

# Biomass to L

## 38. Biomass to Liquid (BTL) Fuels

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We introduce a strategy for biomass fractionation and refinery co-processing. Some of the leading conversion technologies are reviewed, including pretreatment-hydrolysis (for 2nd-generation biofuels), gasification and Fischer-Tropsch (FT) synthesis, pyrolysis, and aqueous phase reforming (APR), along with some of the current challenges for commercialization. The main objective is to give an overview and recommendations in regard to the co-processing of biomass oil with crude oil that includes some of the developed technologies, as well as providing a new theoretical approach to the co-utilization of these raw materials. This new approach utilizes biomass to undergo 2nd-generation conversion processes where it is fractionated into relatively pure streams of soluble cellulosic/hemicellulosic sugars and residual solid lignin (non-sugar) fractions. The cellulose/lignin fractionation would also facilitate the development of new-generation characterization schemes to reduce interference between sugar and non-sugar components. Upgrading and reforming techniques such as gasification and Fischer-Tropsch (FT) synthesis, pyrolysis, or aqueous phase reforming (APR) can then be adopted for use with these fractions to generate feedstocks such as bio-oils that resemble those used within a petroleum refinery. If treated properly these

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biomass-derived oils have been shown to resemble crude-derived oil feeds and when supplemented in large quantities to process feeds can produce equivalent fuels and chemicals to that of petroleum crude oil. Consequently, dependence on fossil fuels will be reduced, among other advantages such as a reduction in greenhouse gas (GHG) emission, while still utilizing in-place technologies and with lower capital investments compared to earlier generations of biofuels.

Long-term success for a sustainable, clean energy source will require a new approach to the current biofuels trend that has focused on a comprehensive makeover of a billion-dollar industry, invested with trillions of dollars' worth of infrastructure and distribution networks, while having been completely integrated into our society. The goal should not be to merely replace the energy technologies that have been developed over time, but to supplement the feedstock (crude oil) with a cleaner and more sustainable resource that has similarities with regards to chemical make-up (e.g., biomass oil). The challenge with the current technologies lies

with the ability to break down the biomass, *cost effectively*, into its basic monomeric units and gaseous forms so that components may be upgraded or reformed into feedstocks that resemble those used within a petroleum or petrochemical refinery.

Recently, there has been a migration of research and technology from a petroleum foundation towards a more green (or alternative) approach to the energy and chemical industry. Environmental concerns are at the forefront of this need to transfer to a more carbon neutral platform in addition to economic and political backing providing a substantial push. The United States

Department of Energy (US DOE), among other national and international agencies, have laid out a goal to accelerate biomass-to-energy conversion research in order to make biofuels both possible and practical within the coming years [38.1]. There are a variety of pathways that are being considered for alternative routes including solar, wind, geothermal, etc., but the route that will be considered in this overview will be the biomass-to-liquids (BTL) fuel production pathway and how this method can be integrated into the current infrastructure of petroleum refineries.

The biomass used to generate biofuels can cover a broad range of materials that include: food crops (1st-generation biofuels), nonfood crops or nonedible portion of food crops (2nd-generation biofuels), and microalgae (3rd-generation biofuels). The 1st-generation biofuels have achieved a certain degree of success in terms of commercialization, especially under government subsidies or mandates. The bioethanol derived from corn and sugarcane, for example, is unable to replace gasoline completely without major modification to the internal combustion engine, and subsequently, must be blended with gasoline in order to be used within existing engines. Recently introduced biobutanol, which has a heat content close to gasoline and less water affinity, can be blended with gasoline at higher concentrations than bioethanol. Biodiesel produced from animal fats and vegetable oil has performed well in diesel engines, especially when blended with petroleum-derived diesel. However, all of the potential sources for 1st-generation fuels are associated with sustainability and affordability concerns, owing to the fact that they inherently compete with food sources considered to be limited in many regions of the world. The 3rd-generation biofuels that are currently under development have potential issues related to long time scales due to the slow growth-rate of the algae along with the need for an incredibly large photosynthesis area to support the large quantity of feedstock used to generate the extracted oils. Economic removal of excess water presents another challenge for algal fuel production.

The 2nd-generation biofuels can be categorized as a variety of products, namely: agricultural wastes (e.g., corn stover, sugarcane bagasse, etc.), municipal wastes, pulp milling by-products, recycled vegetable oils, as well as true feedstocks generated from under- or non-utilized forestry biomass. In essence, biomass is associated with such things as waste streams, pure feedstocks, recycled materials, as well as some materials that have not found a dedicated use. A large portion of biomass is in the form of lignocellulosics, which is a composite material particularly well suited for energy applications due to large-scale availability,

low costs, and the environmentally benign production. Many of the energy production and utilization cycles based on lignocellulosic biomass have low or near-zero greenhouse gas (GHG) emissions on a life-cycle basis [38.2–4]. This is owed to the fact that the CO<sub>2</sub> produced through the use of these fuels is utilized by the growth of other biomass. An added benefit of these new conversion routes is the generation of new employment opportunities in dwindling economies by consolidating and amplifying agricultural economy through energy crop cultivation as well as reinforcing long-standing industries such as sugar, paper, and forestry that can work synergistically with these conversion technologies.

A much overlooked concept that should increase the popularity of utilizing these biomass feedstocks is the idea of use within a fully integrated biorefinery, much like what has already been developed within petroleum refining [38.5, 6]. Biomass material can potentially integrate itself within existing petroleum refineries and be utilized as a feedstock for many of the products that petroleum has created a monopoly over. The integration could be considered as the 4th generation of biofuels as GHG emissions produced are reduced by sequestration techniques over standard refinery operations and biomass fuel production routes alone. This approach would not only be able to help alleviate the fuel industry but also that of plastics, chemicals, and other products that are derived from petroleum.

The primary obstacle impeding the more widespread production of energy from biomass feedstocks is the general absence of low-cost technology for overcoming the recalcitrance (difficulty to break down) of these materials. Currently, there are only a few lignocellulosic conversion methods that have been looked at for implementation into an adapted refinery. These include the generation of electricity by way of combustion, thermochemical treatment (gasification and/or pyrolysis), biochemical treatment, and a combined physicochemical treatment conversion pathway. A variety of chemicals, temperatures, and pressures are used separately or in combination with any of these processes to pretreat the feedstock and then break down the structures of the lignocellulosics into their monomeric, oligomeric, or gaseous forms so they can be further converted or upgraded into a usable product. Formation of these products can take the form of energy (heat and electricity), fuels (solid, liquid, or gaseous), and/or chemicals and materials. This paper will outline some of the technologies that are currently being investigated, along with a more detailed analysis of the utilization and implementation of gasification and pyrolysis into a fully integrated biorefinery (green refinery), and how these processes can be linked with current petroleum and petrochemical refineries.

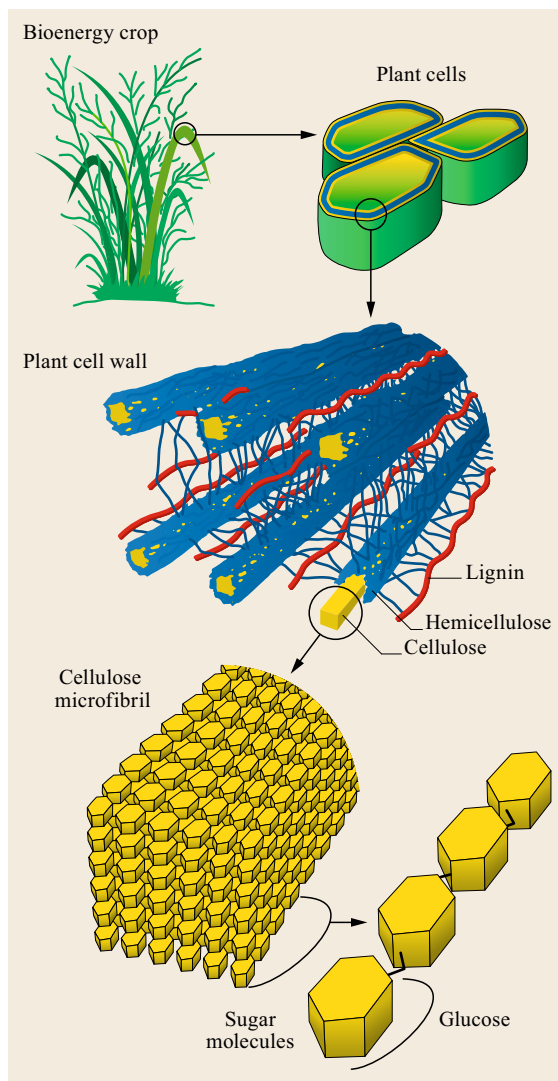
## 38.1 Lignocellulosic Biomass

Before breaking down a complex material such as lignocellulosic biomass something must be known about how it is formed and what the structure is comprised of. Lignocellulose has three primary constituents which are cellulose, hemicellulose, and lignin, with smaller quantities of extractives, proteins, and inorganic materials. The largest of the constituents, cellulose, is a homopolymer composed of *D*-anhydroglucopyranose units (repeated glucose units), linked together by  $\beta$ -(1 $\rightarrow$ 4)-glycosidic bonds. The cellulose chains are packed into microfibrils, stabilized by extensive hydrogen bonds (Fig. 38.1) [38.7]. These fibrils are attached to each other by hemicelluloses (amorphous polymers of various sugars) as well as other polymers such as pectin, and then encased by lignin. Hemicellulose is composed of mainly pentoses (xylose and arabinose) and hexoses (mannose, glucose, and galactose). Lignin is an amorphous polymer whose attributes include providing rigidity to the plant cell wall and resistance to microbial attack. The cellulose microfibrils present in the hemicellulose-lignin matrix are often associated in the form of bundles of macrofibrils.

Necessary information that could prove more important when dealing with some of the thermochemical processes is the ultimate analysis of various feedstocks that could be used (Table 38.1).

The ultimate analysis of the biomass materials is the chemical composition (e.g., carbon, hydrogen, oxygen content) of the feedstocks. A major factor that must be kept in mind during processing, as will be discussed later, is the oxygen content of these materials and its effect in various processing routes, especially when looking into integration within a refinery.

**Fig. 38.1** Schematic representation of the matrix of polymers within lignocellulose that create the plant cells (after [38.7], courtesy of Genome Management Information System/ORNL) ▶



**Table 38.1** Ultimate analysis of various feedstocks

Ultimate analysis (wt%)	Wood and woody biomass			Herbaceous and agricultural biomass			Processed biomass <sup>a</sup>		
	Mean	Low	High	Mean	Low	High	Mean	Low	High
C	52.1	48.7	57.0	49.9	45.2	58.4	53.6	45.4	70.9
O	41.2	32.0	45.3	42.6	34.2	49.0	37.0	16.4	46.1
H	6.2	5.4	10.2	6.2	3.2	9.2	7.3	6.0	11.2
N	0.4	0.1	0.7	1.2	0.1	3.4	1.7	0.2	6.1
S	0.01	0.01	0.42	0.15	0.01	0.60	0.46	0.01	2.33
C/O	1.26	1.52	1.26	1.17	1.32	1.19	1.45	2.77	1.54

<sup>a</sup> Processed biomass includes: shredded currency, demolition wood, furniture waste, and wood yard waste [38.8].

## 38.2 Biomass Processing Routes

There are a few processing routes with regard to the break down of the lignocellulosic biomass into one of many potential products. The three routes that will be discussed herein are: (1) pretreatment-hydrolysis, (2) biomass-to-liquid (BTL) fuels via gasification and Fischer–Tropsch (FT) synthesis, and (3) pyrolysis. A schematic representation of these conversion routes along with the potential pathways that can be implemented for the production of biofuels can be seen in Fig. 38.2 [38.9].

In the pretreatment-hydrolysis route the recalcitrance of the biomass material is first reduced through some type of available pretreatment, followed by hydrolysis of the polymeric sugars into an easier-to-handle soluble fraction. This fraction can then be further treated by means of fermentation, dehydration, or hydrogenolysis to produce liquid fuel substitutes such as hydrocarbons or alcohols. Gasification has been looked at in conjunction with Fischer–Tropsch synthesis, combined as the Biomass-to-Liquid (BTL) fuel process, in order to gasify the feedstock and subsequently convert the gases formed into liquid fuels. Finally, pyrolysis will convert the biomass into a liquid fraction known as bio-oil that can be upgraded to hydrocarbon fuels by a variety of catalytic reactions, as well as having the potential to supplement various streams within a petroleum refinery.

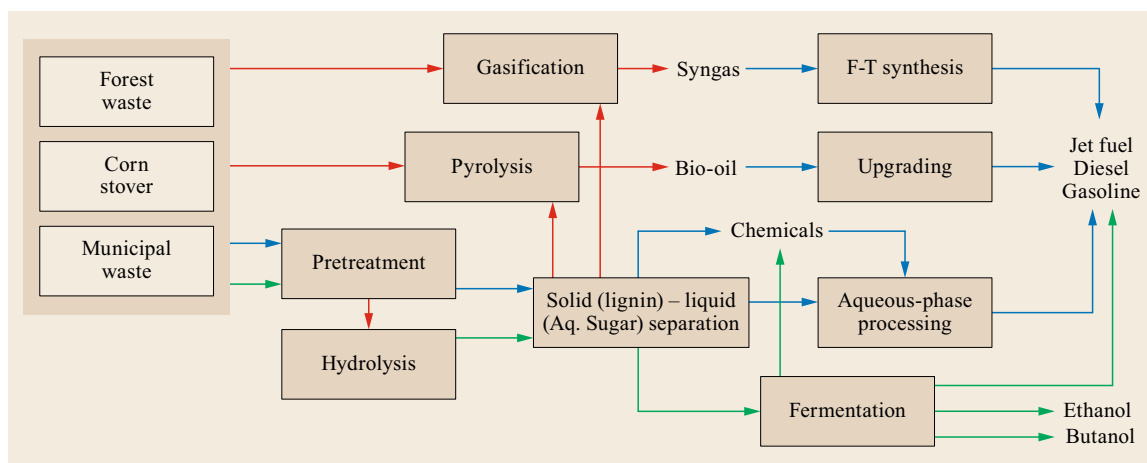
### 38.2.1 Pretreatment–Hydrolysis Pathway (Route 1)

Ultimately, three distinct hurdles (Steps 2, 3, and 4 in Fig. 38.3) must be considered with this type of con-

version pathway that converts the lignocellulosic feed into a usable product, most notably ethanol and butanol, via biological processes. First, there must be some type of (1) pretreatment of the raw material to disrupt the fibrous structure by which the cellulose and hemicellulosic polymers will be made more accessible to be broken down into their monomeric sugars. This digestible lignocellulosic material can then be (2) hydrolyzed (acidically or enzymatically) into the individual subunits of the polymers or fermentable sugars. The fermentable sugars are then converted by one of the (3) oxygenate or alcohol formation pathways, such as fermentation in which microbial *bugs* are used to convert the sugars to products, such as alcohols [38.10].

The current bottleneck lies with the high cost of hydrolysis, owing to either the cost of enzymes or capital investment associated with acid hydrolysis. Currently, enzymatic hydrolysis is the preferred conversion route due to its ability to be specifically tailored to various feedstocks and the low operation costs linked with the reactors. Lowering the enzymatic loadings through the use of higher severity pretreatments without degradation of the feed is the focus of many research groups. The maximization of sugar production at the lowest possible cost can open up multiple routes for hydrocarbon/oxygenate formation [38.9–12].

The strategy that has recently received attention is the idea of fractionating the lignocellulosic biomass into its individual components so as to convert the material into the desired products more effectively [38.13–15]. Fractionation techniques have been used extensively in the pulp and paper industry in order to purify



**Fig. 38.2** Routes for the conversion of lignocellulosic biomass into liquid fuels. *Red arrows* refer to thermal routes, *green arrows* refer to biological routes, and *blue arrows* refer to catalytic routes (adapted from [38.7])

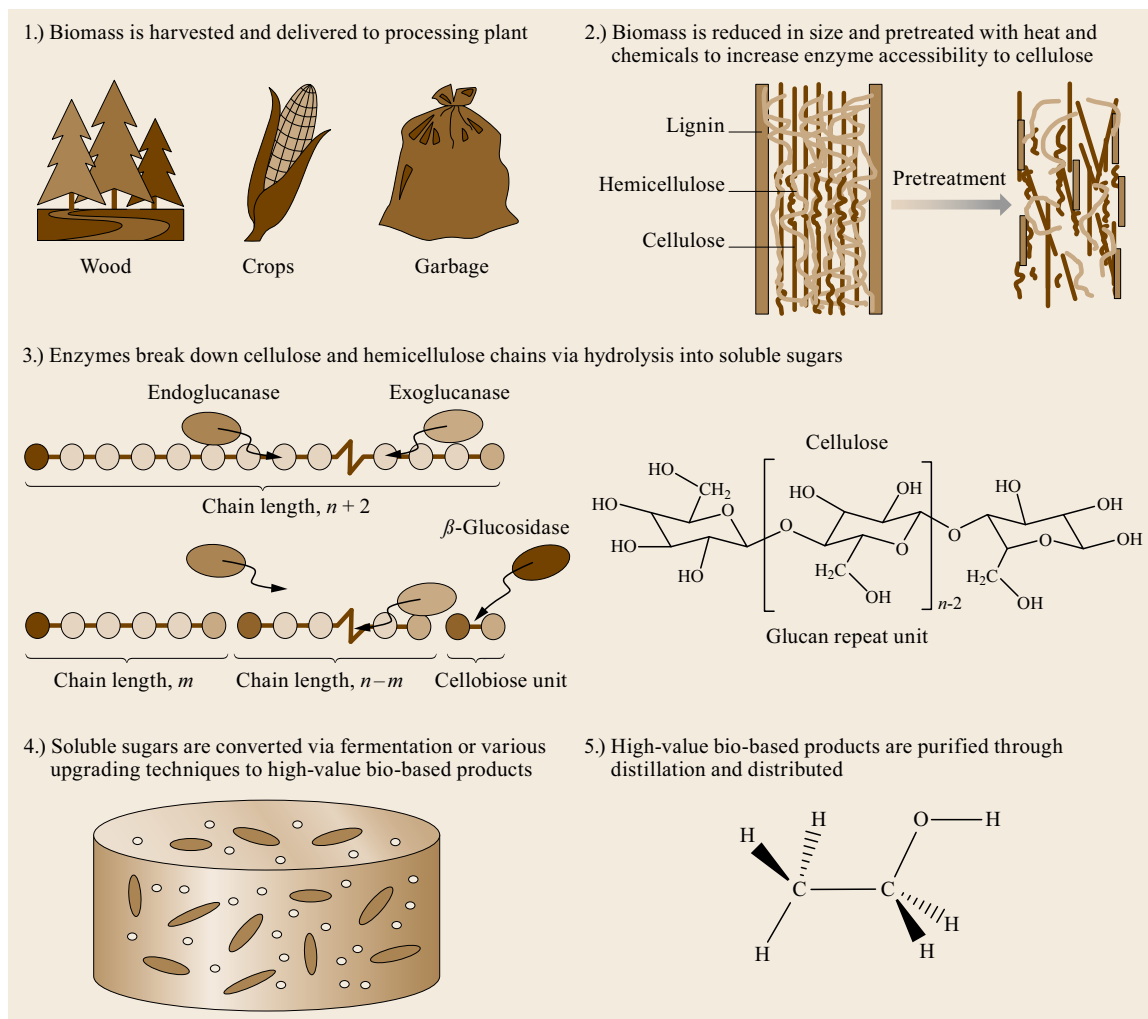


Fig. 38.3 Processing of 2nd-generation biofuels from biomass via the biological route

the cellulosic components of the feedstock, while the residual fraction is mostly burned to generate energy by combustion. However, this method does not effectively utilize the remaining biomass, making upwards of 70% of the total feedstock. These residual solids could potentially be used as feedstocks for gasification or pyrolysis where the material can be upgraded into higher value products.

### 38.2.2 Biomass-to-Liquid (BTL) Fuels (Route 2)

The BTL fuels route can be described almost equivalently to the much older technology of coal-to-liquids or gas-to-liquids (GTLs) conversion. These techniques involve the gasification of the feedstock, whether that is coal, gas, or biomass, followed by Fischer–Tropsch

(FT) synthesis for the production of liquid hydrocarbons.

#### Gasification

The idea of gasification has been around since the mid-19th century where it was originally utilized to convert coal to coal gas (or *town gas*) for lighting and heating purposes, and was used until just after WWII. Recently, the gasification pathway has shifted to producing more synthetic liquid chemicals and fuels through the use of integrated conversion operations. A relatively new approach to the utilization of gasification technology has been developed for use with biomass as a possible clean energy route with a lignocellulosic feed. This method preferentially converts organic-based carbonaceous material (e.g., biomass) into synthesis gas (*syngas* – a mixture of mainly CO and H<sub>2</sub>) through the

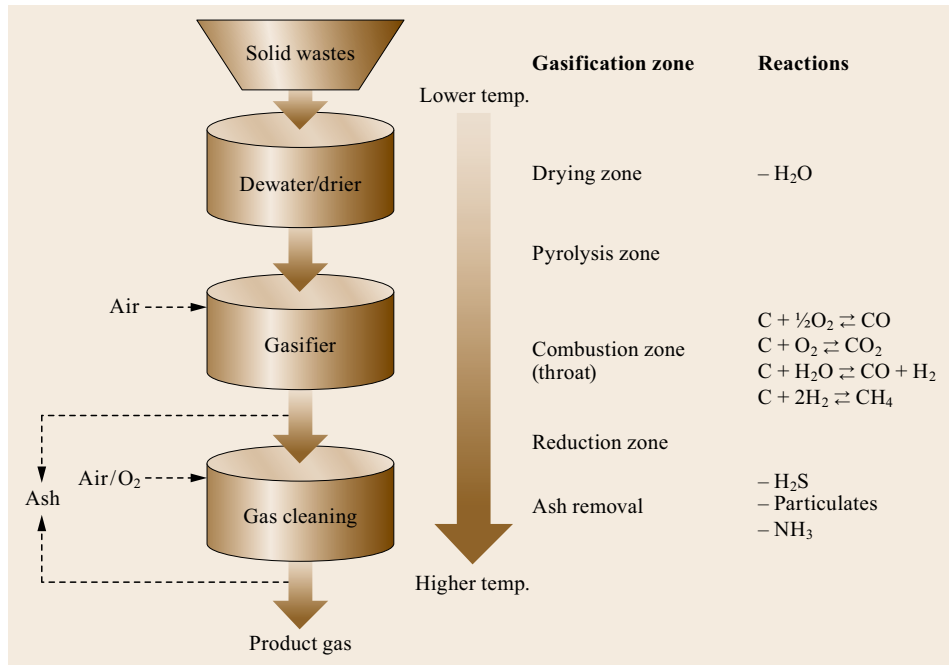
use of high temperatures and the addition of a precise amount of air (or pure oxygen), and to a lesser extent, steam.

One of the attractive features of gasification is the fact that almost any biomass material can be used in this processing route; other routes such as ethanol or biogas production for example, can only use a select type of biomass material. This is due to the process's ability to break down the biomass into a gaseous form as opposed to the intermediates (monomeric sugars) required with the 1st-generation biofuels. A simplified scheme for which solid waste products (or potentially any carbonaceous material) are converted through a downdraft-type gasification system is shown in Fig. 38.4. The syngas produced from this system must first be treated to remove sulfur, nitrogen, and particulates before it can be further converted via FT synthesis. The generation of carbon-based co-products by gasification can be used for chemical upgrading or fertilization in soils (as 4th-generation biofuel production to provide a negative carbon budget in air), limiting waste generation. It is estimated that one ton of carbon (tar or char side-products) produced within this process scheme is equivalent to roughly 3–3.5 t of CO<sub>2</sub> that would normally be released by incineration, greatly reducing GHG emissions when implemented [38.16].

A more concrete definition for gasification would be the partial combustion (or partial oxidation, POX) of a solid fuel (biomass) that takes place at tempera-

tures of roughly 1000 °C in the presence of a controlled amount of oxygen. Complete combustion of the solid fuel will generally produce N<sub>2</sub>, water vapor, CO<sub>2</sub>, O<sub>2</sub>, as well as small amounts of particulate matter considered harmful to both the atmosphere and humans. The *controlled* partial combustion of the biomass produces a preferred mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) with traces of methane (CH<sub>4</sub>) as well as some unwanted side products such as tars and chars, the latter being products of incomplete combustion. The key to a gasifier design is to create a situation in which biomass is reduced to charcoal and subsequently converted to syngas while also limiting the build-up of ash within the reactor. There are four unique processes (reaction zones) that can be considered to take place within a desired gasification process: dehydration, pyrolysis, combustion, and reduction. The break down of the biomass moving through these zones is illustrated in Fig. 38.4.

During the first stage (zone 1) of gasification the water is removed from the biomass feed (having a moisture content of roughly 10–30 % w/w) at temperatures of up to 200 °C, driven by the heat released from the lower zones of the gasifying unit. This is a necessary step as the water within the biomass can drive unwanted reactions during the following steps of gasification due to the presence of the molecular oxygen within the water. High oxygen content in biomass reduces the energy density of the material and for this reason must be removed (similar to the reasoning for the removal



**Fig. 38.4** Simplified schematic of a downdraft gasification unit along with some appropriate reactions and pathways

of oxygen in crude oil for petroleum transportation fuel production) in the form of either CO<sub>2</sub> or H<sub>2</sub>O.

This dehydrated material is then mixed with a gas flow stream where it begins the process of pyrolysis (devolatilization). In this stage, the biomass is converted to large quantities of tars and gases containing carbon dioxide, as well as some methyl alcohols, as the carbonaceous particles are heated up at temperatures ranging from 280–500 °C. Although the gasification process is not necessarily synonymous with pyrolysis, it should be noted that pyrolysis will always occur to some degree within a gasifying reactor generating various condensable hydrocarbons as the material moves from the lower temperature zones to the higher temperature *gasifying* zones. Volatiles are released during this stage while the residual solids form the product char. The material properties of the products and the composition of the char formed during this particular step is highly dependent on the properties of the carbonaceous material that is being supplied to the system and will determine what type of gasification reactions these intermediate products will undergo. The possible reactions that occur during a gasification process can be seen in Table 38.2.

Combustion begins as the volatile products and char begin to react with O<sub>2</sub> to form CO<sub>2</sub> and CO, releasing heat for the subsequent gasification reactions. These reactions are effectively limited in this zone of the reactor by controlling the input rate of O<sub>2</sub>. This limited flow of oxygen to the system will increase the amount of py-

rolysis that occurs in the zone above as the oxygen is consumed initially by the product from pyrolysis (char) that falls from the pyrolysis zone [38.18].

Gasification reactions will be introduced through the combined oxidation and reduction paths in which the carbon sources from the preceding zones are converted to the desired syngas. Solid-phase oxidation reactions will take place at temperatures ranging from 700–1000 °C where heterogeneous reactions (Table 38.2) between oxygen and the residual solid carbon fuel falling through the reactor form CO and H<sub>2</sub>, as well as other by-products. As stated previously, another positive consequence of these reactions is the addition of heat that is necessary for processes within the system. The reduction reactions taking place will require high temperatures (up to 1100 °C) and consume the energy in the system, reducing the heat. Reduction reactions (Table 38.2) such as the Boudouard reaction, water-gas (WG) reaction, water-gas-shift (WGS) reaction, and the methane production reaction (Boudouard and WG preferred) will convert the available carbon to CO and CH<sub>4</sub> with the appropriate reacting material.

It is important to note that there is no distinct separation between the various zones throughout a gasification unit, but an overlap from one zone to the next. These zones may also vary in their order within the reacting system depending on where the air is fed, as well as the configuration of the gasifier. There are several configurations that have been used, most notably: updraft (air fed below gas outlet), downdraft (air fed above gas out-

**Table 38.2** Main reactions during biomass gasification (after [38.17], courtesy of the International Energy Agency)

Reactants	Products	ΔH (kJ/mol)	Process
<b>Primary devolatilization</b>			
Biomass	Primary Tar (CH <sub>x</sub> O <sub>y</sub> ) CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , H <sub>2</sub> O, C		
<b>Tar cracking and reforming</b>			
Primary Tar	Secondary Tar CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , H <sub>2</sub>		
<b>Homogeneous gas-phase-reactions</b>			
Secondary Tars	C, CO, H <sub>2</sub>		
H <sub>2</sub> + 0.5 O <sub>2</sub>	H <sub>2</sub> O	−242	H <sub>2</sub> – combustion (oxidation)
CO + 0.5 O <sub>2</sub>	CO <sub>2</sub>	−283	CO – combustion (oxidation)
CH <sub>4</sub> + 0.5 O <sub>2</sub>	CO + 2H <sub>2</sub>	−110	CH <sub>4</sub> – combustion (oxidation)
CH <sub>4</sub> + CO <sub>2</sub>	2 CO + 2H <sub>2</sub>	+247	Dry reforming reaction
CH <sub>4</sub> + H <sub>2</sub> O	CO + 3H <sub>2</sub>	+206	Steam reforming methanization
CO + H <sub>2</sub> O	CO <sub>2</sub> + H <sub>2</sub>	−40.9	Water-gas-shift reaction
<b>Heterogeneous reactions</b>			
C + O <sub>2</sub>	CO <sub>2</sub>	−393.5	Oxidation of carbon
C + 0.5 O <sub>2</sub>	CO	−123.1	Partial oxidation
C + CO <sub>2</sub>	2 CO	+159.9	Boudouard equilibrium
C + H <sub>2</sub> O	CO + H <sub>2</sub>	+118.5	Water-gas reaction (steam reforming)
C + 2 H <sub>2</sub>	CH <sub>4</sub>	−87.5	Methane production reaction

let), and cross-draft gasifiers (air fed at same level as the gas outlet). *Warnecke* [38.19] provides an extensive review of the various configurations of gasifiers along with their advantages and disadvantages.

Downdraft gasifiers are preferred when dealing with feedstocks such as wood and biomass residues as they tend to be smaller in scale, more affordable, and the tar that is developed during the process has a greater chance of being broken down as it descends through the combustion and reduction zones [38.19, 20]. Some of the other advantages and disadvantages of the various configurations have been highlighted in Table 38.3. Various geometrical configurations within a downdraft gasification unit (straight, single throat, or double throat) are also used depending on the application or feed [38.21].

Research has indicated that many parameters will affect the preferential production of syngas over the less-desired producer gas (mixture of CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>x</sub>H<sub>y</sub>, and N<sub>2</sub>). If producer gas is to form it can be further converted to syngas through other processes such as reforming or tar cracking, but this would add another costly operation step to an already complex process system. The controlling parameters of syngas production to note include the utilization of pure oxygen versus air feed, temperature range, particulate size, system pressure, residence times, as well as the feedstock to be used [38.9, 20]. The production of syngas from biomass for FT synthesis is normally associated

with high temperature, high oxygen content, small particle sizes, high pressure, and low residence times.

Co-firing of biomass with coal has been of recent interest in order to maximize the extent of the water-gas-shift reaction. *Kumabe* et al. observed that when a ratio of 0.5 (coal to biomass) was used, a maximum extent was observed [38.22]. If a further increase of the biomass ratio was introduced, an increase in the amounts of syngas and CO<sub>2</sub>, along with decreases in char, tar, and H<sub>2</sub> were seen. Conversely, CO and hydrocarbon concentrations were left unchanged [38.23].

Syngas has the ability to be used in a variety of processing schemes for a variety of products. Some of the more common conversion routes are FT synthesis, combined heat and power (CHP) technologies, hydrogen production, catalytic synthesis of methanol (and other alcohols), and fermentation to ethanol. The catalytic synthesis of methanol is an interesting option for use with syngas due to the ability of methanol to be used for a range of products such as formaldehyde, dimethylether, and acetic acid. Methanol can also be converted to gasoline when used as the feedstock for methanol to gasoline (MTG) processes [38.24, 25]. FT synthesis however, will be the only option explained in-depth within the confines of this discussion.

### Fischer–Tropsch (FT) Synthesis

FT synthesis is a technology that refers to the conversion of syngas to liquid hydrocarbons using a transition

**Table 38.3** Advantages and disadvantages of various gasifiers (after [38.18])

Gasifier type	Advantage	Disadvantage
Updraft	<ul style="list-style-type: none"> <li>● Small pressure drop</li> <li>● Good thermal efficiency</li> <li>● Little tendency towards slag formation</li> <li>● No carbon in ash</li> </ul>	<ul style="list-style-type: none"> <li>● Producer gas production</li> <li>● Poor reaction capability with heavy gas load</li> <li>● Relatively long time required for startup of internal combustion engine</li> <li>● Great sensitivity to tar, moisture, and moisture content of fuel</li> </ul>
Downdraft	<ul style="list-style-type: none"> <li>● Flexible adaption of gas production to load</li> <li>● Small-scale applications</li> <li>● Low sensitivity to charcoal dust and tar content of fuel</li> </ul>	<ul style="list-style-type: none"> <li>● Design tends to be tall</li> <li>● Not feasible for very small particle size of fuel</li> <li>● Producer gas production</li> </ul>
Cross-draft	<ul style="list-style-type: none"> <li>● Short design height</li> <li>● Very fast response time to load</li> <li>● Flexible gas production</li> </ul>	<ul style="list-style-type: none"> <li>● Very high sensitivity to slag formation</li> <li>● High pressure drop</li> </ul>
Fluidized	<ul style="list-style-type: none"> <li>● Large-scale applications</li> <li>● Feed characteristics</li> <li>● Direct/indirect heating</li> <li>● Can produce syngas</li> </ul>	<ul style="list-style-type: none"> <li>● Moderate tar yield</li> <li>● Higher particle loading</li> </ul>
Circulating fluid	<ul style="list-style-type: none"> <li>● Large-scale applications</li> <li>● Feed characteristics</li> <li>● Can produce syngas</li> </ul>	<ul style="list-style-type: none"> <li>● Moderate tar yield</li> <li>● Higher particle loading</li> </ul>
Entrained flow	<ul style="list-style-type: none"> <li>● Can be scaled</li> <li>● Potential for low tar</li> <li>● Can produce syngas</li> </ul>	<ul style="list-style-type: none"> <li>● Large amount of carrier gas</li> <li>● Higher particle loading</li> <li>● Particle size limits</li> </ul>



metal catalyst. The products that are formed from this process (depending on the type of catalyst used – iron (Fe) and cobalt (Co) being predominant) can include transportation fuels (diesel or jet fuels) as well as higher value chemicals (waxes, lubricants, alcohols, etc.). The FT process can involve a variety of chemical reactions that produce multiple hydrocarbon molecules, however, primary reactions forming species with the formula  $C_nH_{(2n+2)}$  (alkanes) are preferred. A block diagram of this FT synthesis pathway and the generalized products that form from the reactions can be seen in Fig. 38.5.

In order to avoid the production of methane ( $n = 1$ ) the process temperature is normally kept below  $400^\circ\text{C}$  while pressures are kept in the range of  $\approx 150\text{--}580$  psi. Lower temperature synthesis ( $\approx 200\text{--}240^\circ\text{C}$  with Co catalyst) will yield high molecular waxes while higher temperatures ( $\approx 300\text{--}350^\circ\text{C}$  with Fe catalyst) will yield low molecular weight olefins [38.26].

The generation of unreactive gases, short- and long-chain paraffins, olefins, and alcohols can all occur within the FT process. Paraffins produced tend to be straight-chain. However, the distribution of chain lengths (ranging from  $C_1$  up to  $C_{50}$ ) formed tends to be quite large. A positive fact to note with the production of these chains is that the chains will be predominately sweet (sulfur free) with low aromatic content, and can be further converted to automotive fuels through cracking, isomerization, or reforming. A route that has been taken to avoid the large distribution of chain lengths is to produce a more waxy material (larger carbon chains;  $> C_{30}$ ) that can then be cracked into the diesel range by hydrocracking followed by purification using standard petroleum refining techniques. As an example, it has been shown that the syngas that has been converted during this process can be used as a feedstock for the generation of diesel and jet fuels using proprietary techniques developed by companies such as Syntroleum, Rentech, among others.

One of the major hurdles that accompanies BTL fuel processing is the fact that the syngas feed for FT synthesis must be free of impurities as the catalyst system is highly sensitive and is easily deactivated. Multiple, complex purification steps must be used in order to separate the unwanted species such as tars, volatile species ( $\text{NH}_3$  and  $\text{HCl}$ ), sulfur compounds, fine particles, and ashes that normally accompany the syngas produced. The volatile stream derived from biomass gasification will also have a much lower  $\text{H}_2/\text{CO}$  ( $\approx 0.5$ ) ratio than what is normally preferred ( $\approx 2$ ) during FT synthesis [38.9]. Consequently, the gas stream is usually co-fed to an intermediate reactor with water in order to increase the  $\text{H}_2/\text{CO}$  ratio (WGS reaction). Steam reforming may also be used in order to adjust

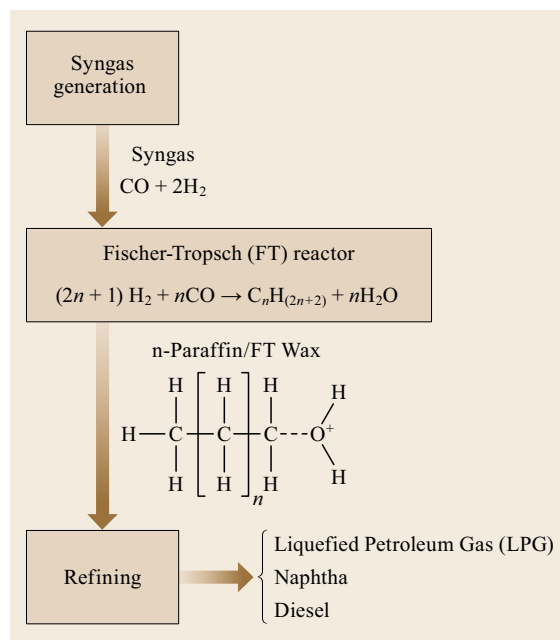


Fig. 38.5 FT synthesis schematic

the  $\text{H}_2/\text{CO}$  ratio if the  $\text{CH}_4$  content is high. This reaction will convert  $\text{CH}_4$  and  $\text{H}_2\text{O}$  to  $\text{CO}$  and  $\text{H}_2$  (Table 38.2).

One example of a multistage gasification unit for biofuel production that is able to utilize a variety of biomass feedstocks is a process developed by Choren. Although this process has had difficulties becoming completely commercialized, it has shown the potential to be expanded upon and optimized in order to be fully functional. In this process, the biomass is first reduced in size, followed by dehydration, before being sent to a relatively low-temperature ( $400\text{--}500^\circ\text{C}$ ) gasifier that forms the carbonization gas (syngas) along with tar and coke (solid state). This gas is then partially oxidized in a combustion chamber at high temperatures ( $> 1400^\circ\text{C}$ ) with a precise amount of oxygen during coke addition, increasing the yield of  $\text{CO}$  and aiding in the break down of the material. After cooling, particulates that are not completely converted to gas are separated, followed by stripping of chlorides and sulfides. The gas stream will then be ready for FT synthesis and ultimately, fuel production [38.27].

Liu et al. [38.28] has shown evidence with performance and cost analysis that the co-generation of FT liquid fuels using coal alongside lignocellulosic biomass can be produced *cost effectively*. These synthetic fuels provide lower GHG emissions and capital investments than a standard fossil fuel power plant implemented with  $\text{CO}_2$  capture. Fuels co-generated are also able to be produced cheaper than through a typical 1st-generation biofuels facility. The analysis shows that

it is possible to develop a scaled up biomass-derived FT fuel production facility with some further commercial optimization.

### 38.2.3 Pyrolysis (Route 3)

Pyrolysis differs from gasification by the fact that there is no air (specifically O<sub>2</sub>) present during the break down of the carbonaceous material. The products that are formed during pyrolysis will also differ from that of gasification. However, the processes do show some similarities due to the overlap in reactions taking place. A lack of gasification within a pyrolysis reactor is usually never possible, as complete absence of oxygen is usually impossible as well as the fact that some oxygen is released from biomass during the reactions taking place. Consequently, some gasification occurs during pyrolysis just as some pyrolysis occurs during gasification. The desired product from pyrolysis is the liquid pyrolysis oils (bio-oils) that rapidly condense from the vapors released. Some other less desirable products will also form as solid residues containing carbon and ash, as well as producer gases.

In order to produce the bio-oil during processing, fast pyrolysis is preferred that utilizes moderate temperatures ( $\approx 450\text{--}600\text{ }^\circ\text{C}$ ) at relatively high heating rates ( $< 2\text{ s}$ ) followed by rapid quenching [38.29, 30]. Slow pyrolysis will produce char rather than bio-oil as the main product. Moisture content should also be strictly controlled, as too little moisture will simply form dust; conversely, too much moisture will form gases, owing to the presence of oxygen from the breakdown of compounds such as water, promoting gasification.

#### Pyrolysis Oil (Bio-Oil)

Pyrolysis oil (bio-oil) is a dark brown, viscous liquid product that is obtained from the pyrolysis of biomass. This bio-oil has a large variation of components dependent on pyrolysis conditions and the composition of the feedstock. A variety of highly oxygenated compounds make up the bio-oil and can be broken down into groups as acids, alcohols, aldehydes, esters, ketones, and aromatic species, along with some unreacted polymeric carbohydrates and lignin fragments [38.31–33]. The typical components of pyrolysis oil is shown in Table 38.4.

The highly complex bio-oil mixture is chemically unstable and can be altered or even degraded during storage due to thermal equilibrium shifts. The quality of the bio-oil is also highly dependent on the starting feedstocks and the pyrolysis reaction conditions need to be tailored to the characteristics of the feed [38.34]. It

**Table 38.4** Typical component of pyrolysis oil (Bio-oil)

Component	(wt%)
Water	27
Ether-soluble organics (aldehydes, ketones, lignin monomers)	25
Volatile acids (mainly acetic)	5
Ether-insoluble organics (anhydrosugars, anhydro-oligomers, hydroxyacids)	28
Lignin derivatives, polymerization products and solids	15
Extractives ( <i>n</i> -hexane soluble organics)	4

**Table 38.5** Comparison of elemental composition of biomass-derived bio-oil and conventional crude oil (after [38.34, 36, 37])

Element (wt%)	Bio-oil	Crude oil
C	55–65	83–86
H	5–7	11–14
O	28–40	< 1
S	< 0.05	< 4
N	< 0.4	< 1

has been shown, however, that if the reaction conditions were tailored to each specific feedstock, the resulting compositions will have similar collections of cyclic hydrocarbons [38.35].

A comparison of the elemental compositions of bio-oil and crude oil has been made, shown in Table 38.5. Some observations can quickly be noted when comparing the elemental compositions of the two oil products. The conventional crude oils have extremely low oxygen content in comparison to the biomass-derived bio-oils that are intended to be co-fed. The high oxygen content within the biomass system can be attributed to the oxygenated functional groups that are prevalent within biomass. It is also estimated that roughly 15–30% of the components of the bio-oil is made up of water because of the high moisture content of the original biomass and the dehydration of the biomass that takes place during hydrolysis [38.38]. Accordingly, the high oxygen and water contents in the biomass-derived bio-oils will lower the heating values (half of that of hydrocarbon fuels) of the oil, and will also cause the streams to be immiscible when co-fed with petroleum-derived oils. For this reason, the products from pyrolysis must first be upgraded via hydrotreatment before being integrated into a petroleum refinery. This is similar to what petroleum-derived oils encounter when hydrotreatment is needed to remove impurities such as nitrogen and sulfur. In the case of biomass-derived bio-oils, however, the hydrotreatment will be used to remove oxygenated compounds.

### 38.3 Biomass Oil and Petroleum Oil Co-processing

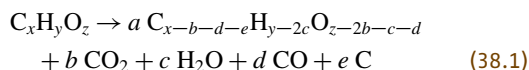
Biomass oils co-processed with petroleum cuts is a novel idea that has been formulated to overcome many of the hurdles that have been realized when developing processing routes that strictly use biomass for fuel production. If the pretreatment-hydrolysis route was simply used in conjunction with a fermentation-type process that converts the soluble sugars to alcohols many alterations would need to occur if the ties with petroleum were to be severed. The trillions of dollars that have been invested in infrastructure such as refineries, vehicles, and transportation networks would all be lost or have to be renovated. Work is still being conducted with regard to the thermochemical routes such as gasification and pyrolysis and being able to implement those technologies in more industrialized locations, as many undesired products are generated during the formation of the desired products.

In order to overcome these disadvantages it is theoretically possible to combine some of the newly developed technologies with the already-in-place petroleum infrastructure to develop biomass/crude co-processing. The idea would be to fractionate the biomass into its respective constituents (cellulose, hemicellulose, and lignin) and preferentially convert the materials by either liquefaction or catalytic conversion techniques. The products generated can then be combined with streams within the in-place petroleum or petrochemical refineries. The fact that biomass, once broken down, or pre-hydrotreated, has a very similar chemical composition and structure to the intermediate feed streams within a refinery makes this quite feasible.

This *co-processing* technique has the ability to add large quantities of feed to an already existent refinery stream with relatively low input in terms of capital costs as well as having a lower environmental impact compared to that which is normally synonymous with fossil fuels production. There are several options that can be used for co-processing that utilize the pretreatment-hydrolysis route, thermochemical route (gasification or

pyrolysis), or even a combination of the two, to generate a feedstock that can be supplemented into the refinery operations.

Fogassy et al. [38.39] has developed a representative reaction scheme (1) for the removal of oxygen in the bio-oil, forming the products CO<sub>2</sub>, CO, C, and H<sub>2</sub>O.



During this processing route a mixture containing 80 wt% vacuum gas-oil (VGO) and 20 wt% hydrodeoxygenated bio-oil was processed in a fluidized catalytic cracking (FCC) unit. The majority of the oxygen within the material was said to be removed in the form of CO<sub>2</sub> and H<sub>2</sub>O by means of decarboxylation and dehydration reactions [38.39]. The impact of this release of CO<sub>2</sub> and CO that is produced during the co-hydrotreatment of petroleum gas oil and lignocellulosic biomass oil has been investigated and it was shown that it can be attributed to some inhibition within the hydrodesulfurization and hydrodenitrogenation reactions [38.40].

Elliot et al. [38.35] have shown that they can dramatically increase the C/O ratio (Table 38.6) over the course of various treatments of bio-oils that could be co-fed into a refinery. The lowest severity treatment, simply hydrotreating the bio-oil (A), focused on low temperatures with a palladium-on-carbon catalyst. The next two treatments made efforts to maximize the C/O ratio. In the first of these cases (B), the oil phase products of the hydrotreated bio-oil were subjected to hydrocracking, where lower pressures and higher temperatures were applied with a sulfide-form catalyst as opposed to directly hydrocracking the bio-oil products. In the second case, nonisothermal hydroprocessing (C) involves a low-temperature hydrotreatment followed by a high-temperature hydrocracking of the bio-oil products without an intermediary product phase separation

**Table 38.6** Ultimate analysis of biomass feed (mixed wood, corn stover, oak, and poplar) and biomass-derived bio-oils, as well as three types of treatment: (A) Hydrotreated bio-oil, (B) Hydrocracked bio-oil, and (C) Nonisothermal hydroprocessed bio-oil (after [38.35])

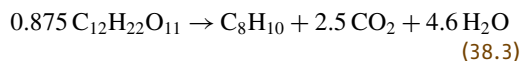
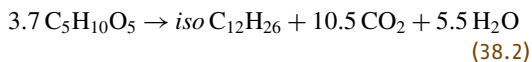
Ultimate analysis (wt%)	Biomass feed		Bio-oil (Moisture free)		(A) Hydrotreatment		(B) Hydrocracked		(C) Nonisothermal hydroprocessing	
	Average	+/-	Average	+/-	Average	+/-	Average	+/-	Average	+/-
C	43.6	9.4	57.9	8.2	75.4	1.5	87.0	0.5	87.6	0.2
H	7.4	0.5	6.2	0.5	9.2	0.6	12.3	0.4	11.7	0.2
O	46.8	7.9	31.9	4.5	14.1	2.3	0.5	0.2	0.4	0.2
N	0.5	0.4	0.6	0.5	1.3	1.1	0.4	0.2	0.2	0.2
S	0.1	0.1	n/a	n/a	0.1	0.1	0.0	0.0	0.0	0.0
C/O	0.93		1.81		5.33		174		202	

processing step. Work is ongoing with regards to optimization of the hydrodeoxygenation, catalytic cracking, and reforming techniques that would enable fully functional integration of the bio-oils into the refining process.

Al-Sabawi et al. [38.41, 42] reviewed co-processing of petroleum-derived and biomass-derived oils to produce clean transportation fuels via FCC [38.41] and hydroprocessing (such as hydrotreating and hydrocracking) [38.42]. The effect of biomass feedstocks on process operations, catalyst performance and deactivation, and product yield and quality were discussed. Even with the added benefit of the ability to use existing refining infrastructure and configurations that offer both economic and environmental advantages, many technical challenges remain. These include the low thermal stability of the bio-oil, compatibility of co-fed feedstocks, effects of the formed water on catalyst activity and stability, corrosion, mass and heat transfer properties, as well as quality and performance of fuels. Thermal stability is one of the biggest issues – the material cokes rapidly under reaction conditions or even in preheaters before reaching the reactor.

### 38.3.1 Aqueous Phase Reforming (APR) – Virent

Virent has developed reaction schemes for the conversion of sugars such as xylose and sucrose into hydrocarbons when utilizing their proprietary catalyst technologies [38.43]. These sugars can be derived from a multitude of biomass feeds by way of the pretreatment-hydrolysis technique, as has been noted. An efficient fractionation technology will be imperative for moving this technology further as it would be preferable to deal with a purified sugar source during these catalytic reactions. The following representative pathways (38.2) and (38.3) are used by Virent for the conversion of sugars, particularly xylose and sucrose, to hydrocarbons



As seen, the xylose  $\text{C}_5\text{H}_{10}\text{O}_5$  sugars can be converted to branched  $\text{C}_{12}$  hydrocarbons and used as a product such as jet fuel, while the sucrose  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  can be converted to the high-octane xylene ( $\text{C}_8$ ) that can be used in gasoline blending [38.42]. The overall process that is in development consists of a multistage conversion for production of gasoline-range hydrocarbons: aqueous phase reforming (APR) of the carbohydrate sugars (glucose, xylose, etc.) and hydrolysates,

catalytic conversion, and fractionation into purified gasoline products. There are a multitude of reactions that are occurring during the APR process that include:

- Reforming to generate hydrogen
- Deoxygenation reactions – dehydration (alcohols), decarbonylation (ketones/aldehydes) and decarboxylation (acids/esters)
- Hydrogenolysis
- Cyclization.

Accordingly, the products formed can be further upgraded using a modified ZSM-5 catalyst to generate a high-octane gasoline, similar to that of the petroleum-derived reformat stream. What makes this processing ideal is the functionality of the products that are developed and the fact that these *drop-in* fuels can potentially replace over 90% of the products that come from a barrel of crude oil. Relatively little infrastructure will need to be implemented and almost none will need to be altered or replaced for the processing of the sugars (i. e., glucose via cellulose; primarily xylose, along with smaller quantities of arabinose, mannose, glucose, and galactose via hemicellulose – see Sect. 38.1) derived from biomass. This is because of the similar chemical compositions of the fuels derived from biomass to that of petroleum-derived fuels along with the in-place technologies that have the ability to upgrade these intermediary chemicals into the necessary feeds for refinery integration.

### 38.3.2 Pretreatment-Hydrolysis/ Thermo-conversion Co-processing

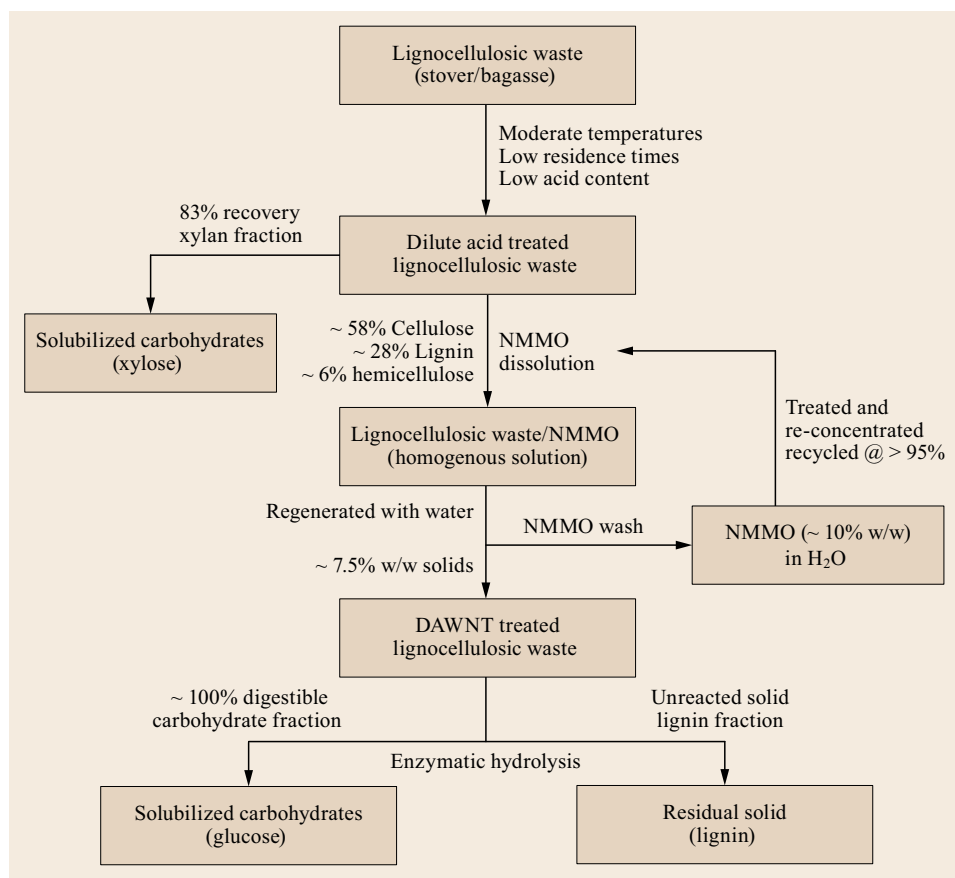
Now, a basis has been set for the idea of breaking down biomass material into purified fractions and then converting or upgrading these fractions through one of the aforementioned processing techniques. We can begin to think about how this can be done. A fractionation scheme that is currently in development utilizes a dual treatment of a lignocellulosic waste stream followed by enzymatic hydrolysis of that waste which is able to theoretically separate the majority of the constituents into three streams [38.44]. In applying this method, the biomass is first fractionated then the various thermochemical conversion techniques can be applied to upgrade these fractions individually where the products will begin to be representative of the crude streams within a petroleum refinery. It is at this point, that the biomass-derived oils and gases could potentially be co-processed with the streams within a refinery. An introduction of these methods will be discussed, followed by a generalization of the conversion method and results.

The first of the pretreatments is a dilute sulfuric acid (DA) treatment that is considered a well-established pretreatment technology within the biomass research community. This method of treatment has been extensively reviewed and refined by several groups and has been established as being able to not only enhance the ability of enzymatic hydrolysis, but also solubilize the majority of the short-chain hemicellulosic structure while leaving the long-chain cellulosic and lignin structures relatively intact for further processing due to the low severity of the treatment [38.10, 45–47]

Next, *N*-methyl morpholine *N*-oxide (NMMO) is used as a solvent to dissolve the DA-treated biomass for a short period of time (< 3 h) followed by an antisolvent regeneration step that will wash away the solvent and precipitate the biomass out of solution. The utilization of NMMO as a pretreatment is a relatively new technique, although it has been used predominately to treat purified cellulose within the fiber industry for several decades by generating Tencel fibers. The effects of this solvent on the lignocellulosic structure of biomass has been of recent interest. What has been discovered is the fact that NMMO is able to effectively and

efficiently decrystallize the cellulosic fibers and swell the lignocellulosic structure to increase the accessible hydrolyzable area for enzymatic attack. The result is that multiple groups have shown that the treatment of biomass with NMMO is able to enhance the rate of hydrolysis of cellulose by fungal enzymes [38.48–51]. However, the point of this discussion is the synergistic utilization of these two treatments to enhance the fractionation and conversion capabilities so that they can enhance the generation of intermediary products where one of the aforementioned conversion techniques will be employed to generate a feed ready for co-processing with crude oil.

The purified product streams generated from this dual treatment (dilute acid with NMMO treatment, or DAWNT) can be fractionated as follows: soluble hemicellulosic sugars (mixture of pentoses and hexoses), soluble cellulosic sugars (mainly glucose – hexose), and a residual solid lignin fraction according to the process design shown in Fig. 38.6. Fractionation is not new to biomass conversion practices, but the idea of a fractionation after enzymatic hydrolysis due to the highly digestible substrate may be considered a novel



**Fig. 38.6** Dilute acid with NMMO treatment (DAWNT) processing of lignocellulosic wastes (after [38.44])

technique. The DAWNT (dilute acid with NMMO treatment) method that uses this type of methodology can be summarized by the following criteria:

- DA Treatment [38.46]
  - $\approx 83\%$  of the hemicellulosic sugars will be solubilized and separated
  - Composition of processed solids: 58% cellulose, 28% lignin, and 6% hemicellulose
- NMMO Treatment [38.10, 44, 52, 53]
  - Unaltered solid composition
  - Highly digestible cellulosic fractionation
- NMMO swells cellulosic fibers enhancing enzymatic digestibility
- NMMO processing can be done at short time scales due to effects based solely on dissolution that occur rapidly due to the initial DA treatment
  - NMMO can be recycled at a rate of  $> 95\%$  while keeping the same treatment efficiency
- Enzymatic Hydrolysis [38.10, 44]
  - $\approx 100\%$  cellulosic conversion to soluble sugars within 48 h at low enzyme concentrations (10 mg<sub>C<sub>Tec2</sub></sub>/g<sub>glucan</sub> enzyme loading)

- The remaining hemicellulosic fraction will also be converted here
- Residual solid lignin fraction and liquid sugar fraction can be easily separated.

This process is currently in development, but one can start to think about the potential applications when moving forward. Solubilized glucose, generated after enzymatic hydrolysis can easily be purified and used with either current 1st-generation conversion techniques or implemented into catalytic reforming processes, such as APR. The solubilized hemicellulosic-derived sugar fraction that is separated during the first treatment can potentially be used in an APR process, as was explained previously. The residual solid lignin fraction can be used in a thermo-conversion process such as gasification or pyrolysis after the solids are extracted post hydrolysis. If the pyrolysis route was to be used, bio-oil could be formed followed by mixing with the vacuum gas oil stream within a refinery process. Consequently, each of these methods will convert the starting biomass material into a usable hydrocarbon fuel, while utilizing the majority of the feedstock.

## 38.4 Conclusion

The majority of the conversion methods discussed here are still in their infancy and have not yet been fully investigated or refined. What can be taken away from this discussion is the fact that it is possible to convert biomass into a usable hydrocarbon fuel through co-processing without the need to convert the already in-place infrastructure and addition of significant capital investment to build independent continuous units (biorefineries). This is highly favorable over other alternative energy routes that would require alterations to an established billion dollar industry as well as an already developed trillion dollar infrastructure, but can simply be subsidized with biomass oil as a feedstock.

There appears to have been no significant breakthrough in 2nd-generation biomass-to-liquid processes in recent years [38.54]. Fractionation of biomass into digestible cellulosic sugars for fermentation and insoluble lignin for pyrolysis/gasification followed by Fischer-Tropsch and co-processing with petroleum oils might provide an alternative for further process development. Cellulose/lignin fractionation would also facilitate the development of new generation characterization schemes for detailed molecular compositional analyses of feedstock, process streams, and products of biofuel/chemical production.

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