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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. Although biochemical processing is often touted as a fundamentally new approach to converting plant materials into useful products and thermochemical processing is often described as "mature" technology with little scope for improvement, in fact both 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 is mature, as the application of biotechnology to improving biochemical processes for industrial purposes has revealed [1]. The petroleum and petrochemical industries have accomplished similar wonders in thermochemical processing of hydrocarbon feedstocks, although the more complicated chemistries of plant molecules have not been fully explored.

Ironically, the domination of thermochemical processing in commercial production of fuels, chemicals, and power from fossil resources for well over a century may explain why it is sometimes overlooked as a viable approach to biobased products. Smokestacks belching

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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 [2], thermal and catalytic sciences also offer opportunities for dramatic advances in biomass processing. 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 [3].

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 decade of the twenty-first century, with worldwide annual production reaching almost 19 billion gallons ($\sim 72 \times 10^9$ L) of ethanol and 4.4 billion gallons ($\sim 16.7 \times 10^9$ L) of biodiesel in 2008 [4]. This 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 advanced 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 cellulosic biomass.

Lipids are a large group of hydrophobic, fat-soluble compounds produced by plants and animals for high-density energy storage. Triglycerides, commonly known as vegetable oils, are among the most familiar form of lipids and have been widely used in recent years for the production of biodiesel. As illustrated in Figure 1.1, triglycerides consist of three long-chain fatty acids attached to a backbone of glycerol. It is relatively easy to hydrotreat triglycerides to yield liquid alkanes suitable as transportation fuels and propane gas. The hydrogenation of vegetable oils has already been proven technically feasible using conventional distillate

Table 1.1 *Comparison of biochemical and thermochemical processing. Adapted from NSF, 2008, Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Next Generation Hydrocarbon Biorefineries, Ed. George W. Huber, University of Massachusetts Amherst. Courtesy: National Science Foundation*

	Biochemical processing	Thermochemical processing
Products	Primarily alcohols	Range of fuels
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)

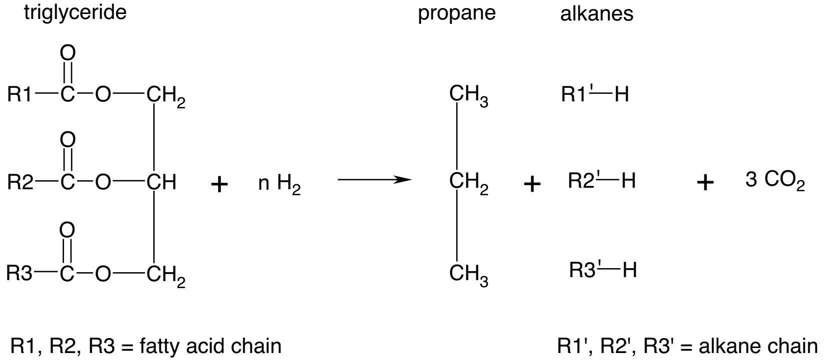

Figure 1.1 *Simplified representation of hydrogenation of triglyceride during hydrotreating*

hydrotreaters at petroleum refineries [6], although the high price of traditional vegetable oils has discouraged companies from producing transportation fuels in this manner. Commercial deployment will require alternatives to traditional seed crops, which only yield 50–130 gal/acre (467.5–1215.5 L/ha) [7]. Suggestions have included jatropha [8] (200–400 gal/acre (1870–3740 L/ha)) and palm oil [9] (up to 600 gal/acre (5610 L/ha)), but the most promising alternative is microalgae, which can be highly productive in natural ecosystems with oil yields as high as 2000 gal/acre (18 700 L/ha) in field trials and 15 000 gal/acre (140 250 L/ha) in laboratory trials [10]. This promise requires considerable engineering development to reduce capital costs, which are estimated to be $100 000 to $1 million per acre ($250 000 to $2.5 million per hectare), and production costs, which exceed $10–$50 per gallon (about $2.60–$13 per liter) [10, 11]. Thus, the challenge of lipid-based biofuels is producing large quantities of inexpensive lipids rather than upgrading them.

Cellulose, on the other hand, is the most abundant form of biomass on the planet. In the form of lignocellulose, a composite of cellulose, hemicellulose, and lignin [12], it dominates most natural ecosystems and is widely managed as sources of timber and animal forage. As illustrated in Figure 1.2, cellulose is a structural polysaccharide consisting of a long chain of glucose molecules linked by glycosidic bonds. Breaking these bonds releases the glucose

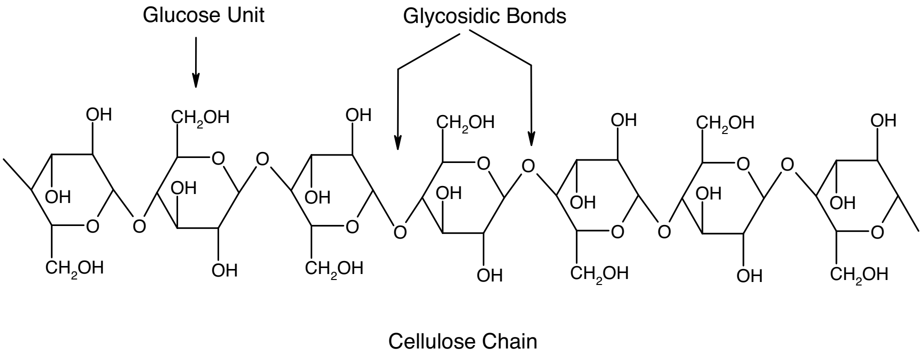

Figure 1.2 *Cellulose is a long chain of glucose units connected by glycosidic bonds*

and makes it available for either food or fuel production. A variety of microorganisms secrete enzymes that hydrolyze the glycosidic bonds of cellulose (and hemicellulose). Many animals, like cattle and other ruminants, have developed symbiotic relationships with these microorganisms to allow them to digest cellulose.

However, cellulose is usually found in nature as lignocellulose, a composite of cellulose fibers in a matrix of hemicellulose and lignin. The lignin, which few microorganisms are able to digest, 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 [13]. 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.

Thermochemical processing occurs at temperatures that are at least several hundred degrees Celsius and sometimes over 1000°C above ambient conditions. At these temperatures, thermochemical processes occur very rapidly whether catalysts are present or not. Although thermochemical processing might be characterized as voracious in the pace of reaction and the variety of materials it can consume (not only carbohydrate, but lignin, lipids, proteins, and other plant compounds), its selectivity is not necessarily as indiscriminate as is sometimes attributed to it. Thermal depolymerization of cellulose in the absence of alkali or alkaline earth metals produces predominately levoglucosan, an anhydrosugar of the monosaccharide glucose [14]. Under certain conditions, it appears that lignin depolymerizes to monomeric phenolic compounds [15]. 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.

As shown in Figure 1.3, thermochemical routes can be categorized as combustion, gasification, fast pyrolysis, hydrothermal processing, and hydrolysis to sugars. Direct combustion of biomass produces moderate- to high-temperature thermal energy (800–1600°C) suitable for electric power generation. Gasification generates both moderate-temperature thermal energy (700–1000°C) and a flammable gas mixture known commonly as producer gas or syngas, which can be used to generate either electric power or to synthesize fuels or other chemicals using catalysts or even microorganisms (syngas fermentation) [16]. Fast pyrolysis occurs at moderate temperatures (450–550°C) in the absence of oxygen to produce mostly condensable vapors and aerosols that are recovered as an energy-rich liquid known as bio-oil. Fast pyrolysis also produces smaller amounts of flammable gas (syngas) and solid charcoal, known as char or sometimes biochar [17]. Bio-oil can be burned for electric power generation or processed into hydrogen via steam reforming or into liquid hydrocarbons via hydroprocessing. Whereas fast pyrolysis requires relatively dry feedstocks (around 10 wt% moisture), hydrothermal processing is ideal for wet feedstocks that can be handled as slurries with solids loadings in the range of 5–20 wt%. Hydrothermal processing occurs at pressures of 50–250 atm ($\sim$5–25 MPa) to prevent

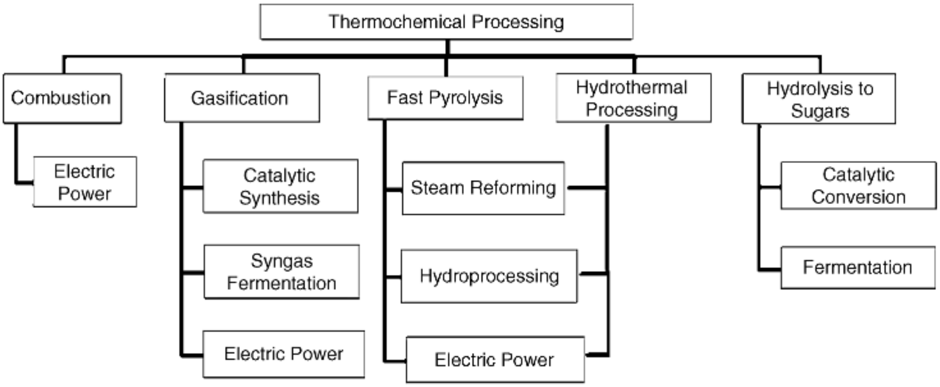

Figure 1.3 *Thermochemical options for production of fuels, chemicals, and power*

boiling of the water in the slurry and at temperatures ranging from 200 to 500°C, depending upon whether the desired products are fractionated plant polymers [18], a partially deoxygenated liquid product known as biocrude [19], or syngas [20]. Finally, hydrolysis of plant polysaccharides yields simple sugars that can be catalytically or biocatalytically converted into fuels. Concentrated acid or the combined action of dilute acid and heat are well known to hydrolyze polysaccharides to monosaccharides. The biotechnology revolution has encouraged the use of enzymes to more efficiently hydrolyze sugars from biomass, but the high cost of enzymes has slowed commercial introduction of so-called cellulosic biofuels by this biochemical route [21]. Although acid hydrolysis qualifies as thermochemical processing, more direct thermal interventions can also yield sugars from biomass. Hydrothermal processing at modest temperatures fractionates biomass into cellulose fibers, hemicellulose dehydration products, and lignin [18]. Further hydrothermal processing of the cellulose can produce glucose solutions. Fast pyrolysis also yields significant quantities of sugars and anhydrosugars under suitable processing conditions [22]. These "thermolytic sugars" can either be fermented or catalytically upgraded to fuel molecules.

1.2 Direct Combustion

Much of the focus on bioenergy in the USA has been production of liquid transportation fuels in an effort to displace imported petroleum. Recently, 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 (BEVs) [23]. Well-to-wheels analyses indicate that BEVs are superior to biofuels-powered internal combustion engine vehicles in terms of primary energy consumed, greenhouse gas emissions, lifecycle water usage, and cost when evaluated on the basis of kilometers driven [24].

Combustion is the rapid reaction of fuel and oxygen to obtain thermal energy and flue gas, consisting primarily of carbon dioxide and water. Depending on the heating value and moisture content of the fuel, the amount of air used to burn the fuel, and the construction of the furnace, flame temperatures can exceed 1650°C. Direct combustion has the advantage that it employs commercially well-developed technology. It is the foundation of much of the electric power generation around the world. In principle, existing power plants could be quickly and inexpensively retrofitted to burn biomass, compared with greenfield construction of advanced biorefineries, which would be based upon largely unproven technologies. Plug-in hybrid electric vehicles will soon be widely available to utilize this biopower. In the long term, high efficiency combined-cycle power plants based on gasified or pyrolyzed biomass will provide power for long-range electric vehicles based on advanced battery technology [25].

However, combustion 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. Chapter 2 is devoted to a description of biomass combustion as a thermochemical technology.

1.3 Gasification

Thermal gasification is the conversion of carbonaceous solids at elevated temperatures and under oxygen-starved conditions into syngas, a flammable gas mixture of carbon monoxide, hydrogen, methane, nitrogen, carbon dioxide, and smaller quantities of hydrocarbons [26]. 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 [27]. 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.

As illustrated in Figure 1.4, 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. The 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

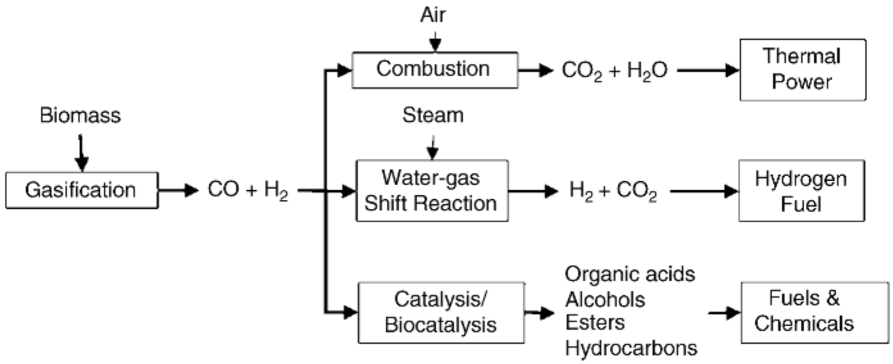

Figure 1.4 *Gasification offers several options for processing biomass into power, chemicals, and fuels*

the gasifier. Gas turbines offer prospects for high-efficiency integrated gasification–combined-cycle power, but they require more stringent gas cleaning [28]. 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.

Chapter 3 describes gasification technologies, Chapter 4 covers gas stream clean-up and catalytic upgrading to fuels and chemicals, and Chapter 9, which covers hybrid thermochemical–biochemical processing, includes a description of syngas fermentation [16].

1.4 Fast Pyrolysis

Fast pyrolysis is the rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, gases, and char [17]. The distribution of products depends on the biomass composition and rate and duration of heating. Liquid yields as high as 72% are possible for relatively short residence times (0.5–2 s), moderate temperatures (400–600°C), and rapid quenching at the end of the process. The resulting bio-oil is a complex mixture of oxygenated organic compounds, including carboxylic acids, alcohols, aldehydes, esters, saccharides, phenolic compounds, and lignin oligomers. It has been used as fuel for both boilers and gas turbine engines, although its cost, corrosiveness, and instability during storage have impeded its commercial deployment.

Its great virtues are the simplicity of generating bio-oil and the attractiveness of a liquid feedstock compared with either gasified or unprocessed biomass. Bio-oil can be upgraded to transportation fuels through a combination of steam reforming [29] of light oxygenates in the bio-oil to provide hydrogen and hydrocracking lignin oligomers and carbohydrate to synthetic diesel fuel or gasoline [30, 31]. Recent technoeconomic analysis [32] indicating that bio-oil could be upgraded to synthetic 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 is primarily a process of deoxygenation, although nitrogen can be significant in some bio-oils. 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 carbohydrate and lignin oligomers are found in bio-oil, which hydrocracking can convert into more desirable paraffin or naphthene molecules. Some researchers are attempting to add catalysis to the pyrolysis reactor to yield hydrocarbons directly. Similar to the process of fluidized catalytic cracking used in the petroleum industry, the process occurs at atmospheric pressure over acidic zeolites. A yield of 17% of C_5–C_{10} hydrocarbons has been reported in a study of upgrading of pyrolytic liquids from poplar wood [33]. Although superior to conventional bio-oil, this product still needs refining to gasoline or diesel fuel. Fast pyrolysis of biomass to bio-oil is described in Chapter 5. Upgrading of bio-oil to transportation fuels is discussed in Chapter 6.

1.5 Hydrothermal Processing

Hydrothermal processing describes the thermal treatment of wet biomass at elevated pressures to produce carbohydrate, liquid hydrocarbons, or gaseous products depending upon the reaction conditions. As illustrated in Figure 1.5, processing temperature must be

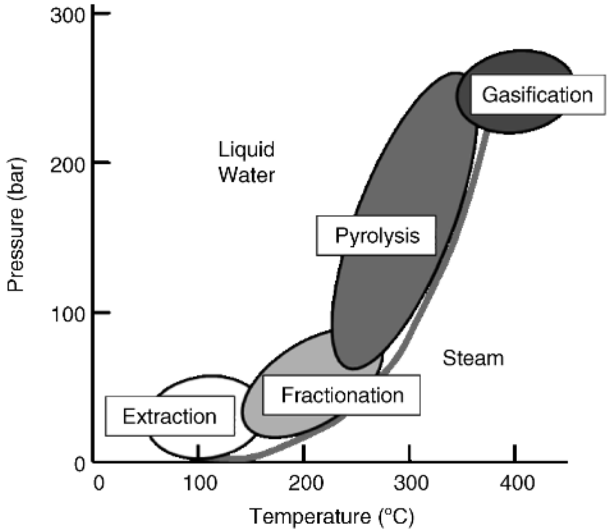

Figure 1.5 Temperature/pressure regimes of hydrothermal processing

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.

Continuous feeding of biomass slurries into high-pressure reactors and efficient energy integration represent engineering challenges that must be overcome before hydrothermal processing results in a commercially viable technology. Chapter 7 is devoted to hydrothermal processing of biomass.

1.6 Hydrolysis to Sugars

Although biochemical processing is sometimes referred to as the "sugar platform," it is possible to thermally depolymerize biomass into monosaccharides and catalytically synthesize fuel molecules from these carbohydrate building blocks. Thus, the so-called sugar platform can be a pure play in biochemical processing (enzymatic hydrolysis of plant carbohydrates to sugar followed by fermentation), a hybrid thermochemical–biochemical process (thermally or chemically induced hydrolysis followed by fermentation of the released sugar), a hybrid biochemical–thermochemical process (enzymatic hydrolysis followed by catalytic synthesis of the sugar to hydrocarbons), or a pure play in thermochemical processing (thermal depolymerization followed by catalytic upgrading of the sugar to fuel molecules).

As described in Chapter 9, fast pyrolysis can produce both anhydrosugars and fermentable sugar from biomass, the yield of which is significantly enhanced if the biomass is washed or otherwise treated to eliminate the catalytic activity of naturally occurring alkali and alkaline earth metals [22]. Limited technoeconomic analysis of the process suggests that fermentation of sugar extracted from bio-oil could yield ethanol at costs competitive with cellulosic ethanol derived from either acid or enzymatic hydrolysis [34]. Similarly, hydrothermal processing under mild conditions can produce aqueous solutions of fermentable sugar [18].

These sugars can also be catalytically converted to fuels. Sugars that exist as five-member rings, like the five-carbon sugar xylose or the six-carbon sugar fructose, are readily dehydrated to the five-member rings of furan compounds [35], some examples of which are illustrated in Figure 1.6. Furans are colorless, water-insoluble flammable liquids with volatility comparable to hydrocarbons of similar molecular weight. Some kinds of furans have heating values and octane numbers comparable to gasoline, making them potential transportation fuel [36]. Catalysts can improve yields by making furan-producing pathways more selective among the large number of competing reactions that can occur during pyrolysis of biomass. 2,5-Dimethyl furan in particular has received recent interest because new catalytic synthesis routes from sugars have been developed [37, 38]. Neither the fuel

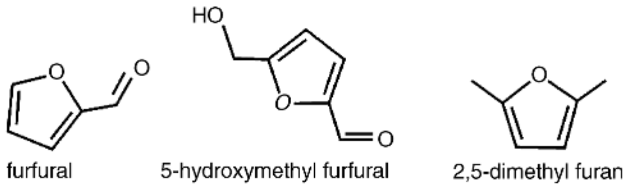

Figure 1.6 *Furans relevant to the production of transportation fuels by thermochemical processing of sugars. Source: Ref. [36]*

properties nor the toxicity of these compounds have been much studied, raising questions as to their ultimate practicality as transportation fuel.

A more promising approach known as aqueous-phase processing reacts monomeric sugar or sugar-derived compounds in the presence of heterogeneous catalysts at 200–260°C and 10–50 bar (1–5 MPa) to produce alkanes, the same hydrocarbons found in gasoline [39, 40]. Catalytic conversion of sugars would have several advantages over fermentation, including higher throughputs, ready conversion of a wide range of sugars, and the immiscible hydrocarbon products could be recovered without the expensive distillations required in ethanol plants. Chapter 8 explores the possibilities of catalytically converting sugars to fuel molecules.

1.7 Technoeconomic Analysis

Of the several technologies explored in this book, only a few are in commercial operation. Although a number of thermochemical technologies have been demonstrated with biomass feedstocks, very limited information on economic performance based on actual construction or operating costs is available in the literature. In the absence of such information, technoeconomic analyses are useful in estimating capital and operating costs for commercial-scale facilities, despite the well-known limitations of such analysis. Although by no means comprehensive, Chapter 10 provides cost estimates for a wide range of thermochemical processes, ranging from electric power generation to the production of biopolymers and hydrogen via syngas fermentation. Although differences in basis years, feedstock costs, financing options, and granularity of the analyses make it difficult to make comparisons among the various technology options, these analyses provide a useful starting point for exploring the feasibility of different approaches to thermochemical processing.

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