Chapter 9

Sustainable Multipurpose Biorefineries for Third-Generation Biofuels and Value-Added Co-Products

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Additional information is available at the end of the chapter

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1. Introduction

The transition to third-generation biofuels is driven by the need to integrate biomass-derived fuels more seamlessly into the existing petroleum based infrastructure. Ethanol, whether derived from corn or sugarcane in first-generation processes or biomass in second-generation facilities, has limited market access due its dissimilarity to conventional petroleum-derived fuels. Limitations include restrictions on ratios in which ethanol can be blended with gasoline, lack of compatibility with diesel and jet engines, inability to transport ethanol through existing pipeline network, and propensity to absorb water. While it is clear that biomass can provide a sustainable and renewable source of carbon to replace a significant portion of petroleum resources currently used to generate fuel, power, and chemicals [1,2], it is also obvious that technologies must be developed to convert biomass into direct replacements for petroleum products. This transition from first- and second-generation biofuels to third-generation biofuels will involve numerous facets [3], the centerpiece likely being a multipurpose biorefinery that utilizes many inputs and produces an even greater number of outputs. The first steps to incorporating each of the individual platforms into one integrated sustainable operation are well underway [4], and this transition promises to be a continuing evolution.

First-generation biorefineries use feedstocks such as corn starch or sugar cane that are renewable, but that also have feed/food uses. As production levels have increased, along with human populations, concerns about competition with food needs have arisen [5,6]. Nevertheless, over the past 30 years these first-generation feedstocks have paved the way for production of biofuels via a more sustainable system without negative impacts on the environment or food supplies [3]. Second-generation biorefineries are based on biomass feedstocks that are more widely available and that are not directly used as food, although some are used as livestock

feed. Technologies are under development to efficiently convert biomass into ethanol as well as valuable co-products. These are leading the way to sustainably meeting energy needs while also supplying materials for chemical and manufacturing industries [3]. Biomass has the unique advantage among renewable energy sources that it can be easily stored until needed and provides a liquid transportation fuel alternative for the near term. However, cellulosic ethanol can displace only the 40% of a barrel of crude oil that is used to produce light-duty gasoline. Research, development, and demonstration on a range of technologies are needed to replace the remaining 60%, which is primarily converted to diesel and jet fuel. About 15% of our current crude oil consumption is used to produce solvents, plastics, cleaners, and adhesives [7]. Thus, cost-effective technologies are needed to produce biofuels that are suitable for drop-in use in cars, trucks, and jet planes. These advanced biofuels can be sustainably produced from cellulosic and algal feedstocks. Biomass conversion technologies are also needed to produce chemical intermediates and high-value chemicals. Compatibility with the existing infrastructure will aid in process integration and increase profitability of biorefineries [7].

Biorefining has been defined as the sustainable processing of biomass into a spectrum of marketable products and energy [3,5]. The biorefinery of the future will conduct many types of processes, including those producing advanced biofuels, commodity chemicals, biodiesel, biomateials, power, and other value-added co-products such as sweeteners and bioinsecticides. With the tools provided by molecular biology and chemical engineering, the types of co-products, chemicals and biofuels that can be derived from biomass may be almost limitless. Biorefineries combine the necessary technologies for fractionating and hydrolyzing biological raw materials with conversion steps to produce and then recover intermediates and final products. The focus is on the precursor carbohydrates, lignins, oils, and proteins, and the combination of biotechnological and chemical conversion processes of the substances [8]. Most of these processes are being developed individually, but have the potential to be more efficient and economical when combined in multi-process crossover regimens using by-products or waste materials from one process to produce advanced animal feeds, human nutritional supplements, high-value peptides, or enzymes needed in other processes [4]. Use of existing infrastructure would significantly decrease the ramp-up time for economical large-scale production of advanced biofuels [7,9].

To fully meet the requirement for safe and sustainable energy production, third-generation biorefineries must be better integrated, more flexible, and operate with lower carbon and economic costs than second-generation facilities [5]. The main areas that must be addressed are biomass production and supply, process optimization and integration, and overall sustainability [10-12]. Technology is developing rapidly in these areas. A major task is to identify the most promising bio-based products, in particular food, feed, value-added materials, and chemicals to be co-produced with energy to optimize overall process economics and minimize overall environmental impact [13]. Challenges to achieving the promise of advanced biofuels include: overcoming biomass recalcitrance, addressing logistics of transportation of raw feedstock and finished products, providing fair prices for crops or agricultural residues, and tailoring crops and production to specific environments and cultures [14].

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2. Biomass production and supply logistics

Feedstock costs represent a large part of biorefinery operating costs, therefore availability of an affordable feedstock supply is crucial for the viability of every biomass processing facility. Economics of biomass production vary with location, feedstock type, political policies, current infrastructure, and environmental concerns. Biofuels may be derived from forestry (thinning and logging), agriculture (residues or dedicated biomass crops), municipal wastes, algal-based resources, and by-products or waste products from agro-industry, food industry, and food services [15]. A key factor is to identify biomass resources that are sustainable because they require minimal water, fertilizer, land use, and other inputs. Feedstocks must be high in energy content, be easy to obtain in large quantities, and be amenable to the conversion processes. Intensive research is in progress on technologies to deliver high-quality, stable, and infrastructure-compatible feedstocks from diverse biomass resources to biorefineries [7].

A strategic analysis was performed in 2005 [16] and updated in 2011 [1] that identified sufficient biomass feedstock availability across the United States to meet near-term and potentially long-term bioenergy goals. The assessment took into consideration environmental sustainability and identified likely costs, assuming a farm-gate or roadside feedstock price of $40-$60 per dry ton. The study did not include additional costs for preprocessing, handling, and transporting the biomass, as these are specific to the feedstock, its condition and form, the type of handling system, and storage conditions. The analysis also did not account for feedstock density or proximity to potential processing facilities. The feedstocks evaluated were those that are currently produced from agriculture and forestry sources, including grain crops (mainly corn for ethanol, sorghum, and barley), sugarcane, sugar beets, oil crops (primarily soybeans for diesel), canola, sunflower, rapeseed, municipal solid wastes, fuelwood, mill residues, pulping liquors, and urban wood wastes, as well as potential forest and agricultural biomass and waste resources. Under conservative assumptions, the combined resources from forests and agricultural lands, assuming feedstock prices of $40-$60 per dry ton, will increase from 138-258 million dry tons in 2012 to 243-767 million dry tons by 2030 [1]. Total energy crops, including perennial grasses such as switchgrass and miscanthus, woody crops such as poplar, willow, southern pine, and eucalyptus, and annual energy crops such as high-yield sorghum, are projected to contribute significantly to this increase, going from less than 4 million dry tons in 2012 to 34-400 million dry tons in 2030. Energy crops have the potential advantages of being produced on marginal lands not used for growing food, requiring essentially no fertilizers or irrigation, and, especially if perennial, requiring little or no tilling [1].

Although sufficient biomass supply is potentially available, continued improvements in biomass feedstocks worldwide are required to achieve viable third-generation biorefineries [5]. Feedstock production improvements include maximizing yield, nutrient (N, P, and K) and water efficiency, and sustainability of production (an area with high potential for rapid gains). Screening of plant species and plant breeding is critically important to increase efficiency of biomass production while minimizing inputs, maintaining soil fertility, managing water

balance, and controlling invasiveness. Techniques to estimate the biomass production potential and to evaluate the impacts and sustainability of production in a given location are required. Logistic-related improvements include increasing efficiency of harvest, addressing the issue of seasonality to provide continuous supply, and ensuring that biomass cultivation helps drive regional development. Costs in transporting biomass to the biorefinery can be reduced by using optimized harvesting equipment, appropriate preparation for shipment, and efficient collection, storage, and transfer networks, especially for multi-feedstock biorefineries [5]. Processing improvements include optimizing the composition and properties of biomass for handling and transport to meet downstream quality requirements, along with imparting traits such as greater digestibility for ease of conversion (an area where basic research has made inroads). New technologies are reducing the cost of preparing biomass for conversion. Each step of the preparation is designed to develop next-generation feedstocks. Mechanical treatments reduce the size of the feedstock, providing fractionation and separation. Thermal and chemical processes control moisture content, remove contaminants, and improve digestibility and stability to reduce fouling in process equipment. Treated or untreated biomass is typically blended or mixed in specific proportions, often with additives to improve conversion efficiency. Temperature and pressure are used to form a high-density, stable feedstock for efficient storage and transport [7].

3. Third-generation biofuels

Advanced biofuels were defined by the Final Rule from the United States Environmental Protection Agency (EPA) Renewable Fuel Standard (RFS) Program as being renewable fuels, other than ethanol derived from corn starch, for which lifecycle greenhouse gas emissions are at least 50% less than the gasoline or diesel fuel it displaces [17]. Advanced biofuels may include any of the following: 1) ethanol derived from cellulose, hemicellulose, or lignin; 2) ethanol derived from sugar or starch (other than corn starch); 3) ethanol derived from waste material, including crop residue, other vegetative waste material, animal waste, food waste, and yard waste; 4) biomass-based diesel; 5) biogas (including landfill gas and sewage waste treatment gas) produced through the conversion of organic matter from renewable biomass; 6) butanol or other alcohols produced through the conversion of organic matter from renewable biomass; 7) other fuel derived from cellulosic biomass. Typically, advanced biofuels are used for transportation, although some may be used in generators to produce electricity and others may eventually replace propane and heating oils [14]. Alcohol can substitute for gasoline in spark ignition engines; biodiesel, green diesel, and dimethyl ether can be used in compression ignition engines; Fischer-Tropsch process produces a variety of hydrocarbon fuels, the main one is a diesel-like fuel for compression ignition engines [15].

Third-generation biofuels, also referred to as drop-in biofuels, are considered advanced biofuels [17]. Third-generation biofuels are direct replacements for gasoline, diesel, and jet fuels currently produced from petroleum, and are, in fact, chemically identical to their petroleum-derived counterparts. This allows third-generation biofuels to be directly substituted for petro-fuels without any alterations to pipelines and infrastructure used to deliver the

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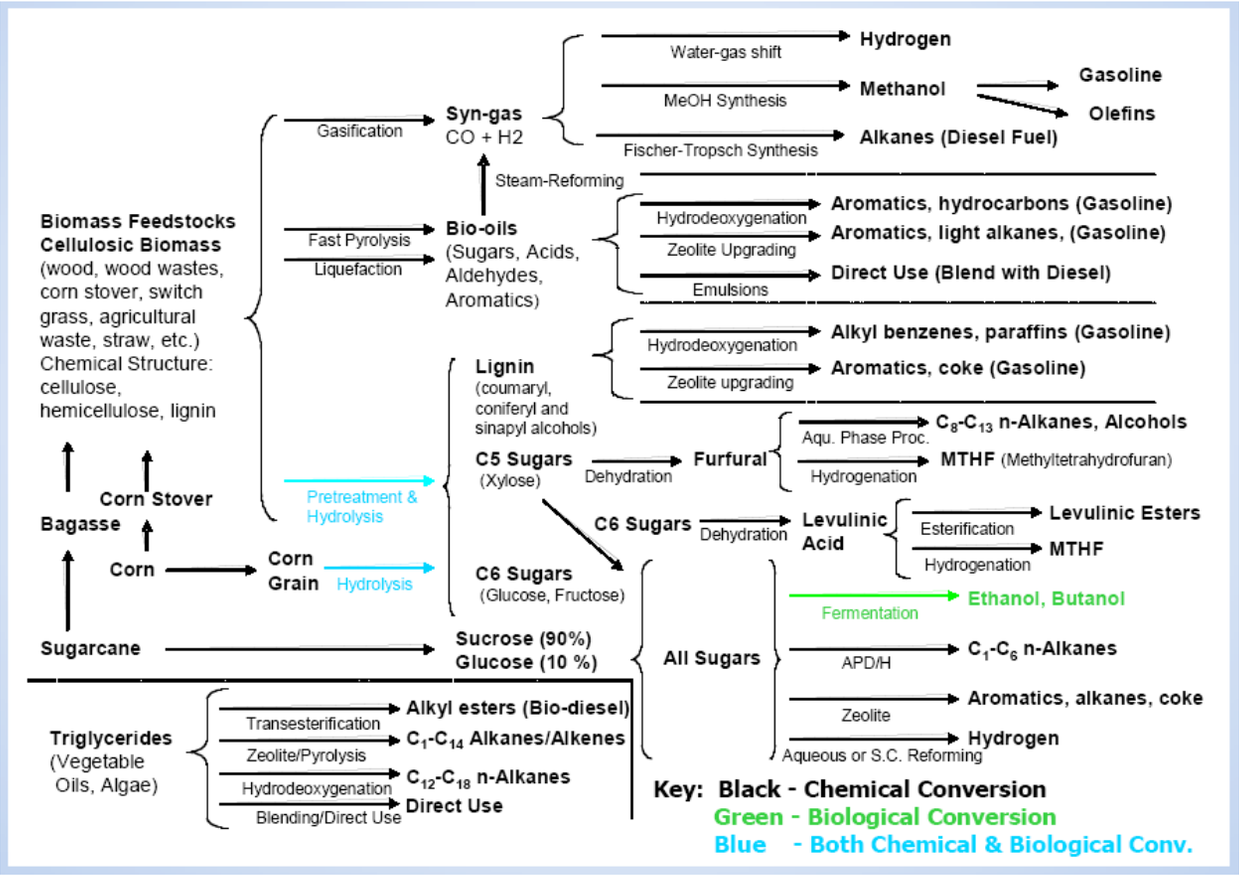
fuel, nor modifications to the engines in which the fuel will be burned. These infrastructure-compatible fuels are derived from biomass or algae, typically through thermochemical processes, although some biochemical processes are being developed as well. These fuels deliver more energy per gallon than ethanol, and conversion processes also yield a range of co-products that help to enhance the economic and environmental sustainability of biorefineries. The knowledge gained and technological advances made through research on cellulosic ethanol have accelerated advances for third-generation biofuels. The previous research on cellulosic feedstock supply, pretreatment, and logistics has helped to improve feedstocks for third-generation biofuels. Similarly, technologies to break down biomass for further processing can be applied to the processing of advanced biofuels. Research on subsequent processing of intermediates and by-products into high-value biological products and chemicals is critical to improving the profitability of third-generation biorefineries [7].

4. Biomass conversion technologies

Lignocellulose is the least expensive and most abundant form of biomass and is cheaper than crude oil on an energy basis. Technically it is possible to convert cellulosic materials and organic wastes into biofuels. Commercialization is limited because low-cost processing technologies that efficiently convert a large fraction of the lignocellulosic biomass energy into liquid fuels have not been developed to date. Thus, it is essential to continue focused research on processes to efficiently and economically convert lignocellulosic biomass into liquid fuels. Three basic routes for this conversion are 1) gasification of biomass to syngas ($CO + H_2$) and further conversion of syngas to liquid fuels, 2) fast pyrolysis or liquefaction of biomass to produce bio-oils followed by upgrading or blending for use as fuels, and 3) hydrolysis of biomass into sugar and lignin monomer units for conversion to targeted products [18]. The conversion technologies for producing liquid biofuels from biomass are outlined in Figure 1.

4.1. Hydrolysis of biomass and fermentation of sugars

Sugar streams for fermentation to biofuels can be obtained directly as sucrose from crops such as sugar cane, sweet sorghum, or energy beets. Alternatively, hydrolysis of starch crops yields glucose and hydrolysis of biomass yields glucose, xylose, and small amounts of other five carbon sugars. Lignocellulosic biomass is composed of cellulose, hemicelluloses, lignin, and proteins bound together in a complex structure that is recalcitrant to enzymatic hydrolysis by cellulase and hemicellulase enzymes. A pretreatment step is required to render the lignocellulosic biomass susceptible to the action of these hydrolytic enzymes [19]. Many factors, such as lignin content, crystallinity of cellulose, and particle size affect the digestibility of biomass. In theory, the ideal pretreatment process produces a disrupted, hydrated substrate that is easily hydrolyzed, but avoids formation of sugar degradation products and fermentation inhibitors. Various pretreatments have been proposed including comminution; delignification by white-rot fungi; chemical pretreatment with acids, alkali, organic solvents or ionic liquids; combined thermal/chemical pretreatment with steam, dilute acid, ammonia, or lime; organosolv-based fractionation treatments; and carbon dioxide or steam explosion [19,20]. Steam pretreatment,



Liquid biofuel production processes use either biochemical or chemical catalysts. Biological catalysts, such as yeast to produce ethanol, are homogenous catalysts in the same liquid phase as the biomass feed. Chemical catalysts range from homogeneous acids to solid heterogeneous catalysts. (Reproduced from [9]; Adapted from [18])

Figure 1. Production of Liquid Biofuels

lime pretreatment, liquid hot water pretreatments and ammonia based pretreatments appear to have the most advantages for biorefinery applications. The main effects are dissolving hemicellulose and altering lignin structure, providing improved accessibility for hydrolytic enzymes [21]. Because the pretreatment process is typically the second most expensive unit cost in the conversion of lignocellulosic biomass, careful analysis and optimization of this process has the potential to significantly reduce biorefinery costs [19].

Genetic engineering of industrial microbes so they are capable of using lignocellulosic feedstocks of variable composition and without catabolite repression is crucial for development of third-generation biorefineries. Since most microbes possess carbon catabolite repression, mixed sugars derived from the lignocellulose are consumed sequentially, reducing the efficacy of the overall process. To overcome this barrier, microbes that exhibit the simultaneous consumption of mixed sugars have been isolated or developed and evaluated for the lignocellulosic biomass utilization. Specific strains of *Escherichia coli*, *Saccharomyces cerevisiae*, and *Zymomonas mobilis* have been engineered for simultaneous glucose and xylose utilization via mutagenesis or introduction of a xylose metabolic pathway. Other microbes, such as *Lactoba-*

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cillus brevis, *L. buchneri*, and *Candida shehatae* possess a less stringent carbon catabolite repression mechanism and show simultaneous consumption of glucose and xylose. Using these phenotypes, various integrated processes have been developed that incorporate both enzyme hydrolysis of lignocellulosic material and mixed sugar fermentation, thereby enabling greater productivity and fermentation efficacy [22,23]. In addition to utilizing multiple substrates, these microbes must tolerate toxic substrate impurities such as by-products from feedstock pretreatment and hydrolysis, as well as potentially inhibitory products produced by the fermentation reaction itself.

At the present time, most recombinant strains for biorefinery applications are based on *E. coli* and *S. cerevisiae* because these organisms have been extensively studied and are relatively easy to engineer with well-developed genetic tools and established physiology [24]. However, the limited range of materials that can be fermented remains an obstacle to cost-effective bioethanol production in spite of substantial investments over the last 30 years in worldwide efforts to engineer xylose utilization in these strains [25,26]. Although several genetically engineered strains of *S. cerevisiae* have been developed that will ferment xylose to ethanol [27-29], further optimization is needed. It will require the simultaneous expression at sufficiently high level of all the enzymes and proteins needed to allow industrial yeast strains to efficiently metabolize pentose as well as hexose sugars under anaerobic conditions. In addition, for cost-effective industrial ethanol production from biomass it will be necessary to express the enzymes required to saccharify the lignocellulosic feedstocks that are the source of hexose and pentose sugars. Genes considered necessary for complete fermentation of xylose and arabinose, the two major pentose sugar constituents of lignocellulosic biomass, include those encoding xylose isomerase (XI), xylulokinase (XKS), arabinose A, arabinose B, and arabinose D [27,29,30]. These genes may be obtained from microorganisms naturally capable of metabolizing these sugars. Saccharification of lignocellulosic feedstocks also requires utilization of hydrolytic enzymes including cellulases and hemicellulases after initial chemical pre-treatment [31,32]. The cost-effectiveness of the fuel ethanol fermentation process could be further enhanced by obtaining high-value co-products and by-products from the process, such as monomers for polymer production and commercially important proteins and peptides. Genes for these proteins and peptides can be mutagenized, placed in an expression system capable of producing high levels of functional proteins or peptides, and screened in high throughput to optimize desired characteristics. [33-36].

Although extensive efforts have been made to engineer *E. coli* and *S. cerevisiae* to use both hexose and pentose sugars [22,37-40], substrate versatility remains a significant issue. Therefore, other strains are being investigated. For example, *Clostridia* strains possess exceptional substrate diversity, utilizing simple and complex carbohydrates, such as cellulose, as well as CO_2/H_2 or CO. In addition, they contain a wide variety of extracellular enzymes to degrade large biological molecules (cellulose, xylans, proteins, lipids) and produce a broad spectrum of chemicals that can be used as precursors to, or directly as, biofuels and industrial chemicals [22,41-43]. *Clostridia* are found in virtually all anaerobic habitats containing organic matter and thus have developed the ability to ferment mono- and disaccharides as well as complex polysaccharides like cellulose and hemicellulose, which makes them ideal platforms for

fermenting biomass feedstocks. They produce metabolites such as butyrate, acetate, lactate, caproate, butanol, acetone, acetoin, ethanol, and many more [24]. *Clostridia* are anaerobic microbes producing a large array of metabolites by utilizing simple and complex carbohydrates, such as cellulose, as well as CO_2/H_2 or CO. Efforts are underway to develop genetic and genomic tools for these microbes, and recent efforts to metabolically engineer *Clostridia* demonstrate their potential for biofuel and biorefinery applications. Pathway engineering to combine established substrate-utilization programs with desirable metabolic programs could lead to modular design of strains suitable for many applications. Engineering complex phenotypes--aerotolerance, abolished sporulation, and tolerance to toxic chemicals--could lead to superior bioprocessing strains [24].

Another significant challenge in using wild-type microbes to convert feedstocks into advanced biofuels is to overcome their endogenous regulation of biofuel-producing pathways that limits yields and productivities. Reconstruction of advanced biofuel pathways in specific heterologous hosts has worked, but use of data-driven and synthetic-biology approaches could further optimize both the host and the pathways to maximize biofuel production from a broader range of substrates. Research will undoubtedly lead to the creation of additional metabolic engineering techniques that can be used to improve pathway flux, and to additional synthetic-biology approaches to optimize microbial hosts for successful commercialization of third-generation biofuels [44,45].

4.2. Gasification

Ethanol and third-generation biofuels can also be produced by a process called gasification. Gasification systems use high temperatures and a low-oxygen environment to convert biomass into synthesis gas, a mixture of hydrogen and carbon monoxide. The synthesis gas, or "syngas," can then be chemically converted into biofuels using the Fischer-Tropsch process or newer advanced catalytic processes. For example, Schmidt and co-workers [46] have combined the three reactions of older thermal gasification processes into a single, small reactor in which gasification takes place over a catalyst to directly produce third-generation biofuels. Synthesis gas can also be microbially converted into biofuels, although the low product tolerance of the microbes has been a limiting factor.

4.3. Pyrolysis

Biomass pyrolysis is the thermal depolymerization of biomass at moderate temperatures in the absence of added oxygen. The biomass is initially converted to a mixture of liquid (pyrolysis oil), solid (biochar), and gaseous fractions that can be used in the production of fuels and chemicals. Fractionation of the pyrolysis oil results in various qualities of oil needed for further upgrading into fine chemicals, automotive fuels, and energy [13]. An updated pyrolysis approach developed by Huber and co-workers uses catalysts to convert biomass into high-octane gasoline-range aromatics in a single step [47,48]. Pyrolysis conditions can be adjusted to optimize the production or chemical composition of a given fraction [49,50].

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4.4. Transesterification of oils and fats to biodiesel

Esterification and transesterification have been used for more than a decade to produce biodiesel from plant or animal-derived lipids. Any feedstock that contains free fatty acids and/or triglycerides such as vegetable oils, waste oils, animal fats, and waste greases can be converted to biodiesel. However, the product must meet stringent quality standards [51]. Consequently, fuel standards such as ASTM D6751 in the United States and EN 14214 in Europe have been implemented to ensure that only high quality biodiesel reaches the marketplace. Similar standards have been adopted elsewhere. Acquisition of refined commodity oils such as soybean oil may account for more than 80% of the cost to produce biodiesel. As a consequence, inexpensive, non-food feedstocks are critically important to improve process economics. Such low-value feedstocks often contain contaminants such as moisture and free fatty acids that render them incompatible with simple, homogeneous, alkaline-catalyzed transesterification. In such cases, alternative methods such as heterogeneous acid catalysis are needed for efficient conversion to biodiesel. An economic comparison between different conversion methods utilizing low-value feedstocks revealed that the heterogeneous acid catalyst process had the lowest total capital investment and manufacturing cost. For biodiesel to expand and mature in the market a number of key issues must be addressed, such as improving production efficiency through development of cost-effective catalysts capable of converting low-quality feedstocks into biodiesel, enhancing availability of low cost feedstocks, and managing agricultural land and water. In addition, biodiesel will require continuous improvement in producing cleaner emissions and reducing environmental impacts, although some of these issues are addressed by exhaust after-treatment technologies such as exhaust gas recirculation (EGR) and selective catalytic reduction (SCR) [52].

4.5. Technologies to convert carbohydrates into mixed hydrocarbons

Dissolved sugars can also be converted into hydrocarbons through routes that resemble petroleum processing more than fermentation. Researchers have developed several technologies in which dissolved sugars react in the presence of solid-phase catalysts under carefully controlled conditions (to avoid unwanted by-products) to produce targeted ranges of hydrocarbons for use as fuels or chemical feedstocks [53,54]. Genetically altered microorganisms have also been developed that ferment sugars into hydrocarbons instead of alcohols [55]. Genes were isolated that, when expressed in *Escherichia coli*, produce alkanes, the primary hydrocarbon components of gasoline, diesel and jet fuel. If commercialized, this single step conversion of sugar to fuel-grade alkanes by a recombinant microorganism would lower the cost of producing drop-in hydrocarbon fuels that are low carbon, sustainable, and compatible with the existing fuel distribution infrastructure. The process does not require elevated temperatures, high pressure, toxic catalysts, or complex operations. The recombinant *E. coli* secretes the hydrocarbons from the cell, so it is not necessary to rupture the cell. In addition, because the hydrocarbons are insoluble in water, they will form a separate organic phase and the microbes are not poisoned by the accumulating fermentation product as occurs with alcohol [56].

4.6. Renewable diesel and gasoline

Traditional petrochemical refinery operations such as catalytic cracking and hydroprocessing (HP) can be applied with modifications to biological feedstocks such as bio-oils and triglycerides to produce non-ester renewable hydrocarbon gasoline and diesel fuels [57]. Fluid catalytic cracking (FCC) may be viewed as continuous pyrolysis (400+ ^{o}C) at atmospheric pressure in the presence of heterogeneous acid catalyst and is used to produce gasoline. During FCC, long-chain hydrocarbons are cracked into smaller molecules, most of which fall within the gasoline boiling range. Among the reactions that occur (both parallel and consecutive) during FCC include protolytic cracking, dehydrogenation, decarboxylation, decarbonylation, scission, cyclization, oligomerization, coking, and hydride transfer [58]. Zeolite-based catalysts have been used for industrial FCC for over 40 years. These catalysts contain a faujasite-type zeolite as the major active component, which is embedded in a silica and/or alumina matrix. This matrix acts a binder, serves as a diluting medium, provides large mesopores for diffusion to the active zeolite crystal and facilitates heat transfer during cracking reactions [58,59].

HP utilizes both high temperature and pressure along with hydrogen and heterogeneous catalysts to remove heteroatoms (such as oxygen, sulfur, nitrogen, and metals) and unsaturation and yields principally diesel and jet fuels [60]. Sulfur in diesel fuels is limited to 10 ppm in Europe (EN 590) and 15 ppm in the United States (ASTM D975). Consequently, an important process that occurs during HP is hydrodesulfurization (HDS), as crude oil may contain up to 2% (by weight) of sulfur [61]. During HDS, chemically bound sulfur is eliminated as H_2S [62]. A two-stage HDS unit is typically employed whereby a Co-Mo/Al_2O_3 catalyst is first used followed by Ni-Mo/Al_2O_3 (or Ni-W/Al_2O_3). HDS over Co-Mo primarily removes sulfur from aliphatic hydrocarbons. The more active Ni-Mo facilitates hydrogenation of aromatic sulfur as well as saturation of aromatic hydrocarbons. The two-stage deep desulfurization needed to produce ultra-low sulfur (<15 ppm S) diesel (ULSD) fuel has caused changes to the chemical composition of ULSD relative to its low sulfur (<500 ppm) diesel (LSD) fuel predecessor, which was historically prepared in only one HDS stage utilizing a Co-Mo catalyst. The resulting ULSD fuel contains fewer aromatics and heteroatom-containing hydrocarbons relative to LSD [60,63,64]. A drawback to applying existing commercial HP catalysts to biological feedstocks is that the lack of heteroatoms (especially sulfur and nitrogen) in the biological feedstocks causes the catalysts to rapidly lose activity. Therefore, to maintain catalyst activity the feedstocks must be doped with dimethyl disulfide (DMDS) and tetrabutylamine (TBA) [65]. This is of course an undesirable solution, especially in an integrated biorefinery setting where substances such as DMDS and TBA represent non-biological inputs. Recently, zeolites such as Pt/H-ZSM5 have shown promise as HP catalysts for triglycerides such as jatropha oil to yield C15-C18 hydrocarbons directly [66].

Both FCC and HP require atmospheric distillation post-production to yield fuels with the appropriate boiling ranges. Current technology for production of biofuels from these processes involves comingling of biological feedstocks with traditional petroleum feeds to produce a hydrocarbon fuel whose carbons are primarily derived from petroleum [58,67]. Direct production of renewable gasoline and diesel fuels from FCC and HP without comingling

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requires development of new catalysts with higher tolerance of biological feedstocks. If such processes are to be performed independently from the classic petroleum refinery, then process economics improvements are needed to reduce production costs. Stand alone units or those integrated into a multi-product integrated biorefinery may become more economically competitive as scale of production increases. Demonstration facilities utilizing a patented Universal Oil Products (UOP) process for conversion of triglycerides to renewable diesel using HP have been reported [68]. Important advantages of renewable hydrocarbon gasoline and diesel fuels relative to ethanol and biodiesel are that the former are indistinguishable from their petroleum counterparts, they have greater storage and oxidative stability, they can be transported via existing pipeline infrastructure, they are not hygroscopic, and they can be blended in any proportion with conventional petroleum-derived fuels [57,68].

4.7. Algal biofuel production

As a result of the interest in developing additional biomass feedstocks, research into the production of liquid transportation fuels from microalgae, is reemerging. These microorganisms use the sun's energy to combine carbon dioxide with water to create biomass more efficiently and rapidly than terrestrial plants. Oil-rich microalgae strains are capable of producing the feedstock for a number of transportation fuels—biodiesel, "green" diesel and gasoline, and jet fuel—while mitigating the effects of carbon dioxide released from sources such as power plants [56]. Research and demonstration programs are being conducted worldwide to develop the technology needed to commercialize algal lipid production. Algae store chemical energy in the form of biological oils, such as neutral lipids or triglycerides, when subjected to stresses such as nutrient deprivation [69]. The oil can be extracted from the organisms and converted into biodiesel by transesterification with short-chain alcohols such as methanol or ethanol [70] or by catalytic deoxygenation/hydrogenation of fatty acids into linear hydrocarbons [71]. Another approach is to engineer algae or cyanobacteria to directly produce fuel compounds, instead of oil [72]. These biofuel replacements for gasoline, diesel, and jet fuel will give higher fuel efficiency than ethanol and biodiesel, and will work in existing engines and fuel distribution networks.

4.8. Anaerobic digestion

Anaerobic digestion is the use of microorganisms in oxygen-free environments to convert organic material into methane and carbon dioxide. This biogas is currently produced from crop residues, food scraps, and manure. Anaerobic digestion is also frequently used in the treatment of wastewater and to reduce emissions from landfills. When functioning well, the bacteria can convert about 90% of the biomass feedstock into biogas (containing about 55% methane), which is a readily useable energy source (combusted for thermal energy and/or used to power electrical generators). Solid remnants of the original biomass input, which are left after the digestion process, are typically used as a fertilizer (although it should be chemically assessed for toxicity and growth-inhibiting factors). Biogas production can be part of sustainable biochemicals and biofuels-based biorefinery platform, since it can derive value from low-

value by-product or waste streams. Value can be increased by optimizing methane yield and economic efficiency of biogas production [13,73].

5. Platform integration

A key factor in achieving a successful biomass-based economy will be the development of biorefinery systems allowing efficient and cost-effective processing of biological feedstocks into a range of bio-based products that integrate seamlessly into the existing infrastructure [12]. Within the operation of a biorefinery, significant opportunities exist to produce commodity and high-value chemicals in conjunction with the production of bioenergy and biofuels [13]. From a technical point of view, almost all industrial materials made from petroleum resources could be replaced by their bio-based counterparts. However, the bio-based products must be no more expensive, perform at least as well, and have lower environmental impacts. Production of these materials in integrated multi-purpose biorefineries offers the most cost-effective approach to achieving this goal. In general, biofuels, both conventional and advanced, can be produced sustainably in the future only with a significant reduction in costs, which potentially can be accomplished by integrated co-production of value-added products [13]. By producing multiple products, a biorefinery can take better advantage of the intrinsic chemical complexity of biomass components and intermediates to maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products as well as a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use and perhaps enough for sale of electricity. The high-value products enhance profitability, while the high-volume fuel provides economies of scale and helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions [74].

The development of promising and innovative bio-based chemicals and polymers depends on the feedstock and the resulting process stream or platform [13]. These platforms include: 1) single carbon molecules such as biogas or syngas that can give rise to methanol, dimethylether, ethanol, or Fischer-Tropsch diesel, 2) six carbon carbohydrates from starch, sucrose, or cellulose and mixed streams with five and six carbon carbohydrates from hemicelluloses that can potentially produce succinic, itaconic, adipic, glutamic, and aspartic acids, and 3-hydroxypropionic acid or aldehyde, isoprene, and farnesene, plus more from the chemical processing of glucose, 3) lignin whose structure suggests it could form supramolecular materials and aromatic chemicals, 4) oils (plant-based or algal) that produce glycerol for propylene glycol, epichlorohydrin, and 1,3-propanediol and that are being developed for manufacture of polymers (polyurethanes, polyamides, and epoxy resins), 5) organic solutions from grasses such as clover or alfalfa that contain proteins, amino acids, carbohydrates, and 6) pyrolytic liquids that are expected to produce phenols, organic acids, furfural, hydroxymethyl furfural, and levoglucosan [13]. The continued growth in biobased chemicals and materials will give impetus to the cost-effective production of biofuels in a biorefinery setting. Given the expanding range of feedstocks, platform technologies, and co-products, numerous combinations for third-generation biorefineries are possible [12].

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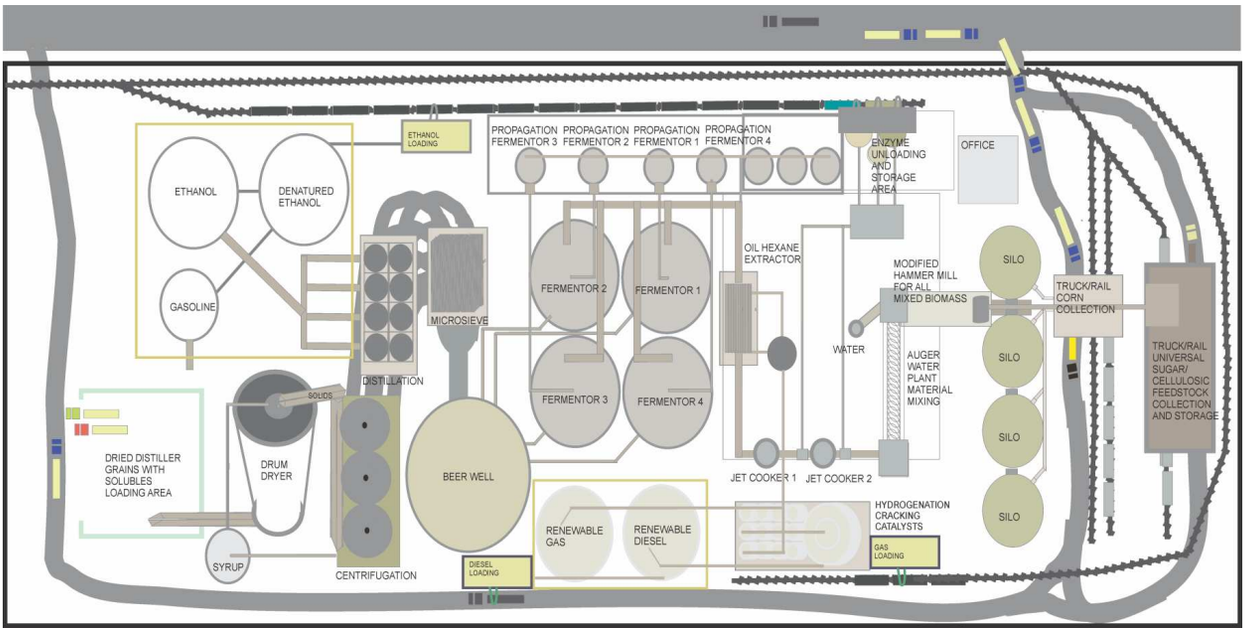
5.1. Multipurpose biorefinery based on starch and cellulosic biofuel platforms

Multipurpose advanced biorefineries that hydrotreat plants oils and animal fats into renewable fuels can be combined with cellulosic ethanol production via fermentation by optimized yeast strains. Concomitant production of high-value bio-based products and advanced animal feeds would be accomplished from by-products from the facility. Cellulosic n-butanol could be produced from mutant strains of *Clostridium acetobutylicum* and *C. beijerinckii* developed to tolerate high concentrations of butanol. Furthermore, engineered algae could be used for urea and ammonia production for emissions control technologies for diesel-operated trucks, for fertilizer, and for production of sucrose and algal oils. The multipurpose biorefinery would require construction of support areas, including research and pilot facilities, a strain collection building, and distillation and post-fermentation processing facilities. Unusable waste streams would be utilized as pyrolysis or biomethane feedstocks to power the biorefinery. Ideally, the biorefinery would produce third-generation biofuels that would be distributed through existing infrastructure. A high-volume animal feed station could be established for distribution to local farms. A possible arrangement of the components of a multipurpose biorefinery combining several of these platforms is shown in Figure 2.

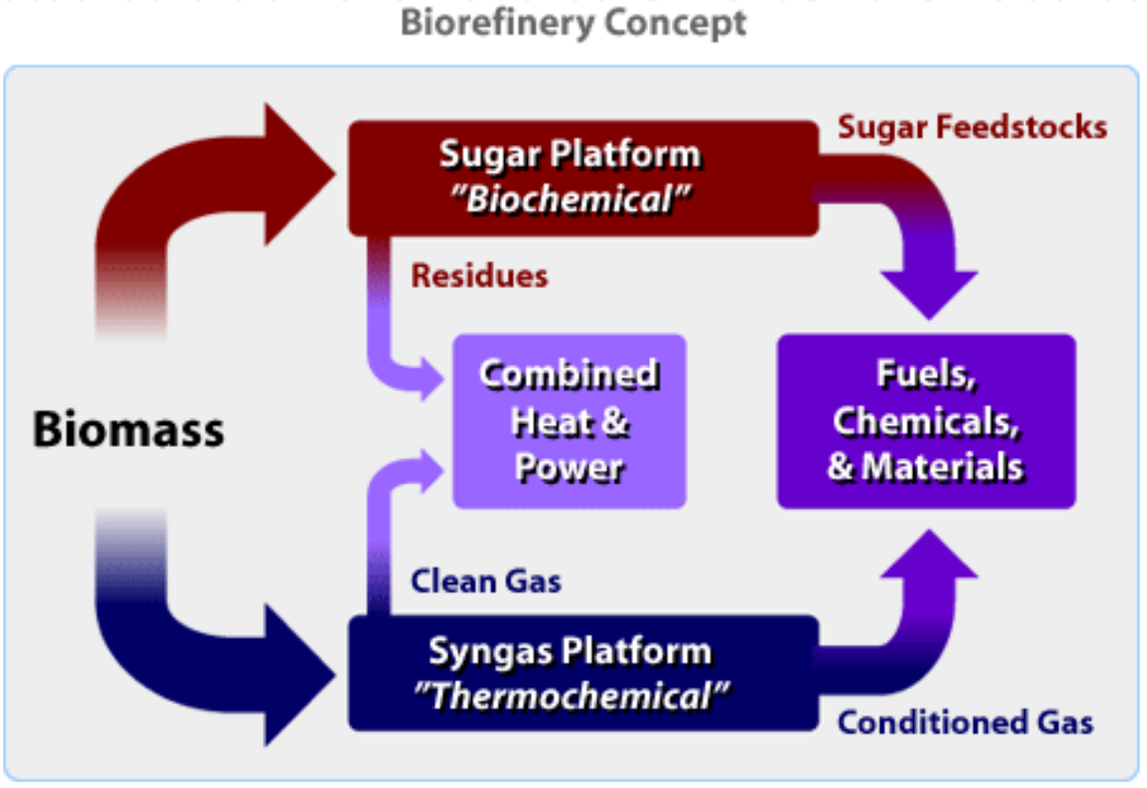


Cellulosic ethanol or n-butanol production by optimized yeast or *Clostridium* strains is combined with an existing starch ethanol production facility. Concomitant production of high-value bio-based products and advanced animal feed is also accomplished from by-products at the integrated facility.

Figure 2. Multipurpose Biorefinery Combining Starch and Cellulosic Biofuel Platforms

5.2. Multipurpose biorefinery based on sugar and syngas platforms

Another example of a multipurpose biorefinery is built on two different platforms, sugar and syngas, to promote different product slates [74]. The sugar platform is based on biochemical conversion processes and focused on fermentation of sugars extracted from biomass feedstocks. The syngas platform is based on thermochemical conversion processes and focused on gasification of biomass feedstocks and by-products from conversion processes. A diagram of this integrated biorefinery is shown in Figure 3.



The sugar platform uses biocatalysts such as yeast to produce liquid biofuels from fermentation of sugars. The syngas platform uses high temperatures and a low-oxygen environment to convert biomass into synthesis gas that can then be chemically converted into biofuels. (Reproduced from [74])

Figure 3. Integration of Sugar and Syngas Platforms

Projects developing this concept are focused on new technologies for integrating the production of biomass-derived fuels and other products in a single facility. The emphasis is on using new or improved processes to derive products such as ethanol, 1,3 propanediol, polylactic acid, isosorbide, and various other chemicals. These projects include facilities to develop and validate process technology and sustainable agricultural systems to economically produce sugars and chemicals such as lactic acid and ethanol. These facilities will also develop 1) a novel biomass technology to utilize distiller's grain and corn stover blends to achieve significantly higher ethanol yields while maintaining the protein feed value, 2) a biobased technology to produce a wide variety of products based on 3-hydroxypropionic acid, produced by

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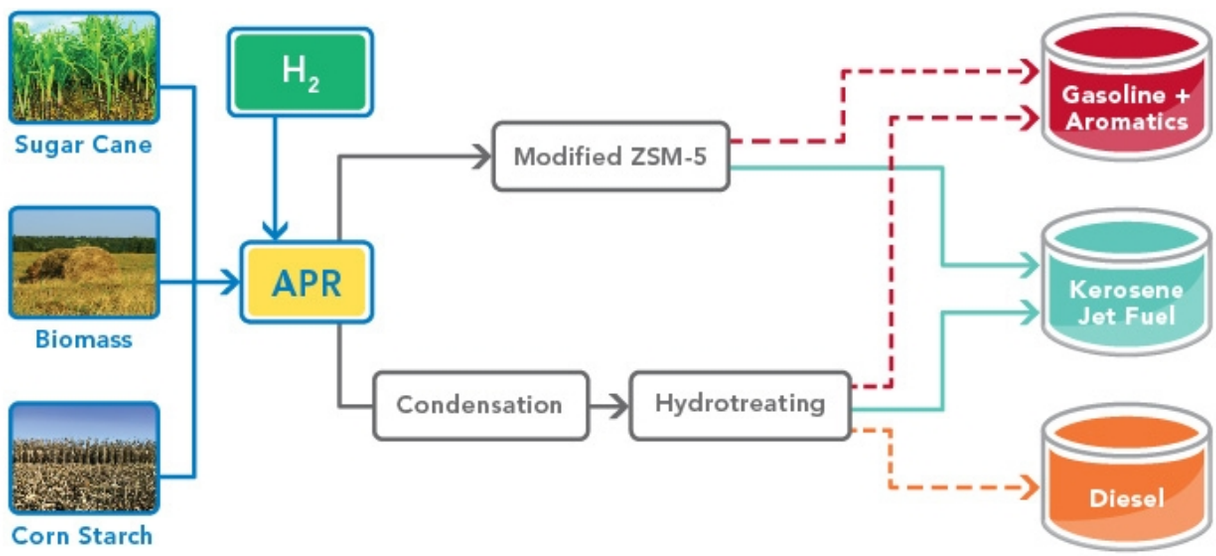
fermentation of carbohydrates, and 3) an integrated process for recovery of the hemicellulose, protein, and oil components from corn fiber for conversion into value-added products [74].

5.3. Conversion of biomass sugars to hydrocarbon chemicals and fuels

Figure 4 shows an example of an integrated biorefinery that produces third-generation biofuels via chemical catalysis to convert plant-based sugars into a full range of hydrocarbon products identical to those made from petroleum, including gasoline, diesel, jet fuel, and chemicals for plastics and fibers. The biofuels are drop-in replacements that enable full utilization of existing processing, pipeline, storage, and transportation infrastructure. The process converts aqueous carbohydrate solutions into mixtures of hydrocarbons and has been demonstrated with conventional sugars obtained from existing sugar sources (corn wet mills, sugarcane mills, etc.) as well as with a wide variety of cellulosic biomass from nonfood sources. The process can accommodate a broad range of compounds derived from biomass, including C5/C6 sugars, polysaccharides, organic acids, furfurals and other degradation products generated from the deconstruction of biomass. The soluble carbohydrate streams are processed through the aqueous phase reforming (APR) step. The APR step utilizes heterogeneous catalysts at moderate temperatures and pressures to reduce the oxygen content of the carbohydrate feedstock. The reactions in the APR step include: (1) reforming to generate hydrogen, (2) dehydrogenation of alcohols / hydrogenation of carbonyls, (3) deoxygenation, (4) hydrogenolysis, and (5) cyclization [75].



Catalytic chemistry converts plant-based sugars into a full range of hydrocarbon products identical to those made from petroleum, including gasoline, diesel, jet fuel, and chemicals for plastics and fibers. (Reproduced from [75])

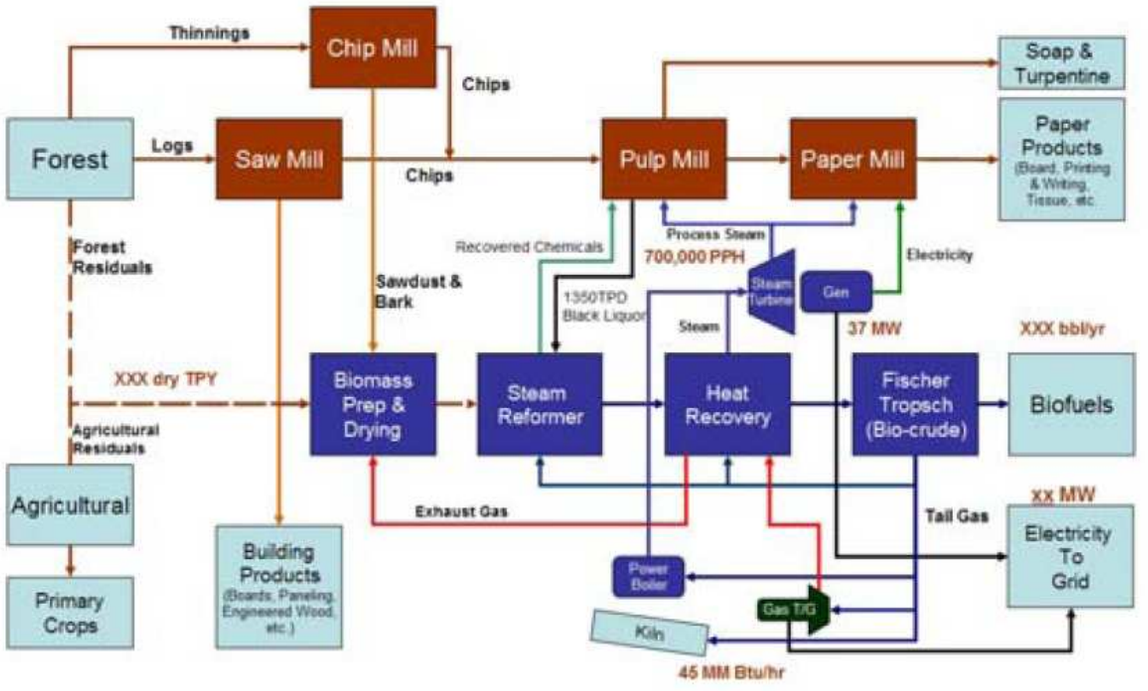
Figure 4. Biomass Conversion to Hydrocarbon Chemicals and Fuels

An advantage to this process is the ability to produce hydrogen in-situ from the carbohydrate feedstock or utilize other sources of hydrogen such as natural gas for higher yields and lower costs. The product from the APR step is a mixture of chemical intermediates including alcohols,

ketones, acids, furans, paraffins and other oxygenated hydrocarbons. Once these intermediate compounds are formed they can undergo further catalytic processing to generate a cost-effective mixture of nonoxygenated hydrocarbons. A modified ZSM-5 catalyst is used to convert the chemical intermediates from the APR step to a high-octane gasoline blendstock that has a high aromatic content similar to a petroleum-derived reformate stream. The chemical intermediates from the APR step can also be converted into distillate range hydrocarbon components through a condensation step followed by conventional hydrotreating [75].

5.4. Integrated forest biorefinery

An integrated forest biorefinery is diagrammed in Figure 5. In ths example, a facility processing biomass to syngas to biofuels is integrated into a pulp and paper mill [76]. The biomass feedstocks for this biorefinery are forest and agricultural residuals. The biomass is dried and sized prior to gasification and then fed into the fluidized bed stream reformer through a screw feed system. It is gasified to produce syngas with the correct hydrogen to carbon ratio for gas-to-liquids processing. The syngas passes through a conventional heat recovery and gas clean-up train. The gas-to-liquids technology is the Fischer-Tropsch (FT) process, a mature technology. In the reactor the syngas, under pressure and temperature, with the FT catalyst is converted to straight chain hydrocarbons that range from light gases to heavy waxes, including gasoline, naphtha, and diesel [76].



Biomass feedstocks from an existing pulp and paper mill are used to create new revenue streams by producing high-value products such as biofuels and biochemical and at the same time improving the efficiency of the core paper-making operations (Reproduced from [76])

Figure 5. Integration of Paper Mill with Biomass Gasification for Biofuels

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The gasification process is ideal for use in a forest products biorefinery because it is configured for high-performance integration with pulp and paper facilities and is capable of handling a wide variety of cellulosic feedstocks, including mill by-products (spent liquor), woodchips, forest residuals, agricultural wastes, and energy crops. The syngas can be used as a substitute for natural gas and fuel oil and as a feedstock for the production of value-added products such as biodiesel, ethanol, methanol, acetic acid, and other biochemicals [76].

6. Conclusion

A crucial step in developing a worldwide bio-industry is to establish integrated third-generation biorefineries that are capable of efficiently converting a broad range of biomass feedstocks into commercially viable biofuels, biopower, commodity and high-value chemicals, and other bioproducts. Integrated biorefineries are similar to conventional refineries in that they produce a range of products to optimize both the use of the feedstock and production economics. Third-generation biorefineries will use novel technologies and diverse biomass feedstocks - requiring significant investments in research, development, and deployment to reduce costs and improve performance to achieve competitiveness with petroleum fuels. These biorefineries will employ various combinations of feedstock and conversion technologies to produce a variety of products, with the main focus on producing biofuels. Co-products can include chemicals (or other materials), animal feed, and heat and power. As pretreatment, conversion, and integration technologies continue to improve, sustainable third-generation biorefineries will become a reality.

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