80% of the energy content of this plant material because some of the polysaccharides and all of the lignin pass through the gut undigested. Biochemical processing has many similarities to the digestive system of ruminant animals. Physical and chemical pretreatments release cellulose fibers from the composite matrix, making them more susceptible to enzymatic hydrolysis, which releases simple sugars that can be fermented or otherwise metabolized [17].
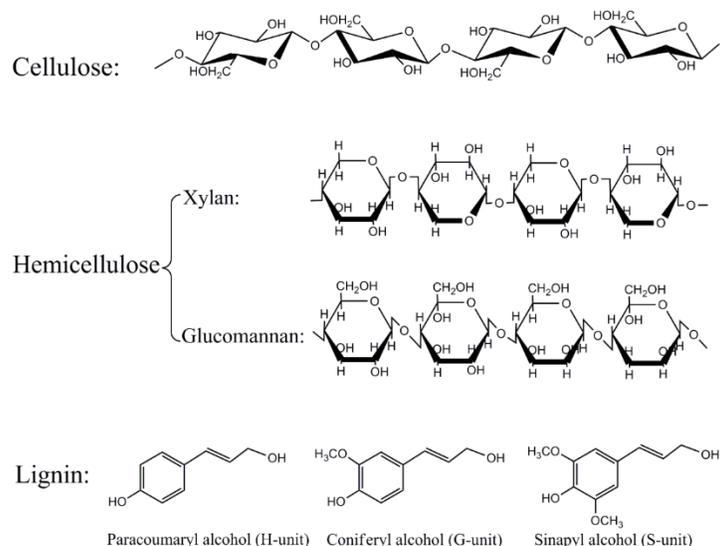
Figure 1.2 *Three main components of lignocellulosic biomass: cellulose, hemicellulose, and lignin* [16].

Thermochemical processing occurs at temperatures that are several hundred degrees Celsius and sometimes over 1000°C. At these temperatures, thermochemical processes occur very rapidly whether catalysts are present or not. In contrast, biochemical processes occur at only a few tens of degrees Celsius above ambient temperature, with the result that they can take hours or even days to complete even in the presence of biocatalysts. Thermal depolymerization of cellulose in the absence of alkali or alkaline earth metals produces predominately levoglucosan, an anhydrosugar of the monosaccharide glucose [18]. Under certain conditions, it appears that lignin depolymerizes to monomeric phenolic compounds [19]. Under conditions of high-temperature combustion and gasification, chemical equilibrium among products is attained. Thus, thermochemical processing offers opportunities for rapid processing of diverse feedstocks, including recalcitrant materials and unique intermediate feedstocks, for production of fuels, chemicals, and power.

1.2 Thermochemical Conversion Technologies

Thermochemical conversion can be categorized as combustion, gasification, pyrolysis, and solvent liquefaction as shown in Figure 1.3. The key operating parameters governing these routes are degree of oxidation, temperature, heating rate, and residence time. End products from various technologies include electric power, heat, fuels and chemicals [20].
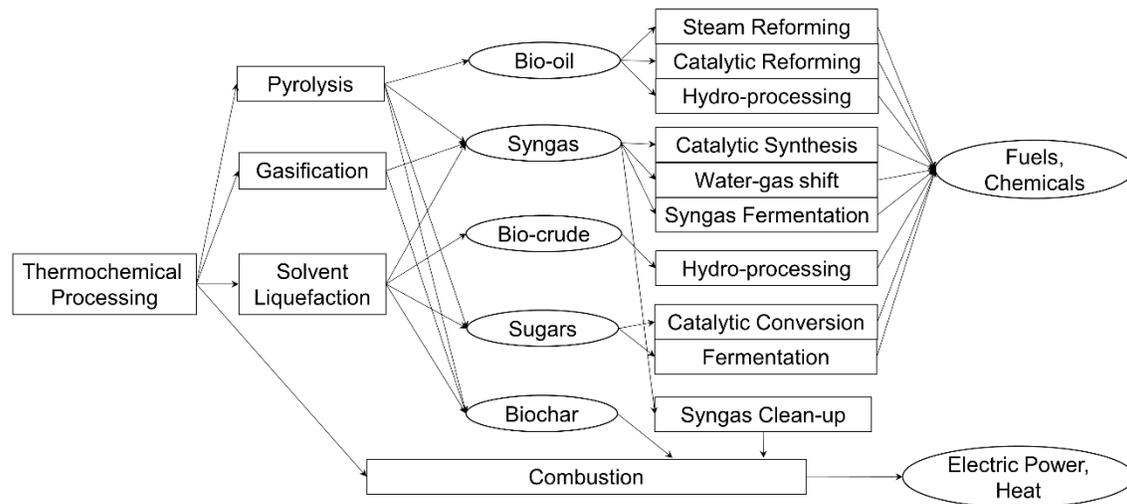
Figure 1.3 *Thermochemical options for production of fuels, chemicals, and power. Text in black indicate technologies and text in red indicate products or intermediate products.*

1.2.1 Direct Combustion

Direct combustion of biomass produces moderate- to high-temperature thermal energy (800–1600°C) suitable for heat and power applications. This is realized by rapid reaction of fuel and oxygen to obtain thermal energy and flue gas, consisting primarily of carbon dioxide and water. Depending on heating value and moisture content of the fuel, the fuel-to-air ratio and the construction of the furnace, flame temperatures can exceed 1650°C. Direct combustion of biomass has the advantage of employing well-developed and commercially-available technology. Combustion is the foundation of much of the electric power generation around the world. Direct combustion of biomass is burdened by three prominent disadvantages. These include penalties associated with burning high-moisture fuels, agglomeration and ash fouling due to alkali compounds in biomass, and difficulty of providing and safeguarding sufficient supplies of bulky biomass to modern electric power plants.

While most of the focus on bioenergy has been on the production of liquid fuels, it has been argued that a better use of biomass would be to burn it for the generation of electricity to power battery electric vehicles (BEV) [21]. Well-to-wheels (WTW) analyses indicate that BEV's are superior to biofuels-powered internal combustion engine (ICE) vehicles in terms of primary energy consumed, greenhouse gas (GHG) emissions, lifecycle water usage, and cost when evaluated on the basis of kilometers driven [22]. However, this is contingent on further development of batteries that can store sufficient electricity to match the power, range and cost of internal combustion engine vehicles.

1.2.2 Gasification

Thermal gasification is the conversion of carbonaceous solids at elevated temperatures (700–1000°C) and under oxygen-starved conditions into syngas, which is a flammable gas mixture of carbon monoxide, hydrogen, methane, nitrogen, carbon dioxide, and

smaller quantities of hydrocarbons [23]. The produced syngas can be used to generate either electric power or to synthesize fuels or other chemicals using catalysts or even microorganisms (syngas fermentation) [24]. Gasification has been under development for almost 200 years, beginning with the gasification of coal to produce so-called "manufactured gas" or "town gas" for heating and lighting. Coal gasification has also been used for large-scale production of liquid transportation fuels, first in Germany during World War II and then later in South Africa during a period of worldwide embargo as a result of that country's apartheid policies.

Gasification can be used to convert any carbonaceous solid or liquid to low molecular weight gas mixtures. In fact, the high volatile matter content of biomass allows it to be gasified more readily than coal. Biomass gasification has found commercial application where waste wood was plentiful or fossil resources were scarce. An example of the former was Henry Ford's gasification of wood waste derived from shipping crates at his early automotive plants. An example of the latter was the employment of portable wood gasifiers in Europe during World War II to power automobiles. With a few exceptions, gasification in all its forms gradually declined over the twentieth century due to the emergence of electric lighting, the development of the natural gas industry, and the success of the petroleum industry in continually expanding proven reserves of petroleum. In the twenty-first century, as natural gas and petroleum become more expensive, gasification of both coal and biomass is likely to be increasingly employed.

One of the most attractive features of gasification is its flexibility of application, including thermal power generation, hydrogen production, and synthesis of fuels and chemicals. This offers the prospect of gasification-based energy refineries, producing a mix of energy and chemical products or allowing the staged introduction of technologies as they reach commercial viability.

The simplest application of gasification is production of heat for kilns or boilers. Often the syngas can be used with minimal clean-up because tars or other undesirable compounds are consumed when the gas is burned and process heaters are relatively robust to dirty gas streams. Syngas can be used in internal combustion engines if tar loadings are not too high and after removal of the greater part of particulate matter entrained in the gas leaving the gasifier. Gas turbines offer prospects for high-efficiency integrated gasification–combined-cycle power, but they require more stringent gas cleaning [25]. As the name implies, syngas can also be used to synthesize a wide variety of chemicals, including organic acids, alcohols, esters, and hydrocarbon fuels, but the catalysts for this synthesis are even more sensitive to contaminants than are gas turbines.

1.2.3 Pyrolysis

Pyrolysis is a thermal conversion technology that can either be considered an initial step for other thermal conversion processes, such as gasification and combustion, or a conversion process in its own right for production of bio-fuels. Pyrolysis decomposes biomass in the absence of oxygen, within a temperature range of 300–900°C [26] and a heating rate that varies greatly from less than 0.005°C/s to more than 10,000°C/s [27]. Depending on operating conditions, pyrolysis can be classified as slow, intermediate, fast, or flash pyrolysis. Slow pyrolysis operates at relatively low heating rate, low temperature, and long residence times with the main product being solid char. Fast pyrolysis is characterized by high heating rate, high temperature, and short

residence time compared to slow pyrolysis. Intermediate pyrolysis is a technology with moderate operating temperature and heating rate. Flash pyrolysis has the highest heating rate and shortest residence time, which requires special reactors to achieve [20].

Bio-oil is an energy-rich liquid recovered from the condensable vapors and aerosols produced during fast pyrolysis. It is a complex mixture of oxygenated organic compounds, including carboxylic acids, alcohols, aldehydes, esters, saccharides, phenolic compounds, and lignin oligomers. Other products include flammable gas (syngas) and biochar [28]. However, bio-oil is the majority product with yields as high as 70-80 wt% [20]. Under suitable processing conditions, fast pyrolysis can also yield significant quantities of sugars and anhydrosugars [29]. These "thermolytic sugars" can either be fermented or catalytically upgraded to fuel molecules.

The great virtues of fast pyrolysis are the simplicity of the process and the attractiveness of a liquid as intermediate product for upgrading to finished fuels and chemicals compared to either syngas from gasification or raw biomass. Early attempts to use bio-oil as fuel for both boilers and gas turbine engines were stymied by its cost, corrosiveness, and instability during storage. More recent strategies upgrade bio-oil to either heavy fuel oil substitutes or transportation fuels. For example, light oxygenates in bio-oil can be steam reformed to provide hydrogen [30] while the heaviest fraction of bio-oil can be cracked to gasoline and diesel fuel [31]. Techno-economic analysis [32] indicating bio-oil could be upgraded to gasoline and diesel for $2–$3 per gallon (about $0.53–$0.79 per liter) gasoline equivalent has spurred interest in fast pyrolysis and bio-oil upgrading.

Hydroprocessing bio-oil into hydrocarbons suitable as transportation fuel is similar to the process for refining petroleum. Hydroprocessing was originally developed to convert petroleum into motor fuels by reacting it with hydrogen at high pressures in the presence of catalysts. Hydroprocessing includes two distinct processes. Hydrotreating is designed to remove sulfur, nitrogen, oxygen, and other contaminants from petroleum. When adapted to bio-oil, the main contaminant to be removed is oxygen. Thus, hydrotreating bio-oil from pyrolysis of lignocellulosic biomass is primarily a process of deoxygenation. Hydrocracking is the reaction of hydrogen with organic compounds to break long-chain molecules into lower molecular weight compounds. Although fast pyrolysis attempts to depolymerize plant molecules, a number of oligomers especially from lignin are found in bio-oil, which hydrocracking can convert into more desirable paraffin or naphthene molecules. Some researchers have employed catalysts in pyrolysis reactors to directly produce hydrocarbons. Similar to the process of fluidized catalytic cracking used in the petroleum industry, the process occurs at atmospheric pressure over acidic zeolites. Yields of C_5–C_{10} hydrocarbons as high as 17% have been reported for catalytic pyrolysis of poplar wood [33]. Although superior to conventional bio-oil, this product still needs refining to gasoline and diesel fuel.

1.2.4 Solvent liquefaction

Solvent liquefaction is the thermal decomposition of biomass in the presence of a solvent at moderate temperatures and pressures, typically 105-400 °C and 2-20 MPa, to produce predominately liquid or solubilized products with smaller amounts of gaseous and solid co-products. Like pyrolysis, solvent liquefaction can produce sugars from carbohydrate

and phenolic compounds from lignin. A wide range of solvents can be employed including non-polar solvents, such as toluene and tetralin, polar aprotic solvents such as gamma-valerolactone and tetrahydrofuran, and protic solvents, such as water and ethanol, and ionic liquids, such as 1-ethyl-3-methylimidazolium chloride.

Solvent liquefaction in water, referred to as hydrothermal processing, is particularly attractive for wet feedstock, which can be handled as slurries with solids loadings in the range of 5–20 wt%. Hydrothermal processing occurs at elevated pressures of 50–250 atm (~5–25 MPa) to prevent boiling of the water in the slurry and at temperatures ranging from 200 to 500°C, depending upon whether the desired products are fractionated and hydrolyzed plant polymers [34], partially deoxygenated liquid product known as biocrude [35], or syngas [36]. As illustrated in Figure 1.4, processing pressure must be increased as reaction temperature increases to prevent boiling of water in the wet biomass. At temperatures around 100°C, extraction of high-value plant chemicals such as resins, fats, phenolics, and phytosterols is possible. At 200°C and 20 atm (~2 MPa), fibrous biomass undergoes a fractionation process to yield cellulose, lignin, and hemicelluloses degradation products such as furfural. Further hydrothermal processing can hydrolyze the cellulose to glucose. At 300–350°C and 120–180 atm (~12.2–18.2 MPa), biomass undergoes more extensive chemical reactions, yielding a hydrocarbon-rich liquid known as biocrude. Although superficially resembling bio-oil, it has lower oxygen content and is less miscible in water, making it more amenable to hydrotreating. At 600–650°C and 300 atm (30.4 MPa) the primary reaction product is gas, including a significant fraction of methane.
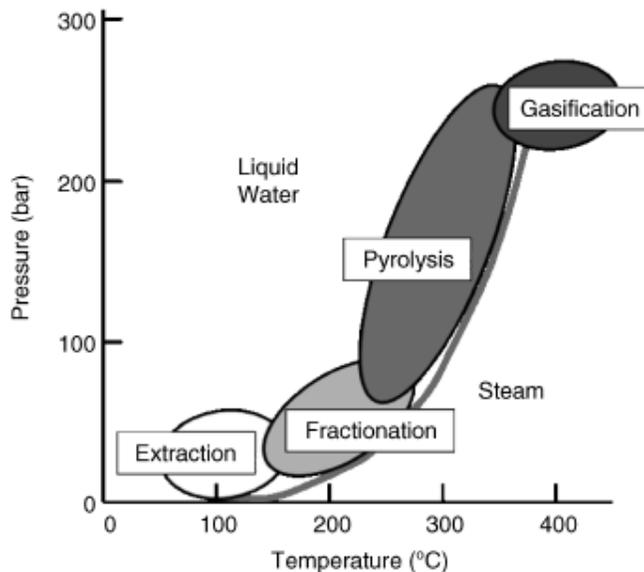

Figure 1.4 *Temperature/pressure regimes of hydrothermal processing.*

Continuous feeding of biomass slurries into high-pressure reactors, efficient energy integration, and product separation from solvent are significant engineering challenges to be overcome before solvent liquefaction results in a commercially viable technology.

1.3 Diversity of products: Electric Power, Transportation Fuels, and Commodity Chemicals

Theoretically, biomass is a resource that can be used to produce all types of products: heat, electricity, transportation fuels and commodity chemicals. Currently, heat is the major product of biomass utilization, with roughly 60% of worldwide bioenergy comprising traditional applications for cooking and heating in developing countries [37]. With regard to electricity production from biomass, dedicated biomass power plants or biomass co-firing plants are feasible means of reducing CO_2 emissions and producing green energy. Much of the recent research focus worldwide on bioenergy has been liquid transportation fuels in an effort to displace imported petroleum.

1.3.1 Biopower

Biopower can help reduce the use of coal, which is expected to decline from 40% of world net electricity generation in 2015 to only 31% by 2040 [38]. Several examples can be cited. Drax, one of the largest coal-fired power plant in the UK, started co-firing biomass in 2003, eventually achieving 100% replacement of coal. Atikokan Generating Station in Canada achieved 100% conversion to biomass in 2014. DONG Energy in Denmark announced in February 2017 that their thermal power plants (all of which employ cogeneration) would completely replace coal with biomass by 2023 [39].

Plug-in electric vehicles utilizing bio-power provides a promising option as well-to-wheels analyses indicate that battery electric vehicles (BEVs) are superior to biofuels-powered internal combustion engine vehicles in terms of primary energy consumed, greenhouse gas emissions, life-cycle water usage, and cost when evaluated on the basis of kilometers driven [40].

Combined-cycle power based on gasification of biomass is another route to biopower. Although gasification can efficiently convert a wide range of feedstocks into a flammable mixture of carbon monoxide and hydrogen, it also contains contaminants including tar, solid particulates, alkali compounds, sulfur, nitrogen and chlorine that must be removed before the gas can be burned for power generation to avoid in-plant corrosion and air pollution emissions. Currently, syngas clean-up is the key barrier for the reliable and cost-efficient operation of power plants based on biomass gasification [20].

1.3.2 Biofuels

Biofuels are defined as transportation fuels derived from biomass. Second generation biofuels are illustrated in Figure 1.5 [20]. These are predominantly liquids at ambient conditions to be compatible with the existing transportation fuels infrastructure, but also includes methane and hydrogen, gases at ambient conditions but which can be compressed or liquefied for use as transportation fuels. The liquid fuels can generally be categorized as alcohols, drop-in biofuels, and fuel additives.
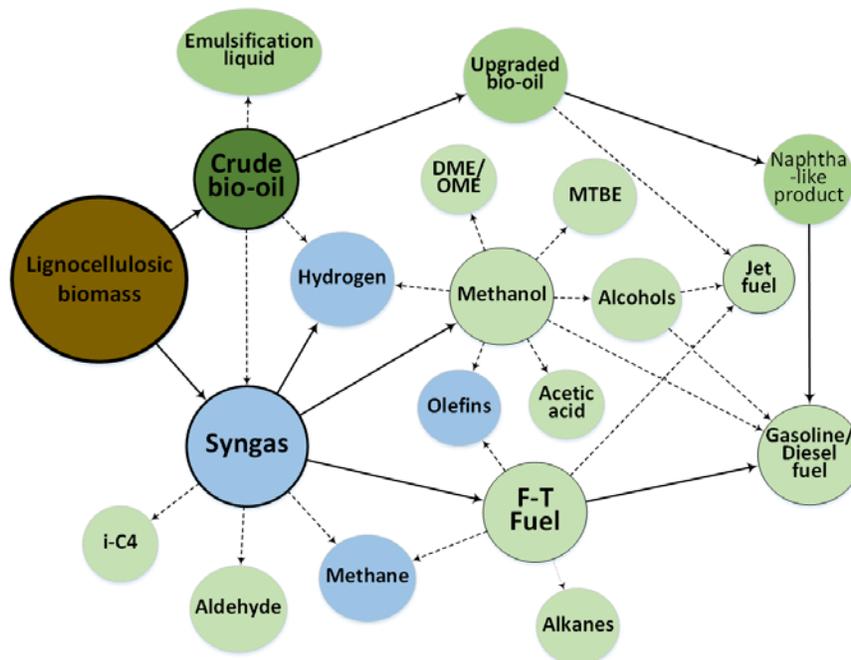
Figure 1.5 *Second-generation biofuels. (F-T: Fischer-Tropsch; i-C4: isobutene and isobutane; DME: dimethyl ether; OME: oxymethylene ethers; MTBE: Methyl tert-butyl ether; HRJs: hydro-processed renewable jet fuels)* [20].

Methanol, a C_1 alcohol, is traditionally synthesized from syngas (CO and H_2) derived from biomass gasification. Due to undesirable properties such as toxicity, water solubility, low vapor pressure, and phase separation, methanol has received less attention than ethanol as a substitute for gasoline. Ethanol has been widely integrated in transportation fuel infrastructures of Brazil, Europe, and the Unites States although it is currently derived from biochemical processing of sugars and starches from sugar cane and grains [41]. Ethanol is typically blended with gasoline is ratios of 10% (E10), 15% (E15), and 25% (E25). Flexible-fuel vehicles are able to use up to 100% ethanol fuel (E100).

Drop-in biofuels are fully compatible with existing fuel utilization systems. Thus, they are liquids containing very little oxygen and are completely miscible in petroleum-derived gasoline and diesel fuel. Drop-in biofuels that are pure hydrocarbons are usually referred to as renewable or green gasoline and diesel. An example of a low-oxygen content drop-in biofuel is butanol. Drop-in biofuels would address concerns about first-generation biofuels damaging fuel systems and causing phase separation of water in gasoline pipelines.

Biomass can also be processed into fuel additives to improve engine performance. Examples include methanol, ethanol, butanol, dimethyl ether (DME), and oxymethylene ethers (OME). Blended with diesel fuel, these oxygenated compounds help reduce soot and NOx emissions [42]. Blended with gasoline, they serve as octane boosters.

Hydrogen has been of interest as a carbon-free energy carrier for several decades. Although it is currently produced mostly from fossil fuels, it could also be produced from biomass gasification. The resulting syngas could be converted into a mixture of carbon dioxide and hydrogen by the water-gas shift reaction (CO + $H_2O \rightarrow CO_2 + H_2$) and the carbon dioxide removed to yield a pure stream of

hydrogen. An alternative route for hydrogen production from biomass is pyrolysis followed by catalytic steam reforming of the bio-oil. The overall yield of hydrogen from biomass via bio-oil reforming is lower than direct gasification of biomass feedstock although it lends itself to distributed processing of biomass.

1.3.2 Biobased Chemicals

Although biofuels represent much larger volume products from biomass, commodity chemicals from biomass (biobased chemicals) potentially represent much larger revenue from biomass. The production of a wide range of chemicals from biomass has been demonstrated [20]. For example, olefins, which can be produced from syngas, are platform molecules to produce plastics and detergents; the water-insoluble fraction of bio-oil, referred to as pyrolytic lignin, can be converted into resin; the biomass-derived carboxylic acids can be used to produce calcium salts as road de-icers, even the conversion has not been commercialized, however, it has the potential to be scaled up [20]. Additionally, bio-methanol is a widely used platform material to produce biobased chemicals such as acetic acid and formaldehyde [43].

Despite the high value of many biobased chemicals compared to biofuels, they must be produced in high yields and efficiently separated at high purity. The growing interest in replacing fossil fuels with renewable resources should encourage the further research and development needed move society toward a bioeconomy [44].

1.4 Economic consideration

Among the thermochemical technologies, combustion is the most widely deployed in commercial practice. Gasification was commercially deployed for heating and lighting over two hundred years ago, but mostly using coal rather than biomass as feedstock. Development of more convenient and cleaner petroleum and natural gas resources has mostly displaced gasification with a few exceptions around the world. Gasification has gained renewed interest as a way to efficiently utilize solid biomass resources. However, most schemes to convert syngas into fuel and power require gasifiers to operate at elevated pressures and produce syngas with very low contaminant levels, both of which contribute to high capital costs [43]. Solvent liquefaction has found few commercial applications, in part due to the capital costs associated with high pressure reactors but also relatively high operating costs associated with the use of large amounts of solvent and recovering products from the solvent. Fast pyrolysis is a relatively simple process that can be operated at small scale, lending itself to distributed processing of biomass and reducing investment risk compared to more capital intensive investments of gasification or biochemical processing of cellulosic biomass. Nevertheless, it has not achieved cost parity with petroleum-derived fuels.

The commercialization of second-generation biofuels are widely limited by their high cost of production, which can be as much as 2–3 times higher than for fossil fuels [20]. As might be expected for recalcitrant feedstock, processing costs are much higher for lignocellulosic biomass than sugars and starches. Feedstocks also show considerable variability across species and production regions including the relative amounts of carbohydrate and lignin, differences in composition of lignin, and variations in ash

composition and amount. All of these factors influence the ability to process the biomass with attendant influences on capital and operating costs.

1.5 Environmental consideration

Biofuels produced from sustainably grown biomass has several environmental benefits compared to petroleum-derived gasoline and diesel [45]. Among the most important of these is net reductions in life cycle greenhouse gas emissions, which arises from the fact that the carbon in biofuels is taken up from the atmosphere through photosynthesis of growing biomass. GHG emission and the relevant net energy assessment are the main focus of life-cycle-analysis (LCA) studies. Typical GHG emissions for several pathways are shown in Figure 1.6 [20]. First-generation biofuels reduce GHG emissions on the order of 40-80% compared to petroleum-derived fuels while second-generation biofuels can even achieve negative GHG emissions [20]. Biofuels have a larger variation in GHG emissions compared to conventional fuels, mainly due to the different maturity levels of these technologies and the several potential routes for producing biofuels.
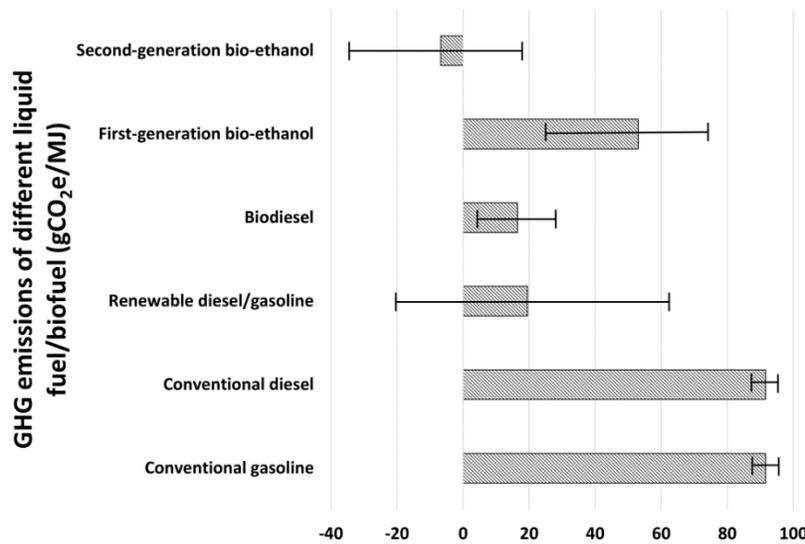

Figure 1.6 GHG emissions (gCO2e/MJ) asssociated with production of several kinds of biofuels and compring with conventional diesel and gasoline [20].

The use of fossil fuels in the production of biomass (application of fertilizer and use of farm machinery) and the processing of biomass (natural gas burned for process heat to support drying and distillation operations) contributes to net GHG emissions associated with the use of biofuels. Furthermore, conversion of farmland from food production to biofuels production can indirectly encourage the conversion of forests and grasslands in other parts of the world to cropland, which often is associated with release of GHG to the atmosphere due to burning of standing biomass or oxidizing soil carbon during tillage of the land [47]. The extent of this so-called "indirect land use change" to the net emissions of GHG from biofuels production is unclear and much debated [48, 49]. Similarly, the effect of biofuels production on water resources, biodiversity, and socioeconomic impacts such as income and employment should also be considered in comparing impacts of biofuels to fossil fuels [46,].

1.6 Organization of Book

Thermochemical processing is distinguished by a large number of approaches to converting lignocellulosic biomass into fuels, chemicals and power. This book is a compilation of review articles on distinct approaches to thermochemically deconstructing biomass into intermediates and their upgrading into final products. Chapter 1 is an overview of these technologies. Chapter 2 reviews the science of thermal deconstruction of biomass, both from experimental and modelling perspectives. Chapter 3 is devoted to biomass combustion including fundamentals, combustor types, operational issues, and power options. Chapter 4 focuses on gasification, including fundamentals, gasifier types, and the state of the technology development and commercialization. Chapter 5 explains the issues associated with syngas cleaning and upgrading with detailed descriptions of the kinds of contaminants found in syngas, the unit operations associated with removal of each of these contaminants, and the synthesis of fuels and chemicals from syngas. Chapter 6 covers fast pyrolysis of biomass including current understanding of the chemistry of pyrolysis, different kinds of pyrolyzers, and the state of development and commercialization. Chapter 7 explores stabilization and upgrading of bio-oil by physical, chemical and catalytic means to transportation fuels. Chapter 8 discusses solvent liquefaction of carbohydrate and lignin to liquids and solubilized products. Chapter 9 describes hybrid processing of biomass, which is defined as the integration of a thermochemical process to deconstruct lignocellulosic biomass into an intermediate suitable as substrate for biochemical upgrading to finished products. Chapter 10 provides cost estimates for a wide range of thermochemical processes, ranging from electric power generation to the production of liquid biofuels and other chemicals. These analyses provide a useful starting point for exploring the feasibility of different approaches to thermochemical processing. Chapter 11 reviews the literature on life cycle analysis of thermochemical processes, including air and water impacts and GHG emissions.

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