

1

An Overview of Biorefinery Technology

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1.1 Introduction

Fossil fuel resources are being depleted and, whether we have 50, 100 or 200 years' worth of petroleum reserves, irrefutably, at some point in time, there will be no more oil to extract in an economical fashion. The world is gradually adapting to this new paradigm, and the price of petroleum-based energy systems is steadily increasing. The developed and developing nations alike are seeing a transition to renewable-based energy forms, with solar panels installed on buildings and wind turbines part of the landscape. Liquid fuels that are produced from renewable feedstocks, in the form of ethanol or biodiesel, are now commercially available. Fuels containing 10–85% w/w ethanol are available to power internal combustion engines throughout the US. Most of the commercially available ethanol, produced from corn in the US and from sugar cane in Brazil, is often referred to as first-generation biofuel. In 2011, nearly 14 billion gallons of ethanol were sold in the US. A thorough discussion of corn, other grains, and sugarcane-to-ethanol processes are described in the chapters prepared by Rausch, Dunford and Prado, and Meireles, respectively. Thus, this chapter will concentrate on second-generation biofuels.

Second-generation biofuels are characterized as fuels that are produced from non-food biomass systems, such as forestry and agricultural residue, and dedicated herbaceous and

wood energy crops. Some of the second-generation fuels are in the mid to late stages of becoming commercially available. As examples, pilot- and demonstration-scale production facilities are now operational at POET, LLC in South Dakota and Iowa, and DuPont in Tennessee. The conversion technologies for these second-generation fuels use non-food crops, or lignocellulosic feedstocks, and are centred around:

1. the hydrolysis of plant cell wall polysaccharides into their single sugar components, followed by fermentation of the resulting sugars to fuels like ethanol or butanol;
2. the gasification of the plant material to produce syngas (synthesis gas), followed by the conversion of CO, CO₂ and H₂ to ethanol or other alcohols by fermentation or catalyst-based processes; or
3. the conversion of organic compounds in biomass through fast-pyrolysis to a dark-brown liquid, called pyrolysis oil, which can be upgraded for transportation fuels.

Depending on the conversion technology, 10–25 million tons of dry cellulosic biomass will be required to produce 1 billion gallons of liquid fuel. Partially replacing our consumption of gasoline with renewable fuels will require huge quantities of feedstock that will be obtained from both cultivated and collected biomass resources. Regardless of which conversion platform is selected, colossal masses of feedstock will pass through the door of a conversion facility. As an example, a 50 million gallon second-generation cellulosic facility will require about 2000 dry tons per day of biomass for processing. To complicate matters, it is very likely that the composition and quality of the feedstock stream will vary throughout the year. An annual biorefinery feedstock cycle could consist of agricultural residues in the fall, woody residues or crops in the winter, cover crops, like rye, in the spring, and energy crops, like sorghum or switchgrass, in the summer. Some of these bioenergy-destined feedstocks will contain valuable compounds that can be extracted prior to or after the conversion process. These compounds or products are often referred to in the literature as value-added biorefinery co-products.

In order to appreciate the array of possible biorefinery-related co-products presented throughout this book, this chapter will provide an overview of various feedstocks, as well as the steps involved in biochemical and thermochemical conversion processes. This chapter will also provide insight as to where co-product generation can be integrated in the biofuel manufacturing process.

1.2 Feedstock

If the US is to produce, as a target, more than 21 billion gallons per year of second-generation biofuels, more than 250 million dry tons per year of biomass will be required. Biomass will be available annually in the form of forest residues, mill residues, dedicated woody and herbaceous energy crops, urban wood waste, and agricultural residues (Bain *et al.*, 2003; Perlack *et al.*, 2005). It is important to note that most dedicated energy crops need time to be established. As an example, perennial warm season crops will take two to five years to establish (Propheter *et al.*, 2010). Herbaceous energy crops include, amongst others, switchgrass (*Panicum virgatum*), sorghum (*Sorghum bicolor*), and miscanthus (*Miscanthus* spp). Woody energy crops include, amongst others, maple (*Acer saccharinum*), sweetgum (*Liquidambar styraciflua*), sycamore (*Platanus occidentalis*), and hybrid poplar (*Populus* spp.).

Switchgrass is a warm season perennial, metabolizes CO₂ via the C4 cycle and remains an important component of tallgrass prairie that has a wide distribution from southern Canada to northern Mexico. There are two main switchgrass ecotypes. The lowland ecotype grows better in the wetter southern habitats, whereas the upland ecotype develops in drier mid and northern latitudes. Kanlow and Alamo are prevalent lowland ecotype cultivars, while Cave-in-Rock is a common upland switchgrass ecotype cultivar. Switchgrass yields of $8.7 \pm 4.2 \text{ Mg ha}^{-1}$ and $12.9 \pm 5.9 \text{ Mg ha}^{-1}$, respectively, for upland and lowland ecotypes were reported (Wullschleger *et al.*, 2010). Propheter *et al.* (2010) reported the yield of the Kansas-grown Kanlow of 9.2 Mg ha^{-1} . Wullschleger *et al.* (2010) reported that, of the agronomic parameters, ecotype, temperature, water supply, and nitrogen fertilization affected the switchgrass yields.

Miscanthus is a perennial rhizomatous grass that also metabolizes CO₂ via the C4 cycle. Heaton, Dohleman, and Long (2008) established miscanthus seedlings in 2002, and monitored the yields for three years, 2004, 2005, and 2006, at three Illinois locations, north, central, and southern. Their reported overall three-year state average was 38.2 Mg ha^{-1} . The maximum miscanthus yields in the trials located in Sweden, Denmark, England, Germany, and Portugal were 10.7, 7.9, 12.1, 17.0 and 26.9 Mg ha^{-1} , respectively, where it was observed that the trials in northern latitudes tended to mature slower than those located in more southern locations (Clifton-Brown *et al.*, 2001). In the Illinois trials, yields were independent of rainfall, nitrogen fertilization, and growing degree days (Heaton, Dohleman, and Long, 2008), whereas irrigation was a key in obtaining the maximum yields in Portugal (Clifton-Brown *et al.*, 2001). Further European trials showed that the peak yields in Austria, Belgium, France, Germany, Ireland, The Netherlands, Portugal, Spain, and England were 23, 25, 21, 25, 18, 25, 15, 18 and 23 Mg ha^{-1} , respectively (Clifton-Brown, Stampfl, and Jones, 2004). Similar to switchgrass, miscanthus translocates its nutrients to roots and rhizomes at the end of the growing season. The clone selected for the trials in Illinois survived at -30°C in the winters, while the clone used in the 2001 European study did not survive Danish and Swedish winters, indicating that clonal selection is critical to overcome the harsh winter. It is important to note that although miscanthus is an attractive energy crop because of its high biomass yields, there are some concerns with respect to its invasive potential (Raghu *et al.*, 2006).

Sorghum (*Sorghum bicolor* L. Moench) is a drought-tolerant crop that has wide distribution in the world; in the US, sorghum is cultivated in the Midwest where rainfall is often scarce (Ananda, Vadlania, and Prasad, 2011). There are different *S. bicolor* cultivars which are commonly referred to as grain, sweet or forage sorghum; what sets these cultivars apart is the flowering period, which is highly dependent on the photoperiod. As an example, the photoperiod-sensitive forage sorghum, capable of producing high lignocellulosic yields without the production of grain, will not flower until the day length becomes shorter than 12 h and 20 minutes, and this, in the Midwest, occurs when seasonal frosts takes place, impeding the reproductive flowering stage (Propheter *et al.*, 2010). Sweet sorghum is desirable because readily fermentable carbohydrates can be extracted from its stalks and processed into biofuels following the sugarcane-processing methods. Sugar yields from sweet sorghum of 4.1 and 4.8 Mg ha^{-1} were obtained in Nebraska and Kansas, respectively (Wortmann *et al.*, 2010; Propheter *et al.*, 2010). Grains obtained from grain sorghum can be processed into biofuels following the same starch-based methods used for corn or wheat. Wortmann *et al.* (2010) reported a maximum grain yield of 6.62 Mg ha^{-1} . Propheter *et al.* (2010) reported on sorghum grown side by side in two Kansas locations for two years using photoperiod-sensitive, sweet,

dual-purpose forage and brown midrib. The yields were 26.8, 32.6, 20.7 and 14.8 Mg ha⁻¹, respectively, indicating that, in this study, sweet sorghum showed the highest potential.

With respect to woody energy crops, hybrid poplars, *Populus deltoides*, are hardwoods that often grow in the forest areas that are logged for softwood, and can be cultivated with a short term horizon, 3 to 6 years, or for a longer term period for 15 to 20 years. Plantation densities can average 18 000 stems ha⁻¹ and yield, within a six-year time frame, 16.9 Mg ha⁻¹year⁻¹ (Fortier *et al.*, 2010). In Sweden, the productivity of poplar stands could be in the range of 70 Mg ha⁻¹ after a 10- to 15-year time frame (Johansson and Karačić, 2011). After seven years of growth, yields of 17.5 and 41.6 Mg ha⁻¹ were reported for sweetgum (*Liquidambar styraciflua*) and sycamore (*Platanus occidentalis*), respectively (Davis and Trettin, 2006).

1.3 Thermochemical Conversion of Biomass

In the thermochemical conversion processes elevated temperature and pressure are utilized to break the chemical bonds in the biomass matrix to either release its energy content directly, as in combustion, or to be chemically converted to fuel precursors, as in pyrolysis, gasification and liquefaction. These outputs are usually considered fuel precursors (or crude) as they require further cleaning, reforming, and fractionation to generate stable drop-in fuels. Generally speaking, fast pyrolysis or hydrothermal liquefaction are the terms used to describe processes that directly produce a liquid bio-crude, while gasification is used to describe processes that produce a synthesis gas consisting primarily of CO, CO₂, and H₂. The following sections will briefly review the principles, limitations, and state-of-the-art developments in these technologies.

1.3.1 Fast Pyrolysis and Hydrothermal Liquefaction

Pyrolysis can be understood as the thermal depolymerization of biomass in the absence of oxygen followed by rapid quenching to produce char, gas, and, more importantly, condensable oils. In fast pyrolysis, the temperature, around 500 °C, the heating rate, over 100 °C min⁻¹, and the residence time, 2–3 seconds, are instrumental in minimizing cracking of condensable vapours into permanent gases; hence the name “fast” or “flash” pyrolysis. The bio-oil, also known as bio-crude, is essentially a mixture of over 100 chemical species (Evans and Milne, 1987) with a wide range of molecular weights that are formed by primary and secondary reaction mechanisms. The oils are highly oxygenated, which is characteristic of the biomass feedstock, and also high in water content. Bridgwater, Meier, and Radlein (1999) present the typical elemental composition and properties of fast pyrolysis oils, which are also shown in Tables 1.1 and 1.2. As is noted, the liquid is relatively viscous, with a medium heating value.

Numerous reactor configurations have been investigated for biomass pyrolysis, with an emphasis on high heat transfer rates and short residence times for both solids and vapours. Examples of such reactors include bubbling fluidized bed and circulating fluidized bed, both of which have high heat transfer rates. Other reactors under investigation are ablative, vortex, rotating cone, and rotating blade reactors (Meier and Faix, 1999).

An important area of research associated with thermochemical conversion is catalysis. The use of suitable catalysts significantly increases the yields and also optimizes the composition

Table 1.1 Typical elemental composition of fast pyrolysis bio-oils (Bridgwater, Meier, and Radlein, 1999). Reprinted with permission from Bridgwater et al., 1999 © Elsevier (1999).

Element	Wt %
Carbon	44–47
Hydrogen	6–7
Oxygen	46–48
Nitrogen	0–0.2

of the output products. Catalysts can be incorporated during or after the production process, or in both stages. In pyrolysis, the use of catalysts can help overcome the problematic qualities of bio-oil, mainly thermal and temporal instability, through the hydrodeoxygenation process. This step essentially converts oxygenates in pyrolysis oil, aided by catalysts, into more stable species. Several studies have investigated the effects of catalyst addition to a pyrolysis reaction; mainly activated alumina, silicate, beta, Y-zeolite and ZSM-5 (Williams and Horne, 1995; Carlson *et al.*, 2009). ZSM-5, an acid–base zeolite, is a prime example of this class of catalysts which was reported to increase the yield of aromatic species in the bio-oil by up to 30% wt (Carlson *et al.*, 2009; Zhang *et al.*, 2009). Aromatic species such as naphthalene and benzene are more stable and industrially significant, with a higher calorific density than un-catalyzed bio-oil oxygenates, phenols and carboxylic acids. Another approach is the downstream treatment of bio-oils in an aqueous, high-pressure, catalyzed environment (Elliott, 2007). Catalysts used in such techniques include sulfide NiMo, sulfide CoMo, and, more recently, Ru/C catalyst (Wildschut *et al.*, 2009; Mercader *et al.*, 2011), which was reported to yield more bio-oils and higher deoxygenating levels.

According to reports, pilot-scale and full-scale pyrolysis facilities are gradually going into uninterrupted operation worldwide. Ensyn Technologies has constructed six circulating fluidized bed plants, with the largest having a nominal capacity of 50 tons/day (DOE, 2005).

Table 1.2 Typical properties of fast pyrolysis bio-oils (Bridgwater, Meier, and Radlein, 1999). Reprinted with permission from Bridgwater et al., 1999 © Elsevier (1999).

Property	Analysis
Moisture content	25%
pH	2.5
Specific gravity	1.20
Elemental Analysis (moisture free basis)	
Carbon	56.4%
Hydrogen	6.2%
Nitrogen	0.2%
Sulfur	<0.01%
Ash	0.1%
Oxygen (by difference)	37.1%
Higher heating value (moisture free basis)	22.5 MJ kg ⁻¹
Higher heating value (as produced)	17.0 MJ kg ⁻¹
Viscosity (at 40 °C)	30–200 cp
Pour point	–23 °C

In 2008, Ensyn and Honeywell's UOP LLC established a joint venture (Envergent Technologies, LLC) to commercialize pyrolysis conversion facilities (trademarked as rapid thermal processing; RTP™). DynaMotive Corporation (Vancouver, Canada) has established two fluidized-bed pyrolysis plants in Canada; first in West Lorne in 2002 at a capacity of 100 tons day⁻¹ and then in Guelph in 2007 with 200 tons day⁻¹ capacity. BTG (The Netherlands) developed the rotary cone reactor (RCR) system for biomass-to-liquid (BTL) conversion with an operational capacity of 50 kg h⁻¹, that was later scaled up to 250 kg h⁻¹ capacity in 2001 (Venderbosch and Prins, 2010). In Finland, a 2 MW integrated pyrolysis plant was built in collaboration with Metso, UPM, Fortum, and VTT. This plant went into operation in 2009–2010, with sawdust and forest residue as the feedstock, generating around 90 tons of bio-oil by the summer of 2010 (Lehto *et al.*, 2010).

Fast pyrolysis occurs at moderate thermal conversion temperatures, 500 °C or so, and produces a liquid product, pyrolysis oil or bio-oil, which may be used as a chemical intermediate, or directly used as a liquid fuel. The US DOE (2005) reported the reactor technologies, including bubbling fluid beds, circulating, and transported beds, cyclonic reactors, and ablative reactors that can achieve a 75% conversion of the biomass to liquid fuels.

Direct hydrothermal liquefaction also produces an oily liquid by bringing biomass into contact with liquid water at moderate thermal conversion temperatures such as 300 °C. The water is maintained in the liquid phase by elevating the pressure. In contrast to fast pyrolysis, residence times of up to 30 minutes are required. The oily liquid is once again available as a liquid fuel, but large quantities of water are also present. The technology is being developed for use on algae, as well as waste biomass. According to US DOE (2005) technology developers include Changing World Technologies (West Hempstead, NY), EnerTech Environmental Inc (Atlanta, GA), and Biofuel B.V. (Heemskerk, Netherlands).

1.3.2 Gasification

Historically, gasification was developed more than 100 years ago to generate gaseous fuel, town gas, from coal and peat. To compensate for petroleum shortages during World War II, gasification was implemented in Europe by converting woodchips to gas to operate vehicles and to generate electricity. Similarly, in the aftermath of the energy crisis in the seventies, interest was renewed in biomass gasification, particularly wood and forestry residue, as an alternative energy strategy. Since then, studies have investigated a wide range of biomass feedstock, including agricultural and crop residue, farm and livestock wastes, industrial and processing by products, municipal and landfill wastes, and, more recently, marine and aquatic biomass.

In principle, biomass gasification is simply the incomplete combustion of biomass, due to low oxygen, to produce CO, CO₂, and H₂ instead of CO₂ and water. In reality, the process is much more complex as it involves overlapping reactions and stages such as drying, pyrolysis, char gasification, and oxidation. This operation converts biomass chemical energy to energy-carrier gases, such as CO, H₂, CH₄, and other hydrocarbons that are known as syngas, while minimizing formation of tar, pollutant oxides, and polycyclic aromatic hydrocarbons.

This conversion typically occurs at elevated temperatures, varying from 500 to 1400 °C, and pressures ranging from atmospheric pressure to as much as 30 atm. Much like combustion, an oxidant is used: air, pure oxygen, steam or a mixture of these gases. Air-blown gasifiers are most common due to their simple design, and relatively low operating costs. However, syngas

yields are diluted by the atmospheric nitrogen, with a typical heating value of 100–150 Btu ft⁻³ (3–5 MJ Nm⁻³). Oxygen- and steam-blown gasifiers produce syngas that is richer in CO and H₂, with a heating value of 250–500 Btu ft⁻³ (8.4–16.7 MJ Nm⁻³). Van der Drift, van Doorn, and Vermeulen (2001) conducted a gasification study, using a fluidized-bed gasifier, on ten types of biomass residues, and reported their syngas composition, heating value and conversion efficiency, as shown in Table 1.3.

The physical and chemical properties of the feedstock are some of the major factors affecting the quality of syngas and the gasification process efficiency in general. The fact that there are large variations in moisture content, ash, and organic species between different biomass types adds to the complexity of this process configuration. In general, high moisture and ash content are considered problematic, as they consume a fraction of the heat supplied without contributing positively to syngas formation. Hughes and Larson (1998) illustrated, through modelling, that the gasification process efficiency in integrated gasification combined cycle (IGCC) increases with a decrease in moisture content of the input biomass down to 30%, where further moisture decreases had negligible influence. However, Brammer and Bridgwater (2002) showed that the high overall efficiency (at a moisture content of 35% in their case) is due to the sensible heat carried by the water vapour. They demonstrated that the cost of an electrical power unit will be higher, compared to a biomass feed with 10% moisture, since the output gas heat will not contribute to power generation.

Similarly, the presence of ash minerals in the biomass can be problematic to gasification, causing agglomeration, fouling, and corrosion in the gasifier bed. Furthermore, catalyst poisoning occurs as a result of mineral oxides deposition on the active site. Priyadarsan *et al.* (2004) studied the gasification of poultry and feedlot manure in an air-blown gasifier, and reported agglomeration in the bed due to the high alkaline oxides, such as sodium and potassium, in the ash. Leaching of high mineral biomass streams to improve the thermal characteristics under gasification conditions (Garcia-Ibanez, Cabanillas, and Sanchez, 2004) is another approach to minimize ash generation.

An important process parameter is the operational mode of the gasifier. Generally, gasifiers operate in a fixed bed, fluidized bed, or entrained flow mode. However, there are many variations to these basic designs. For instance, fixed-bed gasifiers can be operated with updraft or downdraft configurations. Similarly, fluidized-bed reactors can be either bubbling beds or circulating beds. Each of these designs has its pros and cons: a summary of these considerations is presented by Ciferno and Marano (2002). Also, Reed and Das (1987) presented a comprehensive review of biomass gasification modes with the emphasis on downdraft gasifiers. Generally, fixed-bed reactors are known for their ease of operation, with downdraft preferred to updraft gasifiers as they produce syngas with a lower tar content. Although more complex in operation than fixed-bed gasifiers, fluidized-bed gasifiers are commonly preferred in large-scale conversion plants. Fluidized-bed gasifiers essentially keep the biomass and inert bed material (usually alumina) suspended by air flow (or oxidizing agents), thus ensuring a fluid-like state, which greatly improves the heat transfer rate to the biomass particles.

Catalysis Role in Gasification

As stated earlier, the use of a catalyst greatly improves thermochemical conversion by facilitating a preferred reaction mechanism. In gasification, the main role of catalysts is

Table 1.3 Syngas composition of different biomass residues^a (Van der Drift, van Doorn, and Vermeulen, 2001). Reprinted with permission from Van der Drift et al., 2001 © Elsevier (2001).

Biomass	CO	H ₂	CO ₂	CH ₄	C ₂ H ₄ (Vol.% dry)	C ₂ H ₆	Benzene	Toluene	Xylene	HHV - calculated (MJ m ⁻³)	Cold-gas efficiency (%)
Willow	9,400	7,200	17,100	3,300	1,100	0,100	0,210	0,065	0,013	4,92	66
Demolition wood	11,350	7,050	15,750	3,250	0,850	0,030	0,210	0,031	0,005	4,77	58
Park wood	11,650	6,770	15,510	3,170	0,990	0,040	0,250	0,043	0,009	4,93	66
Chip board materials	9,640	6,420	15,630	2,770	0,870	0,030	0,220	0,040	0,007	4,41	59
verge grass	9,890	7,280	15,610	2,580	1,150	0,050	0,120	0,035	0,004	4,64	58
Demolition wood + paper residue sludge	9,240	6,080	16,110	2,810	1,020	0,040	0,190	0,054	0,070	4,51	56
Demolition wood + sewage sludge	10,530	8,020	15,020	3,190	1,120	0,040	0,230	0,058	0,008	5,13	58
Woody excess fraction of ODW	5,340	1,800	16,090	1,240	0,400	0,020	0,120	0,019	0,008	2,05	37
Park wood (bio-dried)	8,310	5,380	16,040	1,720	0,600	0,020	0,140	0,040	0,007	3,28	47
Railroad ties	10,570	5,850	13,940	2,880	0,950	0,030	0,280	0,110	0,110	4,97	60
Cacao shells	8,000	9,020	16,020	2,340	1,130	0,050	0,160	0,060	0,030	4,61	62

^a These feedstocks were tested in a 500 kW circulating fluidized-bed gasification facility [Energy Research centre (ECN) in the Netherlands, in co-operation with a Dutch company (NV Afvalzorg) and the Dutch agency for energy and environment (Novem)]. The process temperatures were approximately 850 °C for all tests to facilitate comparison. The process pressure was atmospheric.

the reduction of condensable organic vapours (that later form tar contamination) by favouring their cracking into permanent gases, such as H_2 and CO . Sutton, Kelleher, and Ross (2001) reviewed gasification catalysts and classified them into three groups: dolomite, alkali (metal), and nickel catalysts. Catalysts could either be added to the gasification bed, or to separate catalytic reforming beds after conversion. The use of independent catalytic reactors is advantageous as it minimizes catalyst fouling and facilitates catalyst regeneration in large-scale unit operations. Both dolomite and nickel catalysts are suited for downstream separate catalytic reformers, while alkali metals can be impregnated into the biomass feed directly. Devi, Ptasiński, and Janssen (2003) listed gasification char as an effective bed catalyst that has been found to reduce tar formation. In addition to the catalysts used, a variety of mechanical separation methods are employed to remove entrained particles from the product syngas. The end use of the syngas generally dictates the necessary quality of the syngas, and in turn, the downstream cleaning stages. In general, cyclones and bag filters are used to separate entrained fly-ash from the gas stream. Furthermore, condensers, scrubbers and strippers are used to remove pollutants and contaminants from the gas stream.

Synthesis Gas Usage

The configuration of the gasification facility depends largely on the intended use, or uses, of the syngas stream. These uses include direct combustion in boilers, turbines or internal combustion engines (ICE) to generate electricity, heat or both. More sophisticated, and capital intensive, implementations include gas-to-liquid (GTL) processes to produce various liquid fuels. Also, syngas can be used to produce hydrogen by separation, or a range of other chemical industry products (non-energy carriers), such as ammonia, by chemical synthesis. Examples of large-scale biomass gasification implementations include the following.

A Battelle/FERCO (Vermont) gasifier demonstration plant was built in 1994, using a fluidized bed reactor unit, where the char was combusted in a second bed to provide reaction heat to the gasification bed by heating the sand (Paisley *et al.*, 1989). The output syngas stream was intended for power generation via gas turbines. Unfortunately, the operation of this facility was discontinued due to operational and logistical issues. The RENUGAS[®] process was developed by GTI (Gas Technology Institute) and essentially consisted of a pressurized, fluidized-bed gasification unit with either air or oxygen as the oxidizer and a hot-gas cleaning unit (Lau and Carty, 1994). A demonstration unit, with a maximum capacity of 91 metric tons day^{-1} , was constructed in Hawaii, using sugarcane bagasse to power a combustion turbine for electricity generation. Unfortunately, the operation of this facility was also discontinued due to lack of funding (Rollins *et al.*, 2002). The U-GAS[®] process, patented by GTI, was implemented in Tampere, Finland by Enviropower, Inc., now Carbona, Inc. This is a high-temperature ($\sim 1000^\circ C$), high-pressure fluidized-bed conversion process, of which the syngas is used to power combined-cycle turbines for district heating. The facility can run on a variety of feedstocks, including coal, paper-mill waste, straw, and willow. A series of gasification systems were manufactured by Primenergy LLC (US) to convert biomass by products, such as rice hulls and corn fibres, into energy and steam. Riceland Foods Inc., located in Stuttgart, AR, operates three Primenergy-built gasifiers, gasifying 600 tons day^{-1} of rice hulls to produce 68 039 $kg\ h^{-1}$ of steam and 12.8 MW of electricity (UCR, 2009).

Syngas can also be used as feedstock to produce liquid fuels through the Fischer–Tropsch (F–T) process. This process requires only hydrogen and carbon monoxide as input

components, which requires additional purification steps to remove other syngas components such as CO_2 , CH_4 , and N_2 . A H_2 and CO mixture, preferably at a ratio of H_2 : CO of 2, are exposed to specific temperatures, in the range 200–350 °C, pressure, in the range 15 to 40 bar, and catalytic agents, such as Co, Fe, Ni. This generates a distribution of saturated hydrocarbons, referred to as alkanes, including: methane (CH_4), ethene (C_2H_4), ethane (C_2H_6), LPG (C3–C4, propane and butane), gasoline (C5–C12), diesel fuel (C13–C22), and light waxes (C23–C33) (Demirbas, 2007). This process has been developed and utilized on an industrial scale by SASOL Ltd. (South Africa) since the 1950s to produce petroleum liquids from coal and natural gas. To our knowledge, no large-scale conversion facilities have been established for biomass-to-liquid via the F–T process. Modelling studies showed that converting biomass into F–T fuels was not economical; however, with the incorporation of green energy premiums, production costs may become competitive (Tijmensen *et al.*, 2002).

1.4 Biochemical Conversion

As opposed to thermochemical processing, biochemical processing does not require temperatures in the realm of 500 °C. On the other hand, this processing platform is based on the saccharification of sugars that make up the plant cell wall into high-quality sugar streams that will then be converted to bio-based fuels or chemicals. To produce fuels using biochemical processing technologies, feedstock must be reduced in size, pretreated, hydrolyzed with enzymes, and fermented (Lynd *et al.*, 2008). A schematic of the plant cell wall and its ensuing components is presented in Figure 1.1. Specific pretreatment methods attack different components of the cell wall, with ammonia and lime treatments resulting in the disruption of lignin, while water and dilute acid cause hemicellulose solubilization (Wyman *et al.*, 2009). The efficacies of pretreatments are rated according to their production of reactive fibre, utility of the hemicellulose fraction and limitation of the extent to which the pretreated material

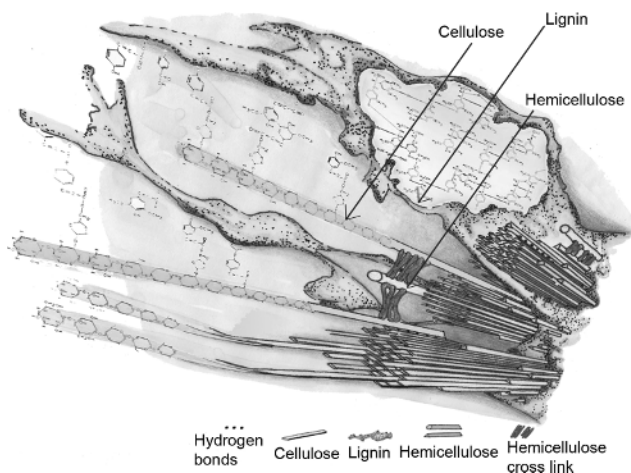


Figure 1.1 A close up of the plant cell wall where lignin, hemicellulose, and cellulose are intertwined.

inhibits enzymatic hydrolysis and growth of the fermentation microorganism (Laser *et al.*, 2002). Pretreatment can lead to the generation of inhibitory products such as lignin derivatives and xylose degradation products, such as furfural and formic acid (Du *et al.*, 2010). Leading pretreatments include: ammonia fibre explosion, ammonia recycling, controlled pH, dilute acid and lime.

1.4.1 Pretreatment

Ammonia fibre explosion (AFEX) pretreatment expands the plant cell wall, facilitating the work of the hydrolyzing enzymes (Balan *et al.*, 2009; Teymouri *et al.*, 2005). This disruption is very important because the enzymes during subsequent hydrolysis will cleave the monomeric sugars from the cellulose microfibrils and the hemicellulose backbones, respectively. AFEX pretreatments are usually performed with an ammonia:biomass ratio of 1:1, 2:1 or 3:1 in high-pressure vessels that can sustain pressures from 1.4 to 4.8 MPa, and temperatures from 60 to 200 °C for 5 to 45 min. AFEX pretreatments usually do not lead to the generation of inhibitory products. On the other hand, because of the use of pressurized vessels, this pretreatment is quite costly.

Lime pretreatments are usually conducted with a 0.5:1 Ca(OH)₂:biomass loading, at temperatures ranging from 25 to 150 °C, for reaction times that can vary from hours to weeks in oxidative and non-oxidative environments. As expected, the processing time is inversely related to temperature. When conducting the pretreatment at a temperature of 25 °C, the processing time is in terms of weeks, requiring vast biomass holding areas. On the other hand, processing at temperatures in the range of 150 °C results in reaction times in terms of hours. Because the loosening of the plant cell wall of the feedstock can be carried out at 25 °C, this process can be set up as an on-farm operation. Lime pretreatment solubilizes lignin and results in the production of very few degradation products (Kim and Holtzaple, 2005).

Controlled pH pretreatment requires a loading of 1:6.2 biomass:water, with reaction temperatures between 170 and 200 °C, and reaction times of 5 to 20 min. Under these conditions, xylan is solubilized as oligomers that will later be hydrolyzed into their monomeric components by enzymatic hydrolysis. Very few degradation products are produced during this pretreatment method (Kim, Mosier, and Ladisch, 2009; Mosier *et al.*, 2005).

Dilute acid is a pretreatment that can be conducted at a range of sulfuric acid concentrations, 0.22 to 0.98%, at temperatures varying between 140 to 200 °C for times between 1 min and 1–2 hours. This pretreatment results in the solubilization of hemicellulose, exposing the cellulose microfibrils and the lignin in the plant cell wall. The cellulose is ready to be hydrolyzed by the enzymatic action. The xylose fraction will be released in the form of xylose monomers or as xylose degradation products, which need to be removed or at least minimized for further processing. Although dilute acid pretreatments present many drawbacks, this technology is likely to be adopted at the deployment scale because of its low cost and ease of use (Lloyd and Wyman, 2005; Wyman *et al.*, 2009).

Ammonia recycle pretreatment is usually conducted at a loading of 3.3 mL of ammonia 15% (w/w) per g of biomass, residence times between 10 to 12 min, processing temperatures between 170 and 220 °C and a processing pressure of 2.3 MPa. This process will result in the solubilization of lignin, leaving the hemicellulose and cellulose fractions ready to be hydrolyzed by the enzymes. Because the lignin content of grasses, 15–20%, is lower than

Table 1.4 Sugar recovery of corn stover and poplar recovered with leading pretreatment technologies. Conversion for the corn stover using 15 FPU enzyme cocktail.

	Corn stover	Poplar
Dilute acid	92% ^a glucose 94% ^a xylose 160 °C, for 20 min (Lloyd and Wyman, 2005)	87% ^a glucose 72% ^a xylose 190 °C, for 1.1 min (Wyman <i>et al.</i> , 2009)
Controlled pH	91% ^a glucose 82% ^a xylose 190 °C, for 15 min (Mosier <i>et al.</i> , 2005)	56% ^a glucose 96% ^a xylose 200 °C, for 10 min (Kim, Mosier, and Ladisch, 2009)
AFEX	96% ^a glucose 92% ^a xylose 1,7MPa 90 °C, for 5 min (Teymouri <i>et al.</i> , 2005)	52% ^a glucose 53% ^a xylose 4,8 MPa 180 °C 30 min (Balan <i>et al.</i> , 2009)
Lime	93% ^a glucose 76% ^a xylose 55 °C, for 4 wk (Kim and Holtzapple, 2005)	78% ^a glucose 96% ^a xylose 2,3 MPa 140 °C 120 min (Sierra, Granda, and Holtzapple, 2009)
Ammonia recycling	90% ^a glucose 88% ^a xylose 170 °C, for 10 min (Kim and Lee, 2005)	49% ^a glucose 69% ^a xylose (Gupta and Lee, 2009)

^aIndicates percentage recovery of available xylose and glucose, respectively.

that of hardwoods, 20–35%, this pretreatment is advantageously used with herbaceous materials (Gupta and Lee, 2009; Kim and Lee, 2005).

Table 1.4 presents side-by-side comparison of monosaccharide release from corn stover and poplar that were subjected to these pretreatments. It can be observed that the processing conditions, as well as the monosaccharide release are different for the five leading pretreatments using the same feedstock. It appears to be easier to release the carbohydrates from a feedstock like corn stover as compared to that of a woody feedstock such as poplar.

1.4.2 Enzymatic Hydrolysis

Pretreatment opens the tightly woven biomass plant cell wall by separating cellulose, hemicellulose, and lignin, thereby increasing the internal surface area. With more available surface area, enzymes can have access to the carbohydrate polymers, hydrolyzing hemicellulose into the five-carbon xylose, and cellulose into the six-carbon glucose. The hydrolysis of the treated cellulose is performed with an enzymatic cocktail composed of β -glucosidase, endo-cellulase and exo-cellulase. These enzymes hydrolyze cellobiose as well as the middle and extremities of the cellulose polymer, respectively. Loadings of 15 FPU g⁻¹ glucan and

30 FPUg⁻¹ glucan of cellulase and β -glucosidase, respectively, are reported as being utilized (Gupta and Lee, 2009). Xylan cocktails including endo- β -(1,4)-xylanases, β -xylosidases, acetylxylanesterases, and feruloyl esterase are used to cleave the hemicellulose, including their attached monosaccharides (Bauer *et al.*, 2005). The enzyme α -glucuronidase is used to remove glucuronic acid residues from the hemicellulose. Specific activities related to hemicellulose hydrolysis need to be determined because the hemicellulose composition varies from plant to plant. It is critical to digest the plant cell wall monosaccharides with the least amount of cellulase and xylanase enzymes; these biocatalysts account for the most costly component of the biochemical process and, if not used sparingly, could forfeit the economic viability of the biorefinery.

Although pretreatment is critical, this processing step unfortunately can lead to the production of inhibitory compounds that restrain the enzymatic saccharification of the carbohydrate polymers. The enzymatic saccharification step is obstructed mainly by three groups of compounds: lignin derivatives that cause non-productive binding of the saccharification cocktail (Berlin *et al.*, 2006); xylose-derived compounds inhibiting the enzyme cocktail (Cantarella *et al.*, 2004); and oligomers and phenolic-derived compounds deactivating the enzymes over time (Kumar and Wyman, 2008; Berlin *et al.*, 2006 and Ximenes *et al.*, 2011). To lessen the effect of these inhibitory compounds and minimize the amount of enzymes used, the inhibitors must be removed by separation methods, for example, washing the pretreated biomass with successive volumes of water (Hodge *et al.*, 2008).

1.4.3 Fermentation

After biomass is pretreated and the ensuing plant cell wall components are saccharified, the released sugars can be fermented into biofuels or other desired bio-based products. It is critical that both five-carbon and six-carbon sugars are fermented to alcohol because the process could never achieve economic viability if only the more easily fermented six-carbon sugars are metabolized. Desirable performance metrics of ethanol titre and rate are 40 g L⁻¹ and 1 g L⁻¹ h⁻¹, respectively (Lau *et al.*, 2010). To achieve these performance metrics, glucose and xylose must be processed by the microorganism.

Unfortunately, no native organism can metabolize simultaneously both carbon streams. Native *Saccharomyces cerevisiae*, which is a leading microorganism for ethanol fermentations, metabolizes glucose into ethanol, but cannot process xylose. On the other hand, *Pichia stipites* is a native microorganism that metabolizes xylose into ethanol (Jeffries, 2006). There are two scientific approaches to make sure that both glucose and xylose are processed into ethanol: (1) genetically introduce the missing xylose pathway into the target organism, such as *S. cerevisiae*; (2) co-culture xylose and glucose metabolizing organisms, such as *S. cerevisiae* with *P. stipites*.

There are a number of microorganisms into which the xylose-metabolizing pathway was introduced, amongst others: *Escherichia coli*, *Zymomonas mobilis*, and *S. cerevisiae*. Lau *et al.* (2010) reported on the side-by-side comparison of these three strains using AFEX pretreated corn stover; ethanol titers of 30, 40 and 30 g L⁻¹ were reported for *E. coli*, *S. cerevisiae*, and *Z. mobilis*, respectively, during 80, 160, and 40 hours of fermentation. From these results, *S. cerevisiae* appeared to be the least troubled by the fermentation inhibitors that are produced during pretreatment.

If desirable ethanol yields are to be obtained via the co-culture route, one must be cognizant of two important considerations: (1) the strains must not be toxic to each other, such as a *S. cerevisiae* and *P. stipites* combination; and (2) the strains must be cultured at similar temperatures and pH, also such as a *S. cerevisiae* and *P. stipites* combination. The *Z. mobilis* and *P. stipites* system is an example of an unsuccessful co-culture combination; although both require a temperature of 37 °C, the former requires an optimum pH 7 and the latter needs an optimum pH 5, illustrating well the impasse. Guidelines as to how to set-up a *S. cerevisiae* and *P. stipites* co-culture system include: (1) initial total sugar concentration between 20 and 100 g l⁻¹ with xylose varying between 20 and 50%; fermentation temperature of 30 °C; and 2 mmol l⁻¹ h⁻¹ of oxygen. These cultivation conditions resulted in a volumetric ethanol productivity of 0.94 g l⁻¹ h⁻¹ and an ethanol yield of 0.50 g g⁻¹ over a 40-hour fermentation cycle (Chen, 2011).

Although the discussion has been centred mostly on ethanol production, it is important to bear in mind that the biorefinery could be centred on other fermentation products. When the biomass plant cell wall is saccharified and the sugars are released, the nature of the fermentation organism determines the produced product. *Clostridium tyrobutyricum* can be used to produce butyric acid from carbohydrates, and then *C. acetobutylicum* can be used to ferment the butyric acid to butanol. With this two-step approach, yields of 0.40–0.47 g acetone:butanol:ethanol products per g sugar utilized (g g⁻¹) are common (Ramey, 1998).

1.4.4 Pre-Pretreatment

As mentioned earlier in this chapter, pretreatment is a critical operation in the biochemical processing operations; without some sort of pretreatment, it is almost useless to perform enzymatic hydrolysis because the cell wall will not be loosened, and the cellulase and xylanase enzymes will not have sites to bind to. In addition to standard pretreatments, the biomass feedstock can undergo a “pre-pretreatment,” where the biomass is soaked in water or dilute acid before being subjected to the actual pretreatment operation. The pre-pretreatment step can be, in a sense, compared to the soaking of a stained garment before washing. The wash water from the pre-pretreatment step can sometimes contain phytochemicals; this can be an opportunity to extract high-value speciality chemicals, while improving pretreatment and adding value to the overall biorefinery operation.

Ground early fall-harvested switchgrass var. Cave-in-Rock was extracted in 90 °C water for 20 min prior to dilute acid pretreatment; the flavonoids, quercitrin (quercetin-3-O-rhamnoside), and rutin (quercetin-3-O-rutinoside), were detected and their concentrations were 193 and 186 mg kg⁻¹ of dry biomass, respectively (Uppugundla *et al.*, 2009). The extracts were subsequently purified by centrifugal partition chromatography, using a ethyl acetate:ethanol:water (2:1:2, v/v/v) solvent system, into quercitrin and rutin fractions; these purified flavonoids decreased by 78 and 86%, respectively, the oxidation of low-density lipoprotein as measured by the thiobarbituric reactive substances (TBARS) assay (Uppugundla *et al.*, 2009).

Ground spring-harvested Switchgrass var. Alamo was extracted in 85 °C water for 2 h; neither rutin nor quercitrin was detected, but quercetin was noticed at concentrations of 140 and 120 mg kg⁻¹ of dry biomass, respectively, for leaves and stems (Martin *et al.*, 2011). The pre-pretreated biomass was subsequently pretreated in 1% sulfuric acid in a 2 L Parr bioreactor for 25 min at 130 °C. The coupling of the pre-pretreatment step to that of the pretreatment

resulted in xylose increases of 5 and 23% for stems and leaves, respectively (Martin *et al.*, 2011). These results point to the fact that not only can high value chemicals be recovered in the pre-pretreatment water, but that this operation increases carbohydrate recovery.

Sweetgum (*Liquidambar styraciflua* L.) has a widespread distribution in the southeastern United States. Much of its distribution is as understory amongst planted pines that are grown for softwood lumber and pulp for paper products. However, hardwood competition in the pine forest understory is a major impediment to pine forest growth; therefore, southern pine forests are intensively managed. Instead of being a nuisance, this hardwood understory growth could become an important source of biomass for the upcoming biochemical-based biorefineries, especially in view that sweetgum is a fast-growing hardwood. In addition to being a possible biorefinery feedstock, sweetgum contains shikimic acid, which is a precursor for the drug Tamiflu[®] used in treating avian flu. Water-extracted sweetgum bark and heartwood yielded 1.7 and 0.2 mg g⁻¹ of shikimic acid, respectively. The addition of a 65 °C shikimic acid extraction step coupled to pretreatment with 0.98% H₂SO₄ at 130 °C for 50 min resulted in 21% and 17% increases in xylose percentage recovery from bark and de-barked wood, respectively. These results indicate that, in addition to recovering a high-value product, the 65 °C wash step also increases xylose recovery (Martin *et al.*, 2010).

1.5 Conclusion

The goal of this chapter was to present a general overview of what a thermochemical and a biochemical biorefinery would entail in terms of feedstock and of processing. The reader can appreciate the fact that, although both technology platforms can be conducted with biomass, their processing parameters widely differ. The thermochemical conversion platform is conducted at temperatures of at least 300 °C and results in the production of bio-oils or syngas that can be upgraded into further products. On the other hand, biomass processing following the biochemical conversion platform is, in a sense, more mild because of the requirements of cell wall loosening coupled to enzymatic release of the structural sugars. Because the sugars are further fermented into various products, this technology platform offers the possibility of producing various bio-based products. Hopefully, both platforms will be widely utilized in the decades to come, processing colossal amounts of biomass. The goal of this book is to illustrate that speciality chemicals and other bio-based products could be extracted prior to or after the conversion process, increasing the overall profitability and sustainability of the biorefinery. Therefore, subsequent chapters will describe various classes of secondary metabolites that are present in biomass, present strategies for the extraction and purification of these various phytochemicals, and finally describe examples of biorefinery-destined biomass that contains speciality chemicals.

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