Chapter 19
Partnerships, Future, and Emerging Technologies

Thomas D. Foust

Abstract This chapter will cover the current state and possible futures of the biofuels industry. Technology options for the production of cellulosic ethanol will be explained with comparative economics given for representative biochemical and thermochemical cellulosic ethanol conversion processes. This will be followed by a description of the current state of the biofuels industry with possible future directions outlined and what needs to happen both from a technical and business perspective to provide the best chances of success. Finally, advanced biofuel (hydrocarbon fuels) conversion options will be discussed with preliminary economics provided.

Keywords Biofuels • Bioproducts • Biofuels industry • Cellulosic ethanol • Advanced biofuels • Comparative economics

Overview

The future of industrial crops for biofuels and bioproducts is highly dependent on the current and future direction of the biofuels and bioproducts industry. The biofuels industry is very much in a state of transition with many possible futures. After significant growth in the 2000s decade, first-generation biofuels have entered a period of minimal to stagnant growth due to a variety of factors such as market conditions, concerns about land use, sustainability concerns, and decreasing government policy support. Conventional wisdom was that the stagnation of first-generation biofuels industry would lead to the natural transition to the second-generation biofuels industry, utilization of lignocellulosic crops.

However, the transition to the second-generation biofuels industry is occurring at a much slower pace than anticipated again to a variety of factors such as market and economic conditions as well as renewed debate about the proper role of biofuels in a sustainable world future on food and fuel supplies. Hence, the biofuels and bioproducts industry is currently in a state of flux with many possible future scenarios that are both dependent on technologies and markets.

T.D. Foust (✉)
Department of Biofuels, National Renewable Energy Laboratory, Golden, CO, USA
e-mail: Thomas.foust@nrel.gov

© Springer Science+Business Media New York 2015

V.M.V. Cruz, D.A. Dierig (eds.), *Industrial Crops*, Handbook of Plant Breeding 9,
DOI 10.1007/978-1-4939-1447-0_19

This chapter will explore several possible scenarios for the future of the second-generation biofuels industry and the implications that this will have on approaches for industrial crop breeding for bioenergy and bioproducts. For first-generation biofuels, the relationships between desired crop characteristics and biofuel or bioproduct type are fairly straightforward, i.e., high sugar or starch content correlates to higher yields and better economics. However, this relationship for second-generation biofuels and bioproducts is much more complex and is highly conversion-type specific. For example, for the same product, cellulosic ethanol, high carbohydrate low lignin crops would be preferred if a fermentation-based conversion technology is utilized. However, if a thermal conversion route such as a gasification/catalytic fuel synthesis conversion route is utilized, relative carbohydrate/lignin composition percentages are not that important, but inorganic trace constituents are very important.

Cellulosic Ethanol

Cellulosic ethanol has been the historical focus point of second-generation biofuels. Cellulosic ethanol development efforts date back to the early 1980s [1, 2], with some initial work beginning in the late 1970s [3]. Cellulosic ethanol is the logical biofuel to initially focus on for two main reasons: it builds upon the corn and sugar ethanol industry and it addresses the gasoline market, which is the biggest fuel market worldwide.

Cellulosic ethanol shows a good deal of promise for overcoming many of the limitations of first-generation ethanol technologies that utilize sugar or starch crops as the feedstock. Since cellulosic crops are utilized as feedstocks, the issue of direct competition with food production is negated [4], although land completion issues still exist [5].

Environmental and Sustainability Benefits

Cellulosic ethanol has long been touted for its environmental and sustainability benefits over first-generation ethanol technologies. The two biggest producers of first-generation ethanol are Brazil from sugarcane and the USA from corn. True environmental benefits and effects on food supply and food prices are concerns that are commonly brought up about first-generation ethanol. For example, at the 2011 US production rate of 52.8 billion liters/year, almost 40 % of the US corn crop is utilized for ethanol production [6]. There is considerable debate about the effect this amount of corn crop consumption for ethanol production has on world food prices and supplies, but in any case further significant growth is unlikely.

Cellulosic ethanol also has significant potential greenhouse gas (ghg) emission reduction benefits over first-generation ethanol technologies [7]. Figure 19.1 shows

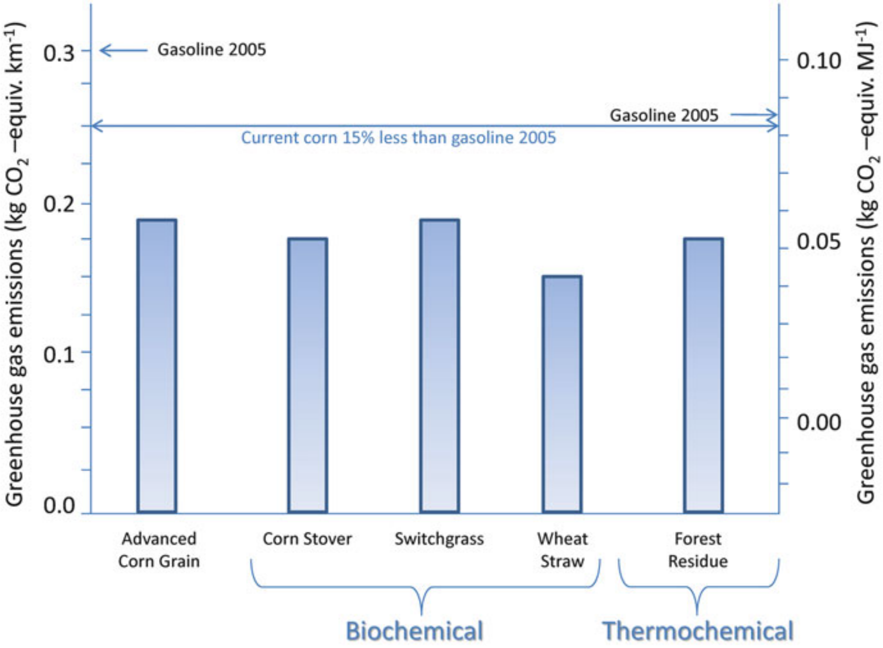

Fig. 19.1 GHG benefits of cellulosic ethanol compared to first-generation ethanol

potential ghg benefits of various cellulosic ethanol technologies, current first-generation corn ethanol, and an advanced future state of the corn ethanol industry as they compare to gasoline based on values given by Hsu et al. [8]. These ghg values incorporate using the lignin component to supply the heat and power needs of the conversion process in the cellulosic ethanol cases and an increased biomass component in the advanced corn ethanol state [9]. Another benefit of cellulosic ethanol over first-generation ethanol is that cellulosic ethanol has a much-improved net energy balance [10], and similar to the ghg emission benefits, much of this benefit comes from utilizing the lignin component to supply the heat and power needs for the conversion process.

Conversion Technologies

Although there are a multitude of variations, there are essentially two main technology approaches for producing cellulosic ethanol from lignocellulosic biomass. The first route, commonly referred to as the biochemical route, utilizes a sugar intermediate, which is fermented into ethanol, and the second route utilizes a syngas intermediate, which can either be fermented or catalytically converted to ethanol. Both routes have received considerable amount of public and private support to develop the technologies to a commercially viable state, and both routes have the potential to make a significant contribution to the world's supply of transportation fuels.

Biochemical

A schematic of a representative biochemical conversion process for cellulosic ethanol is shown in Fig. 19.2.

The biochemical conversion process can essentially be categorized into two main subcomponents: the liberation of the sugars from the biomass and the fermentation of these sugars to ethanol. The efficient liberation of sugars from the carbohydrate portion of the biomass "saccharification" is a significant challenge given the recalcitrant nature of biomass [11]. Saccharification research has received considerable attention over the past couple of decades with significant improvements made in both the efficiency and the cost of the process [12].

Saccharification can essentially be either a chemical process where a concentration acid process or multiple stages of dilute acid are utilized to liberate both the hemicellulose and cellulose sugars [13] or a two-step approach involving a pretreatment step and a enzymatic hydrolysis used to liberate some to most of the hemicellulose sugars and condition the biomass to a state that is amenable for enzymatic hydrolysis [14].

The US Department of Energy (DOE) evaluated the long-term potential [15] of these two approaches and determined that the pretreatment/enzymatic hydrolysis approach had the best potential for efficient conversion at low cost for wide-scale applicability [16]. Although this is true at the macroscale, chemical saccharification technologies such as concentrated acid or multistep dilute acid approaches are certainly viable for special niche applications.

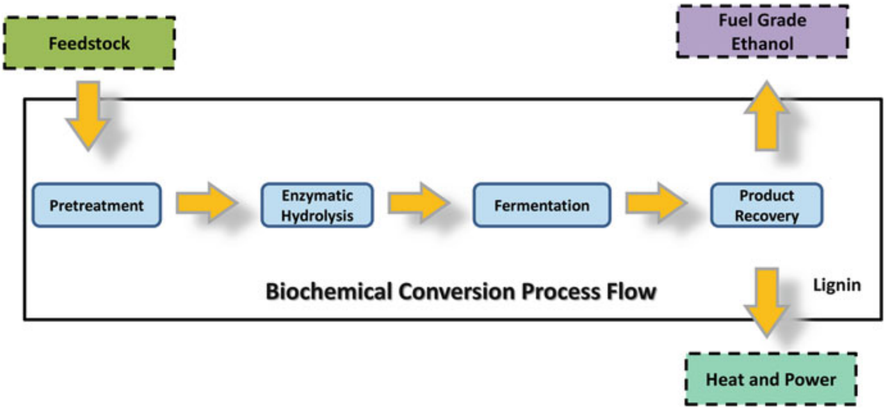

Fig. 19.2 Biochemical conversion process schematic

When effectively coupled, pretreatment and enzymatic hydrolysis can be a very efficient, cost-effective way to liberate monomeric sugars from the carbohydrate portion of biomass with some organizations reporting over 90 % conversion of structural polysaccharides to monomeric sugars [17]. There are a multitude of pretreatment approaches being pursued that cover the gamut of pH ranges from acidic to alkaline approaches as well as temperature ranges (~140–210 °C). All of these approaches have their plusses and minuses when compared on an efficiency and cost basis [18]. However, comparison work has shown that there is really not a "one size fits all" when it comes to a pretreatment approach across the spectrum of suitable lignocellulosic feedstocks. In general, the alkaline or higher severity approaches such as wet oxidation [19] that are more aggressive at depolymerizing the lignin component tend to perform better on higher lignin feedstocks such as softwoods, while the lower severity approaches such as dilute acid or hot water [20] tend to perform better on the low lignin herbaceous feedstocks such as corn stover or switchgrass.

Enzyme development with the goal of low cost-efficient hydrolysis to monomeric biomass sugars has been an area of extensive focus with considerable progress being made [21]. This progress has been critically important in moving the biochemical conversion process towards its goal of economic competitiveness; however, further progress in both specific activity and costs to produce the enzymes is still possible and desirable.

Similarly, with enzyme development, organism development for the cost-effective efficient fermentation of biomass sugars to ethanol has been an area of significant focus, again with impressive, high-impact progress being made [22]. Humbird [15] reported for pilot scale results very effective fermentation results of greater than 90 % of total biomass sugars to ethanol, which would correspond to a total ethanol yield of 330 l/tonne of biomass. At these yields and efficiencies, the overall economics compare favorably to first-generation ethanol technologies. However, this needs to be caveated with the fact that these are pilot plant numbers and the technology still needs to be proven out at commercial scale.

The final step in the biochemical lignocellulosic ethanol conversion process is product recovery, which is envisioned to be standard fractional distillation to the ethanol-water azeotrope, followed by molecular sieve concentration to anhydrous ethanol. These techniques will be very similar to what is currently used in first-generation ethanol processes and hence is a well-proven technology.

Since cellulosic ethanol technology utilizes only the carbohydrate portion of the biomass, the lignin component of the biomass is available for other uses. Initial process designs put forward by a number of organizations [23] dry the lignin and then use it as a fuel for heat and power needs of the conversion process. The Renewable Fuel Standard (RFS) requires that advanced biofuels show a 60 % ghg reduction when compared to conventional gasoline to quality for the RFS credit. Utilization of the lignin component as opposed to using a fossil fuel such as natural gas or coal contributes significantly to ghg reductions for cellulosic ethanol [24].

Feedstock Considerations

Since the biochemical lignocellulosic ethanol conversion process hinges on high sugar conversion to ethanol, desirable feedstocks will have a high carbohydrate content that is amenable to conversion to monomeric sugars that in turn are readily fermented to ethanol. Although this statement is fairly straightforward and may be a bit obvious, it is in reality overly simplistic and may not be a good metric for judging the relative value of feedstocks. Lignocellulosic feedstocks have a great variety as to both physical and chemical properties, and these variations can have significant impacts on the yields and efficiency of the conversion process.

In the early days of biochemical conversion process development, the process was commonly referred to as the sugar platform and organizations and researchers focused on cost of sugars [25]. Research predominantly focused on maximizing sugar yields per mass unit of feedstock. However, since the ultimate goal in any conversion process is to produce the final product at the highest efficiency and yield at the lowest possible cost, history and experience has shown that this singular focus on sugar yields could be misleading. Fermentation inhibitors such as furfural, hydroxymethylfurfural (HMF), or other inhibitory compounds can significantly affect the fermentability of the sugar solution [26]. The presence and concentration of these inhibitory compounds is very much a function of the feedstock type, the pretreatment technology, and finally the severity of the pretreatment. Since some inhibitory compounds such as furfural and HMF arise from thermal degradation of sugars, the higher severity pretreatment approaches that lead to higher sugar yields also lead to high inhibitory compound concentrations. Hence final ethanol yields could actually be lower for higher sugar concentration hydrolysates with these compounds present, then they would be for lower sugar concentration hydrolysates without these compounds being present. Although these inhibitory compounds can be reduced or eliminated by hydrolysate conditioning [27], these processes add cost and complexity to the process as well as lead to sugar losses; hence, it is best to avoid these processes if possible.

For these reasons, there is really not a preferred feedstock since the best choice will be the feedstock that is available at the desired quantities at the lowest cost. The conversion process will need to be well suited for the feedstock. Adding to the complexity will be that feedstock availabilities and cost are geographically dependent as well as weather and time of year dependent. Therefore, it might be cost effective to build robustness into the process conversion plant so that a range of feedstocks can be accommodated based on weather or seasonal variations. Simply building a plant capable of processing the predominant feedstock in the geographical area (i.e., corn stover in the US Midwest or Sugar Cane Bagasse in Brazil) may make the plant difficult to operate economically year in and year out over the 30+ year life of the plant if the feedstock availability drops significantly due to a prolonged drought or other condition that affects the availability of that particular feedstock.

Economics

Since ethanol like any transportation fuel is a commodity with no price differentiation in the market place, price parity with first-generation ethanol as well as ultimately price parity with conventional petroleum-based gasoline on an energy-adjusted basis needs to be achieved before demand-driven market penetration can occur. Achieving price parity has proven to be a very difficult challenge, and fortunately after decades of focused effort, significant encouraging progress is being made. Several companies are going forward with commercial cellulosic ethanol facilities, but private companies are typically resistant or even prohibited, depending on the country regulations where they are located from publicly disclosing feedstock or production costs. Hence, the only method to get production cost numbers is from the open literature. This tends to be somewhat of a mixed bag depending on the source of the numbers and the rigor that was used to develop the production cost numbers as well as the underlying motivation for publishing the numbers. Press releases [28] and other popular press articles [29] exist that show economically competitive production costs, which if taken at face value would indicate that price parity has been achieved or even exceeded. However, peer-reviewed literature on economics of cellulosic ethanol production tends to be more conservative on the costs [30]. Hence, why it is difficult to state a number or even a range of numbers is that range is likely to be so broad that it ceases to be meaningful.

With all these said, probably the best source of public numbers on the production cost of cellulosic ethanol from a biochemical production route is available from the US DOE via the National Renewable Energy Laboratory (NREL). Humbird et al. [22] published a case where a fully loaded production cost of $2.15/gallon (2007 dollars) could be achieved based on technology demonstrated at the pilot plant for a 2,000 tonnes/day commercial plant for an nth plant case.

At these production costs, cellulosic ethanol produced via a biochemical conversion route compared very favorably with first-generation ethanol production costs from sugar or corn. A noticeable difference is the percentage of overall production costs represented by the feedstock component. In the case of first-generation ethanol, feedstock costs represent about 70 % of overall production costs, whereas in the case of cellulosic ethanol, feedstock costs only represent 30 % of overall production costs [29]. Analyses that have been performed on a range of technically mature conversion processes have shown that typically feedstock costs represent 30–50 % of production costs for commodity products [31] such as ethanol. Hence, this would indicate that the long-term potential for further cost reductions is higher for cellulosic ethanol than it is for first-generation ethanol.

Thermochemical

A schematic of a representative thermochemical conversion process for cellulosic ethanol is shown in Fig. 19.3. This conversion route is based upon utilization of catalytic fuel synthesis for ethanol production. An alternative to catalytic fuel synthesis would be fermentation of the syngas to ethanol [32]. The catalytic fuel synthesis option will be covered here primarily because better public data exists for this option.

Similarly to the biochemical conversion process, the thermochemical ethanol conversion process can essentially be categorized into main components: the gasification of the biomass to syngas (H_2 and CO) and then the catalytic conversion of this syngas to ethanol. Biomass gasification is an early-stage commercial technology that has been deployed at a few locations [33]. Biomass gasification technologies cover a fairly broad gamut of simple to sophisticated approaches with, as would be intuitively expected, the sophisticated approaches having higher costs, both from an operating and capital perspective. The simplest biomass gasification technologies, updraft or downdraft air-blown approaches, produce a syngas highly diluted with N_2 that is generally not well suited for catalytic conversion to fuels. Oxygen blown or direct gasification and indirect gasification do not introduce air into the gasification process and hence do not have the N_2 dilution issue; thus, they are the two best gasification technology choices for producing a syngas suitable for catalytic fuel synthesis. Phillips, Dutta, and coauthors did a series of studies [34–36] where they looked at dry ash and slagging direct biomass gasification approaches compared to indirect biomass gasification for mixed alcohol fuel synthesis and concluded that for the scales of biomass (2,000 tonnes/day), indirect gasification was the preferred route on both a cost and an efficiency basis.

A drawback of indirect biomass gasification is the amount of tars and light hydrocarbons produced during the gasification process [37]. Light hydrocarbons and tars are problematic since they represent a carbon and hence an efficiency loss,

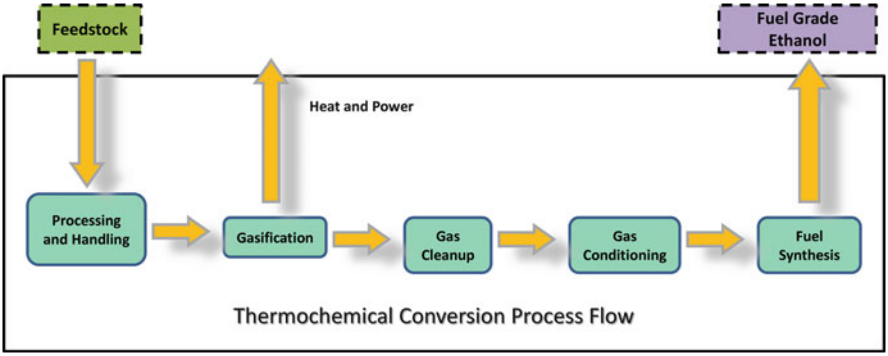

Fig. 19.3 Thermochemical conversion process schematic

but tars are especially problematic since they have the additional detrimental effect of fouling downstream fuel synthesis catalysts and system.

Proven technology approaches for removing the light hydrocarbons and tars from the syngas is a two-step process: water quenching to remove the tars and other particulates from the syngas stream followed by steam methane reforming to change the methane and other light hydrocarbons to additional syngas. Although water quenching is effective for removing tars and heteroatoms from the syngas, it represents a carbon and efficiency loss since the carbon and energy contained in the tars would be lost to the system. However, even more problematic is the large toxic wastewater stream that water quenching would create. Steam methane reforming does not represent a carbon or energy loss or create a problematic waste stream, but it does add additional cost and complexity to the process.

A preferred approach to this two-step process would be to perform integrated tar and light hydrocarbon reforming in a catalytic single-step process. This would have the benefits of increasing the carbon and energy efficiency of the process, reducing process steps and hence the cost and complexity of the conversion process, and finally eliminating a large volume toxic wastewater stream. Although several researchers have published results showing that a number of catalysts look promising for tar and light hydrocarbon reforming [38], the challenge is to maintain the activity in the presence of sulfur. This area has been the focus of considerable effort over that past several years, and a number of researchers and organization are reporting some encouraging results [39].

The next major step in the process after the syngas has been cleaned and conditioned is to perform the catalytic fuel synthesis. Several organizations have developed mixed alcohol synthesis catalysts over the past decade or so [40, 41]. In order to be commercially viable, mixed alcohol synthesis must have good selectivity to the desired product, in this case ethanol, as well as good CO conversion. Several researchers have reported significant improvements in mixed alcohol synthesis catalyst performance [42]. Improvements in catalyst performance that increase single-pass conversion and ethanol productivity are particularly beneficial since these improvements have the added benefit of simplifying the process by requiring fewer recycle loops, hence improving both costs and efficiencies.

Feedstock Considerations

Biomass composition affects thermochemical processing differently than biochemical processing. Unlike biochemical conversion, which only converts the carbohydrate portion, gasification converts the entire organic component of biomass, both carbohydrate and lignin fractions, into syngas, light hydrocarbons and some tars. Trace inorganics predominantly sulfur, salts, and alkaline earth metals can be problematic in a variety of ways. Potassium can be problematic in the gasifier for fluidized bed gasifiers. The potassium interacts with the silica in the system to form K_2SiO_4 which has a low melting point of ~ 500 °C, and its formation will lead to the bed media becoming sticky which in turn leads to agglomeration and defluidization of the bed media.

Sulfur that gets converted into H_2S and alkaline earth metals such as Ca or Na can be significant catalyst poisons for both the tar reforming catalyst and the fuel synthesis catalyst. Depending on their concentration in the feedstock and the sensitivity of the catalysts being utilized, they may need to be reduced or eliminated from the syngas stream by water scrubbing or catalyst guard beds. Although both of these techniques are well-proven technologies, they do add cost and complexity to the process.

Economics

The thermochemical conversion process has not received the same degree of focus as has the biochemical conversion process, and therefore there are less references in the literature on the economics of the process. Similar to the biochemical conversion process, probably the best public source of production cost numbers is NREL. Dutta et al. published a case where a fully loaded production cost of $2.05/gallon (2007 dollars) could be achieved based on technology demonstrated at the pilot plant for a 2,000 tonnes/day commercial plant for an nth plant case [43].

Given these two independent technology approaches for producing cellulosic ethanol, the logical question is how they compare. Several studies have looked at this particular question, and one study [44] specifically did a rigorous comparison of these two technologies based on 2007 reported numbers. Table 19.1 provides some direct comparison numbers for the two processes based on the latest reported results from NREL referenced above.

As can be seen from the values in Table 19.1, the economics of the two processes are very similar. The thermochemical process has a slightly lower MESP (5 % lower) but a higher required capital investment (22.1 % higher). The thermochemical process does have slightly higher yields since the lignin portion is utilized for fuel production as well. Average return on investment is almost identical.

An important point of distinction is that the biochemical results are presented for corn stover, whereas the thermochemical results are for pine. The authors of the referenced studies choose the feedstocks that tended to give the best performance and economics for their conversion technology. Although conversion economics do not exist for pine feedstocks for the biochemical conversion process or corn stover for the thermochemical conversion process, poorer conversion economics would be expected for these cases due to lower carbohydrate content for the pine feedstock for biochemical conversion and higher ash content for the corn stover feedstock for thermochemical conversion. This illustrates the earlier point that there does not appear to be a clear superior conversion technology in terms of yields and/or economics. Hence, the best approach is to best match the conversion technology to the predominant feedstock. Since feedstocks tend to be local, the best conversion technology choice will most likely be feedstock dependent or regionally specific.

Table 19.1 Comparative economics for cellulosic ethanol production

	Biochemical	Thermochemical
MESP[a]	$2.15/gallon	$2.05/gallon
Ethanol yield	79.0 gal/dry ton	83.8 gal/dry ton
Delivered feedstock/cost	$58.50/dry ton (corn stover)	$61.57/dry ton (pine)
Total installed equipment cost	$232 MM	$296.5 MM
Total capital investment	$422.5 MM	$515.85MM
Average return on investment	56.6	57.5
Current yield (actual/theoretical)	76.0 %	40.0 %

[a] MESP defined as a fully loaded production cost with a 10 % IRR

State of Industry

After rapid growth in the 2000s decade, further expansion of first-generation ethanol technology has been fairly stagnant. Future growth in first-generation ethanol production will most likely continue to be slow mainly due to concerns about the percentages of the sugar and corn crop being directed to ethanol production, true environmental benefits, as well as market saturation.

Many companies are proceeding forward with plans to commercially deploy cellulosic ethanol in many parts of the world with several commercial production plants in construction. Since pioneer plants or first-of-a-kind plants have higher costs than mature nth plant cost, many countries such as the USA [45] have incentives in place for the initial commercial production of cellulosic ethanol to offset this initial higher cost.

An important point to make is that since the biofuels industry and especially the cellulosic ethanol industry is in an immature state and as any immature industry, it is highly dynamic and will change and evolve over time. For this reason, mentioning any companies' or organizations' plans is not that useful since it will quickly become outdated. A review of the recent history of the biofuels industry from 2006 to 2012 clearly illustrates this point. In the 2006–2008 timeframe, driven by record high prices for crude oil and aggressive government policies for biofuels development and deployment, there was tremendous growth in the biofuels and bioproducts sector with more than 135 companies [46] being active in the "second-generation" biofuels space. This growth period continued until 2011–2012 where there has been a consideration contraction of the industry. A specific illustrative example of this point is that in the US public company valuations for 13s generation biofuels companies are down more than 66 % in 2012 which translates into a $4B USD decrease in value. Many companies have delayed or even shelved plans to proceed forward with commercial plants leading to layoffs across the industry. Therefore, the industry is clearly in a critical state where it can move on to a successful future state or continue downward to an uncertain future. For the industry to be successful, it must focus on sustainable value creation and learn from and move on from past mistakes.

Initially, the biofuels sector was following the business model set by the biotech and software industries. These industries operate on the investment/capital-lite potentially very high revenues model. A highly successful example of this is Google, which went public in 2004 with only $25MM of total external funding and generating $3.2B in revenues in its first year. Although this is an extreme example for even the software industry, this type of revenues/investment ratio is completely outside the realm of possible for the biofuels industry. Investments in R&D to develop the technology plus the required capital to build and operate a pilot plant to demonstrate the technology will easily run into the $100 s of millions to get the technology to a commercially viable state. Estimates for a pioneer commercial plant are around $500MM or higher so the total investment to get to a commercial state could be around $1B to produce a commodity product that will compete with well-established first-generation ethanol and conventional gasoline. The time period required to go from R&D stage to commercial production can easily be 10 plus years, which also serves as an impediment. Granted government R&D funding or incentives can be leveraged to offset some of the costs as well as help on the revenue side, still the promise of biotech or software industry types of returns on investment simply is not realistic.

The cellulosic ethanol industry needs to abandon this unrealistic model, which has led to overhyping and overpromising, and endorse a more realistic business model based on sustainable value production over the long term. Given the large amounts of resources and time required to develop the technology to commercialization, the industry will need to pool assets either by strategic alliances or consolidation to form strong players with the required resources and strong business positions to be successful. The many small players with weak business plans, poor strategic and intellectual property (IP) positions, and incomplete assets and capabilities are plaguing the industry with too many failures and few to any major commercial successes. This is giving the industry a black eye with the investment community, government policy makers, as well as the fuel industries with a reputation of being long on promises and short on delivery.

To focus on sustainable value production, the biofuels industry needs to reduce costs and risk and focus on ways to increase revenue over both the near and long terms. Pooling expertise, IP, and capital through consolidation and/or strategic alliances can reduce risks. Since the industry grew out of R&D roots, there is too much focus and redundancies in R&D to develop unique processes for unit operations such as pretreatment in biochemical conversion that in reality has minimal impact on overall costs and yields and ultimately business position. Research and development resources would be better spent on ways to increase revenue by creating higher value products that can be sold into chemical, materials, or other higher value markets to maximize potential for commercial success. The industry also needs to look into innovative ways to reduce time to market since failure to deliver on past commitments is adversely impacting the industry.

Limitations of Cellulosic Ethanol

Although ethanol has many benefits as a fuel, i.e., it is readily blended into gasoline the predominant worldwide transportation fuel, it can be used in most cars at low blend levels (<15 % ethanol) without modification, and it has favorable production costs. Compared to conventional gasoline, it does have some drawbacks that have limited its growth as a transportation fuel. Ethanol has only 2/3 of the energy content of gasoline and hence will deliver less mileage on a volumetric basis than gasoline. Additionally ethanol has only limited compatibility with the existing infrastructure, thus requiring new investments in pipeline or refining infrastructure for large-scale deployment.

However, the biggest drawback of ethanol has proven to be limited markets. In the USA, the world's biggest producer and user of ethanol, almost all ethanol is utilized as E10 with E85 usage being almost negligible [47]. Currently, in the USA almost 97 % of motor gasoline is E10; hence, the E10 market is essentially saturated. This situation is commonly referred to as the "blend wall" and is the primary reason potential developers of cellulosic ethanol cite as limiting the deployment of cellulosic ethanol. This is interesting because the common perception is it lacks commercially viable cellulosic ethanol technology, which in reality is not the case. The US Environmental Protection Agency (EPA) did approve the use of E15 in model 2000 and newer cars [48] to address this issue, but the adoption of E15 has been slow due to a number of logistical factors. Brazil has not faced the blend wall issue due to a different fuel strategy that is unique to Brazil [49]. Two fuels are offered in Brazil E25 and E100, and since 2003 most new vehicle sales are rapidly trending towards "flex" vehicles, which can accommodate any amount of ethanol. Transportation experts are mixed in their opinion if this strategy to avoid the blend wall issue could be used outside of Brazil.

Although ethanol is a good blend component for gasoline, it is not a good blend component for diesel and completely not suitable for jet fuel. Since diesel and jet fuels are growth fuels and gasoline demand is leveling off or declining especially in the EU and USA, biofuels that do not face the market issues of ethanol and are suitable for the diesel and jet fuel markets are highly desirable.

Advanced Biofuels

The nomenclature of "advanced biofuels" is somewhat used inconsistently in the literature. As it is used here, it refers to hydrocarbon fuels or "drop-in" fuels that can be directly utilized in the existing gasoline, diesel, and jet fuel pools. Producing advanced biofuels from biomass has a number of advantages over ethanol. Since they are essentially substantially similar to current gasoline, diesel, and jet fuels, they would be completely compatible with the existing fuel distribution and vehicle infrastructure. This compatibility could be extended all the way to processing inside existing petroleum refineries, which will be explained in more detail in the following sections.

Another significant advantage of advanced biofuels is that they do not face any market or new fuel acceptance issues. The challenge to get a new fuel certified can be very significant in a large part due to emission and air quality concerns. For instance, in the USA, the US EPA requires a very rigorous testing program to verify that a new fuel or even a blend limit change, i.e., E10 to E15, does not adversely affect emissions. Additionally, vehicle manufacturers and engine manufacturers are very leery of new fuels or blend limit changes because of possible impacts on performance or reliability. For advanced biofuels, none of these issues or concerns would come into play since the fuels would be simply gasoline, diesel, or jet, which are currently certified and accepted by vehicle and engine manufacturers.

However, in the context of nothing is as simple as it first appears, fuel liability issues would exist and need to be addressed. Most country's fuel liability provisions are structured in a manner that the fuel supplier accepts all liability issues associated with the use of the fuel. Therefore, thorough testing would most likely be required for advanced biofuels before fuel suppliers would be willing to accept them as part of the fuel supply and accept the liability associated with their sale.

The categorization of conversion routes into biochemical routes and thermochemical routes roughly holds for advanced biofuels as it does for cellulosic ethanol with the distinction that the biochemical route is more of a sugar intermediate route because the upgrading to fuels can be by either a fermentation route or a catalytic route.

Sugar Intermediate Routes

Figure 19.4 illustrates the overall process for advanced biofuel conversion via a sugar intermediate. The first part of the process, converting the carbohydrate portion of the biomass to a sugar intermediate, is essentially the same pretreatment/enzymatic hydrolysis process that was explained in detail in the biochemical cellulosic ethanol conversion section. From the sugar intermediate, the upgrading to an advanced biofuel can take two dramatically different routes, either a fermentative route to an isoprenoid [50] that can be upgraded to a diesel fuel in a fairly straightforward manner or a catalytic route that involves a number of catalytic and upgrading steps to produce an advanced biofuel [51].

Feedstock Considerations

The feedstock considerations are similar to biochemical cellulosic ethanol conversion. In general feedstocks with high carbohydrate content and correspondingly lower lignin concentration tend to have better performance. This tends to favor the

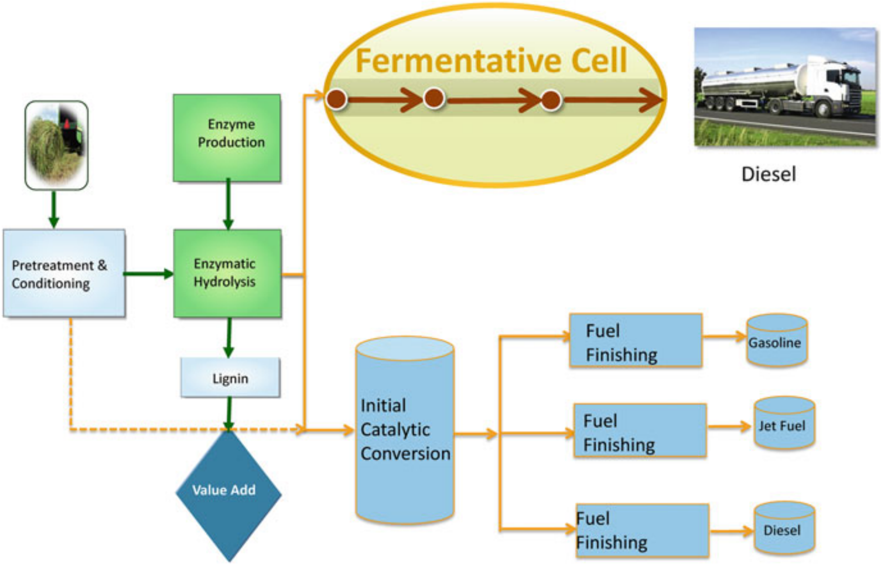

Fig. 19.4 Advanced biofuel routes via sugar intermediate

herbaceous feedstocks such as corn stover or switchgrass. For catalytic conversion, sulfur and alkaline earth metal concentrations can be a significant issue since these compounds can be significant catalyst poisons.

Economics

The economics for conversion to advanced biofuels are much less developed than they are for cellulosic ethanol primarily because the technology is in an earlier state of development. Since the biomass deconstruction to intermediate sugars component is essentially the same as it is for biochemical cellulosic ethanol, these costs are well quantified. However, much less cost specificity exists for the advanced biofuels production step. For the fermentative route, it is fair to say that this will be a higher cost fermentation than ethanol fermentation since isoprenoid fermentations are aerobic which are higher cost both from a capital and operating perspective than anaerobic ethanol fermentations. The final product, hydrocarbon diesel fuel, has higher value than ethanol, so this cost/benefit ratio will determine how the economics compare to cellulosic ethanol. For the catalytic upgrading route, the challenge most likely will be the number of process steps required. Multiple processing steps increase capital cost as well as operationally complexity. Since fuel production like any commodity process requires high plant online time, simpler processes will have the advantage.

Thermal Routes

Thermal routes can be categorized onto three areas based on the intermediate they produce, liquefaction, pyrolysis, or gasification. Figure 19.5 shows the intermediate as a function of severity of deconstruction.

The highest severity thermal deconstruction technique is gasification at temperatures of 600 °C and above, depending on the type of gasification technology used [52]. Once a syngas has been produced and appropriately cleaned and conditioned, there is a multitude of fuel synthesis routes for producing an advanced biofuels [53]. Some of these routes such as Fischer-Tropsch synthesis are well-proven technologies that are being practiced commercially in certain countries such as South Africa. Others are more in the development stage such as single-step olefinic gasoline production that shows better potential for being economically viable at the scale of biomass.

The mid-severity thermal deconstruction technique is pyrolysis which is performed at temperatures in the range of 300–600 °C [54] at atmospheric pressure. Pyrolysis processes produce oil commonly referred to as "bio-oil" or "pyoil" that somewhat resembles crude oil in appearance but has dramatically different physical and chemical properties. The initial biomass pyrolysis process developed was fast pyrolysis. This process is well proven and relatively efficient, but the oil produced has some very undesirable properties that present some significant challenges for upgrading to advanced biofuels [55]. Many of these desirable properties are directly related to the high oxygen content of the bio-oil.

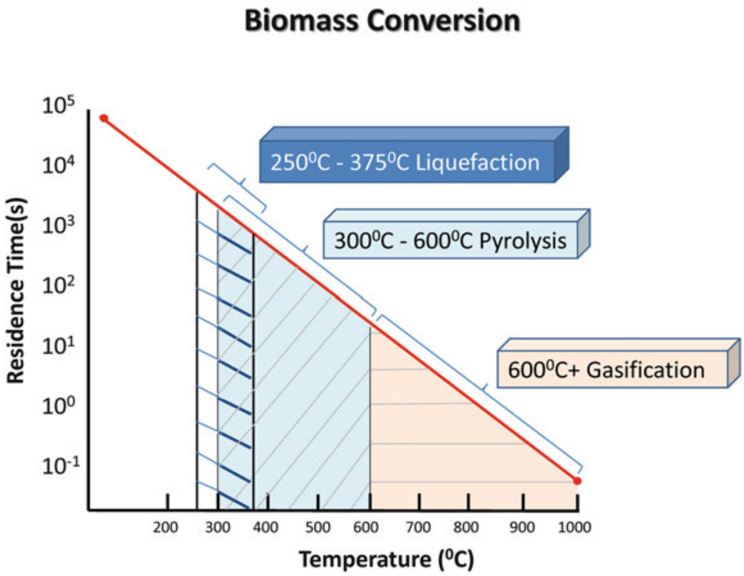

Fig. 19.5 Thermal intermediate as a function of temperature and residence time

To address this issue, several researchers and organizations have developed processes that deoxygenate the bio-oil during the production process such as catalytic fast pyrolysis [56] or hydropyrolysis [57]. Since these processes produce oil considerably lower in oxygen content, the oil has much better properties that make it more amenable for upgrading to an advanced biofuel. These processes are complex from both a physical and chemical perspective, so some technical challenges will need to be overcome before they can be deployed commercially.

The lowest severity deconstruction technique is liquefaction or hydrothermal processing at temperatures in the range of 250–375 °C [58]. Hydrothermal processing requires high pressures in the range or 600–3,200 psi to maintain the water in a liquid state at these temperatures and as shown in Fig. 19.5 requires considerable longer residence times than pyrolysis or gasification. Hydrothermal processing produces oil considerably lower in oxygen content that is more amenable for upgrading to an advanced biofuel.

Economics

Since gasification technologies had been under development for some time, a number of studies exist in the literature on the economics of gasification processes to advanced biofuels. There has been considerable interest over the years to pair biomass gasification with Fischer-Tropsch synthesis since they are both relatively developed technologies, and this pairing could represent a fairly streamlined path to commercialization. Unfortunately, most studies have shown that the economics of this paring are not that attractive primarily due to the fact that Fischer-Tropsch synthesis is a capital-intensive technology and the economies of scale do not match well with the scales of biomass [59]. Studies that have looked at paring biomass gasification with less capital-intensive advanced fuel synthesis routes have shown potentially attractive economics [60].

The economics of pyrolysis processes or liquefaction processes to advanced biofuels are not as well developed since the technology is in an earlier stage of development. A very enticing possibility of these routes is to perform a significant portion of the upgrading to an advanced biofuel inside existing petroleum refineries. Figure 19.6 shows one possible scenario for this. The economic advantages of this are potentially significant. If a large portion of the upgrading could be accomplished utilizing existing petroleum refineries, the capital investment required would be dramatically reduced. A study estimated that a cumulative investment of $95B [61] would be required in new processing facilities to meet the RFSII goals of 21 billion gallons of cellulosic ethanol and/or advanced biofuels by 2022. Although a definitive estimate does not exist as to how much this required investment could be reduced by biofuels processing inside existing petroleum refineries, primarily because this technology is in too early of a stage of development to make this determination, it is fair to say the potential is very significant and warrants further investigation.

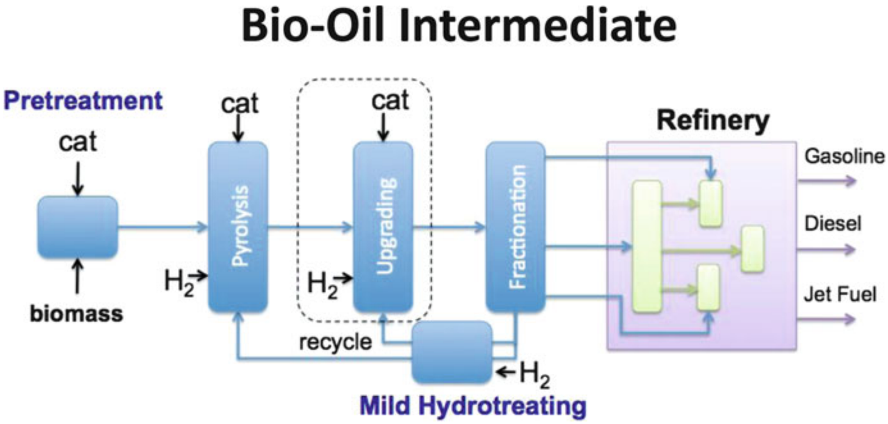

Fig. 19.6 Advanced biofuels integration with petroleum refining

State of Industry

For the most part, the comments made about the cellulosic ethanol industry hold for the advanced biofuels industry as well. One important distinction is that if the approach for processing inside petroleum refineries develops to a state where it is commercially viable, several large petroleum refinery industrial players have stated they would be interested in adopting the technology. This would be a dramatic shift in the biofuels industry because it would constitute a change from many small companies to a few well-established large players. These larger players would address the issue of not having adequate resources to take the technology to commercial deployment.

References

1. Pieber M, Toha JC. A general view of ethanol and methane production from cellulosic residues. J Ferent Technol. 1982;60(3):247–52.
2. Sk T. Process-development for ethanol-production based on enzymatic hydrolysis of cellulosic biomass. Process Biochem. 1982;17(3):36–45.
3. Cysewski GR, Wilke CR. Utilization of cellulosic materials through enzymatic hydrolysis. 1. Fermentation of hydrolysate to ethanol and single-cell protein. Biotechnol Bioeng. 1976;18 (9):1297–313.
4. Gomiero T, Tiziano P, Maurizo G, Pimentel D. Biofuels: efficiency, ethics, and limits to human appropriation of ecosystem services. J Agric Environ Ethics. 2010;23(5):403–34.
5. Searchinger T, Heimlich R, Houghton RA, Dong F, Elobeid A, Fabiosa J, et al. Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land use change. Science. 2008;319:1238–40.
6. Carter CA, Miller HI. Corn for food, not fuel. The New York Times: Opinion Pages, 30 July 2012.

7. Scown CD, Nazaroff WW, Mishra U, Strogen B, Lobscheid AB, Masanet E, et al. Corrigendum: lifecycle greenhouse has implication of US national scenarios for cellulosic ethanol production. Environ Res Lett. 2012;7:014011.
8. Hsu DD, Inman D, Heath GA, Wolfrum EJ, Mann MK, Aden A. Life cycle environmental impacts of selected U.S. ethanol production and use pathways in 2022. Environ Sci Technology. 2010;44:5289–97.
9. Schmer MR, Vogel KP, Mitchell RB, Perrin K. Net energy of cellulosic ethanol from switchgrass. Proc Natl Acad Sci USA. 2007;105(2):464–69.
10. Wang MQ, Han J, Haq Z, Tyner WE, Wu M, Elgowainy A. Energy and greenhouse gas emission effects of corn and cellulosic ethanol with technology improvements and land use changes. Biomass Bioenergy. 2011;35(5):1885–96.
11. Himmel M, Ding SY, Johnson DK, Adney WS, Nimlos MR, Foust TD. Biomass recalcitrance: engineering plants and enzymes for biofuels production. Science. 2007;315:804–7.
12. FitzPatrick M, Champagne P, Cunningham MF, Whitney RA. A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. Bioresour Technol. 2010;101(23):8915–22.
13. Liu ZS, Wu XL, Kida K, Tang YQ. Corn stover saccharification with concentrated sulfuric acid: effects of saccharification conditions on sugar recovery and by-product generation. Bioresour Technol. 2012;119:224–33.
14. Chen Y, Stevens MA, Zhu Y, Holmes J, Maxley G, Xu H. Reducing acid in dilute acid pretreatment and the impact on enzymatic saccharification. J Ind Microbiol Biotechnol. 2012;39(5):691–700.
15. Wright J. Fuel ethanol technology evaluation. Biofuels and municipal waste technology research program summary FY 1986 National Technical Information Service report DE87001140. Solar Energy Research Institute DOE/CH/1093-6.
16. Sheehan J, Riley C. Annual bioethanol outlook: FY 2001. National Renewable Energy Laboratory (NREL). Sponsored by Office of Fuels Development U.S. Department of Energy.
17. Humbird D. Biochemical Platform State of Technology Update. National Renewable Energy Laboratory (NREL) September 2011. Milestone: A.ML.12; 2011.
18. Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol. 2005;96:673–86.
19. Rana D, Ran V, Ahring B. Producing high sugar concentrations form loblolly pine using wet explosion pretreatment. Bioresour Technol. 2012;121:61–7.
20. Kazi FK, Fortman JA, Anex RP, Hsu DD, Aden A, Dutta A, Kothandaraman G. Techno-economic comparison of process technologies for biochemical ethanol production from corn stover. Fuel. 2010;89(1):S20–8.
21. Stephan JD, Mabee WE, Saddler JN. Will second-generation ethanol be able to compete with first-generation ethanol? Opportunities for cost reduction. Biofuels Bioprod Biorefin-Biofpr. 2012;6(2):159–76.
22. Huffer S, Roche CM, Blanch HW, Clark DS. *Escherichia coli* for biofuel production: bridging the gap from promise to practice. Trends Biotechnol. 2012;30(10):538–45.
23. Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A. Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. 2011. NREL/TP-5100-47764.
24. Menon V, Rao M. Trends in bioconversion of lignocellulose: biofuels, platform chemicals and biorefinery concept. Prog Energy Combust Sci. 2012;38(4):522–50.
25. Knauf M, Moniruzzaman M. Lignocellulosic biomass processing: a perspective. Int Sugar J. 2004;106(1263):147–50.
26. Klinke HB, Thomsen AB, Ahring BK. Inhibition of ethanol-producing yeast and bacteria by dehydration products produced during pre-treatment of biomass. Appl Microbiol Biotechnol. 2004;68(1):10–26.
27. Pienkos PT, Zhang M. Role of pretreatment and conditioning processes on toxicity of lignocellulosic biomass hydrolysates. Cellulose. 2009;16(4):743–62.

28. Mascoma. December 14, 2011 Press Release – Mascoma awarded $80 million from the US DOE for construction of commercial-scale hardwood cellulosic ethanol facility in Kinross. Michigan.
29. Chu J. Cellulosic ethanol on the cheap. MIT Technology Review-Business News. 12 May 2009
30. Tao L, Aden A. The economics of current and future biofuels. In Vitro Cell Dev Biol-Plant. 2009;45(1):199–217.
31. Carriquiry MA, Du X, Timilsina GR. Second generation biofuels: economics and policies. Energy Policy. 2011;39(7):4222–34.
32. Henstra AM, Sipma J, Rinzema A, Stams AJM. Microbiology of synthesis gas fermentation for biofuel production. Curr Opin Biotechnol. 2007;18(3):200–6.
33. Kumar A, Jones DD, Hanna MA. Thermochemical biomass gasification: a review of the current status of the technology. Energies. 2009;2(3):556–81.
34. Phillips S, Aden A, Jechura J, Dayton D, Eggeman T. Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass. 2007; NREL/TP-510-41168.
35. Dutta A, Phillips SD. Thermochemical ethanol via direct gasification and mixed alcohol synthesis of lignocellulosic biomass. 2009; NREL/TP-510-45913.
36. Dutta A, Bain RL, Biddy MJ. Techno-economics of the production of mixed alcohols from lignocellulosic biomass via high-temperature gasification. Environ Process Sustain Energy. 2010;29(2):163–74.
37. Carpenter DL, Bain RL, Davis RE, Dutta A, Feik CJ, Gaston KR, et al. Pilot-scale gasification of corn stover, switchgrass, wheat straw, and wood: 1. Parametric study and comparison with literature. Ind Eng Chem Res. 2010;49(4):1859–71.
38. Noichi H, Uddin A, Sasaoka E. Steam reforming of naphthalene as model biomass tar over iron-aluminum and iron-zirconium oxide catalyst catalysts. Fuel Process Technol. 2010;91 (11):1609–16.
39. Magrini-Bair KA, Jablonski WS, Parent YO, Yung MM. Bench- and pilot-scale studies of reaction and regeneration of Ni-Mg-K/AL2O3 for catalytic conditioning of biomass-derived syngas. Top Catal. 2012;55(3–4):209–17.
40. Subramani V, Gangwal SK. A review of recent literature to search for an efficient catalytic process for the conversion of syngas to ethanol. Energy Fuels. 2008;22(2):814–39.
41. Spivey JJ, Egbebi A. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. Chem Soc Rev. 2007;36(9):1514–28.
42. Baldwin RM, Magrini-Bair KA, Nimlos MR, Pepiot P, Donohoe BS, Hensley JE, et al. Current research on thermochemical conversion of biomass at the National Renewable Energy Laboratory. Appl Catal Environ. 2012;115–116:320–9.
43. Dutta A, Talmadge M, Hensley J, Worley M, Dudgeon D, Barton D, et al. Techno-economics for conversion of lignocellulosic biomass to ethanol by direct gasification and mixed alcohol synthesis. Environ Prog Sust Energy. 2012;31(2):182–90.
44. Foust TD, Aden A, Dutta A, Phillips S. An economic and environmental comparison of a biochemical and a thermochemical lignocellulosic ethanol conversion processes. Cellulose. 2009;16(4):547–65.
45. US Energy Policy Act (EPActO of 2005 as amended by the Energy Independence and Security Act (EISA) of 2007. www.epa.gov/otaq/fuels/renewablefuels/index.htm. Last accessed 21 Feb 2013.
46. Biofuels Digest. Industrial database, category: biofuels digest index. 2013. http://www.biofuelsdigest.com/bdigest/category/biofuels-digest-20-index-bdi. Last accessed 25 Feb 2013.
47. Walls WD, Russo F, Kendrix M. Biofuels policy and the US market for motor fuels: empirical analysis of ethanol splashing. Energy Policy. 2011;39(7):3999–4006.
48. U.S. EPA E15 partial waiver January 21, 2011. www.epa.gov/otaq/regs/fuels/additive/e15/. Last accessed 21 Feb 2013.

49. deFreitas LC, Kaneko S. Ethanol demand in Brazil: regional approach. Energy Policy. 2011;39 (5):2289–98.
50. Zurgiggen A, Kirst H, Melis A. Isoprene production via the mevalonic acid pathway in *Escherichia coli* (Bacteria). Bioenergy Res. 2012;5(4):814–28.
51. Alonso DM, Bond JQ, Dumesic JA. Catalytic conversion of biomass to biofuels. Green Chem. 2010;12:1493–13.
52. Bain RL, Broer K. Gasification. In: Brown RC, editor. Thermal processing of biomass: conversion into fuels, chemicals and power. Chichester: Wiley; 2011. p. 47–77.
53. Spaeth PL, Dayton DC. Preliminary screening-technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived synthesis. NREL; 2003. NREL/TP-510-34929.
54. Venderbosch RH, Prins W. Fast pyrolysis, chapter 5. In: Brown RC, editor. Thermal processing of biomass. New York: Wiley; 2011. p. 124–56.
55. Bridgewater AV. Upgrading fast pyrolysis liquids. In: Brown RC, editor. Thermal processing of biomass: conversion into fuels, chemicals and power. Chichester: Wiley; 2011. p. 157–88.
56. Mullen CA, Boateng AA, Mihalcik DJ, Goldberg NM. Catalytic fast pyrolysis of white oak wood in a bubbling fluidized bed. Energy Fuels. 2011;25(11):5444–51.
57. Mortensen PM, Grunwaldt JD, Jensen PA, Knudsen KG, Jensen AD. A review of catalytic upgrading of bio-oil to engine fuels. Appl Catal A Gen. 2011;407(1–2):1–19.
58. Elliot DE. Hydrothermal processing. In: Brown RC, editor. Thermal processing of biomass: conversion into fuels, chemicals and power. Chichester: Wiley; 2011. p. 200–26.
59. Anex RP, Aden A, Kazi FK, Fortman J, Swanson RM, Wright MM, et al. Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification and biochemical pathways. Fuel. 2010;89(1):29–35.
60. Phillips SD, Tarud JK, Biddy MJ, Dutta A. Gasoline from woody biomass via thermochemical gasification, methanol synthesis and methanol-to-gasoline technologies: a technoeconomic analysis. Ind Eng Chem Res. 2011;50(24):11734–45.
61. Bio Economic Research Associates. U.S. Economic impact of advanced biofuels production: perspectives to 2030 bio-era. Bio Economic Research Associates.