CHAPTER TWELVE
BIOFUELS

EXECUTIVE SUMMARY

Conventional biofuels are commercial today and can provide a greenhouse gas (GHG) benefit over fossil fuels. Today the United States has daily production capacity of approximately 14 billion gallons (910,000 barrels per day) of ethanol from renewable resources, namely corn-derived dextrose. In addition, the United States is producing about 2 billion gallons of biodiesel. The potential exists for significant expansion of first generation biofuels as improvements in yields continue to increase; specifically, corn yields are predicted to double by 2030.

Cellulosic biofuels are liquid fuels derived from biomass such as stover, switchgrass, timber, and other agricultural waste and algae. Cellulosic biofuels offer the potential for expanding the feedstock supply and providing greater GHG reduction than conventional liquid transportation fuels. There are significant quantities of biomass available, which if converted to biofuels, could increase the volume of available biofuels several fold from today's levels. Several demonstration plants are under construction to demonstrate the technology for producing advanced biofuels. Biofuels can also provide a significant opportunity to leverage existing vehicle and fueling infrastructure; for example, flexible-fuel vehicles and fueling stations. Algal-based biofuels represent an alternative that holds promise for supplying large quantities of biofuel, but significant technological challenges, and economic uncertainty, qualify this opportunity as longer term than the options described above.

While there are no major barriers preventing expansion of today's biofuels technology, there are significant challenges to the use of cellulosic biofuels. Feedstock logistics and fuel production technologies are well established for conventional biofuels, but additional fuel and vehicle infrastructure will be needed to support increased volumes. While several larger scale research, development, and demonstration plants for cellulosic biomass conversion to ethanol, and pyrolysis, are nearing completion, technological and economic challenges still remain. Routes to biofuel production, using gasification technologies employing biomass feedstock, are also under active research and development. However, significant economic hurdles may limit the applicability of such technologies.

There are two major technology platforms for cellulosic conversion, biological and thermochemical. Each technology platform has several separate pathways under development that will allow for the commercial deployment of cellulosic biofuels in the form of ethanol, isobutanol, and other "drop in" biofuels. However, according to a recent study from the National Academy of Sciences, National Academy of Engineering, and National Research Council (NAS/NAE/NRC), there are technological and economic challenges for advanced biofuels.

Continued development of the biomass supply depends on improving crop yields per acre, arable land availability, and co-product production and utilization. Significant research efforts are underway to increase the yields of cellulosic energy crops such as switchgrass and miscanthus. Infrastructure development to collect, store, transport, and process biomass is critical to the wide-scale adoption of biofuels. It should also be recognized that there will be additional demands on the biomass resource beyond liquid transportation fuels, including power generation, chemical feedstocks, and products.

CHAPTER INTRODUCTION

This chapter discusses the challenges, the opportunities, and the potential role of biofuels as a sustainable source of transportation fuel in the United States through the year 2050. The role of biofuels to meet transportation fuel demands in an economically competitive, sustainable manner, utilizing resources within the United States, will be discussed in further detail. Today the United States has daily production capacity of approximately 14 billion gallons (910,000 barrels per day) of ethanol from renewable resources, namely corn-derived dextrose. In addition, the United States is producing nearly 1 billion gallons of biodiesel. The potential exists for significant expansion of first generation biofuels as improvements in yields continue to increase; specifically, corn yields are predicted to double by 2030. Corn and sugarcane ethanol and vegetable-oil-derived biodiesel have demonstrated the opportunities and potential for biofuels. In order to be competitive with first generation biofuels, second generation cellulosic-derived biofuels will need to overcome key barriers that will drive improved yields and process performance, and economics.

First Generation Biofuels Growth

An examination of the historical growth of the first generation biofuels, corn for ethanol, and oilseeds for biodiesel, can help in predicting the growth of second generation biofuels. Their growth can be traced to the increased need for agricultural production to meet the growing need for food in the United States and abroad.

More recently, the adoption of U.S. biofuels requirements under the Renewable Fuel Standards (RFS) has accelerated that growth. The two mandated biofuels, corn-based ethanol and vegetable oil biodiesel, have seen significant growth since the introduction of RFS2. As a result, first generation biofuels have displaced roughly 4% of U.S. transportation fuel demand in 2010. To the extent that yield increases and crop intensification globally continue to outpace demand, there is significant potential for additional first generation biofuels production. First generation biofuels have GHG benefits—the extent of the benefit is dependent on such factors as the cultivation methods and fertilizer use, land use change, energy used in crop growth, transport, and production of the fuel from the biomass. Agriculture in the United States has reduced the input requirements for first generation biomass by 50% over the past 20 years and technology is making further improvements likely. When calculating the GHG footprint of any fuel, a comprehensive life-cycle analysis should be employed to establish potential GHG savings. This topic is further explored in Chapter Six, "Greenhouse Gases and Other Environmental Considerations."

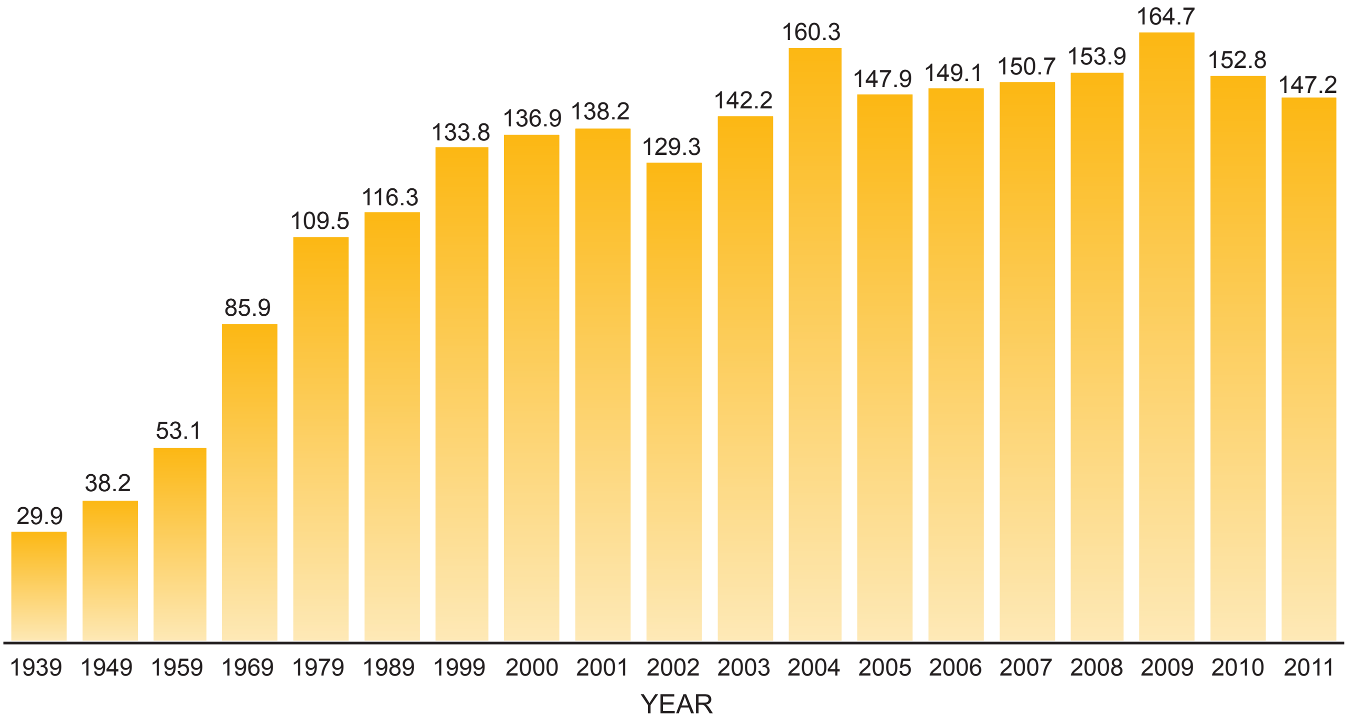
FIRST GENERATION BIOFUELS TECHNOLOGY – CURRENT STATUS

A brief review of the growth of the first generation biofuels industry helps to illustrate the potential growth pattern for second generation biofuels. Critical factors include the development of a robust agricultural supply chain, improved farming and harvesting techniques, and genetic crop modification.

The United States has a sophisticated and well-developed agricultural supply chain. The supply chain includes an efficient infrastructure for delivery of raw agricultural inputs including seed, minerals, and fertilizer. The acreage currently planted for the two primary crops used in biofuels production, corn and soybeans, is about 160 million acres annually. These products are harvested, stored, and distributed through an integrated system including on-site storage, elevator networks, and agricultural processing facilities. The transportation of crops is accomplished primarily via truck, rail, and barge. The infrastructure continues to evolve and expand as yields have improved and the total volume of materials has expanded, making the United States the most efficient agricultural producer, distributor, and processor in the world.

Corn Ethanol

Figure 12-1 shows the increase in corn yields that have occurred in the United States over the past 60 years, starting in 1939. The ethanol industry emerged as an opportunity to convert the ever-growing surplus of corn into fuel and feed. By 1993, the emerging industry had grown to produce nearly 1 billion gallons of fuel per year, consuming an additional 450 million bushels of corn, yet stocks-to-use ratios persisted at nearly 25% on the heels of a record harvest.



Source: U.S. Department of Agriculture, National Agriculture Statistics Service.

Figure 12-1. *Average Corn Yields in the United States (Bushels per Acre)*

Acreage dedicated to corn has ranged from about 65 million acres to 94 million acres over the past 70 years. Figure 12-2 shows the specific acreage planted since 1939. In general, acres planted are a reflection of market conditions and pricing since growers make decisions based on commodity prices, land prices, and input costs.

Corn production in the United States is shown in Figure 12-3. The United States has continued to increase total corn production since the 1930s on a relatively constant amount of farmland. The majority of the growth over the past 10 years has been to support ethanol production as mandated in the Renewable Fuel Standards, which were created in 2005 and revised in 2007.

The advent of biotechnology traits coupled with globalization of germplasm further enabled both increases as well as protection of corn yields as shown in Figure 12-4. Corn's 30-year trend line yield growth began to accelerate over the next interim, averaging nearly 1.5% compounded growth per annum. Biotechnology traits were also introduced in key crops including soybeans, canola, and cotton, further maximizing land productivity. Once again, the biotechnology traits that increase both productivity as well as yield, were rapidly and readily adopted.

One of the critical issues for the continued growth of biofuel production in the United States is biomass supply and the efficient conversion of cellulosic biomass. In the case of ethanol, the feedstock for the industry is largely based on starch and sugar crops with the potential to expand into lignocellulosic feedstocks in the near future as technologies develop. Potential production capacities for biofuels based on cornstarch out to 2030 in the United States are in the range of 30 to 35 billion gallons of ethanol equivalent[1]—well beyond original RFS volumes.

Significant increases in corn supply are expected, based on past trends and expected improvements via biotechnology. An expert panel assembled by the U.S. Department of Energy (DOE) in 2009 agreed that corn yield growth would continue through 2050, as shown in Figure 12-5. "The majority of

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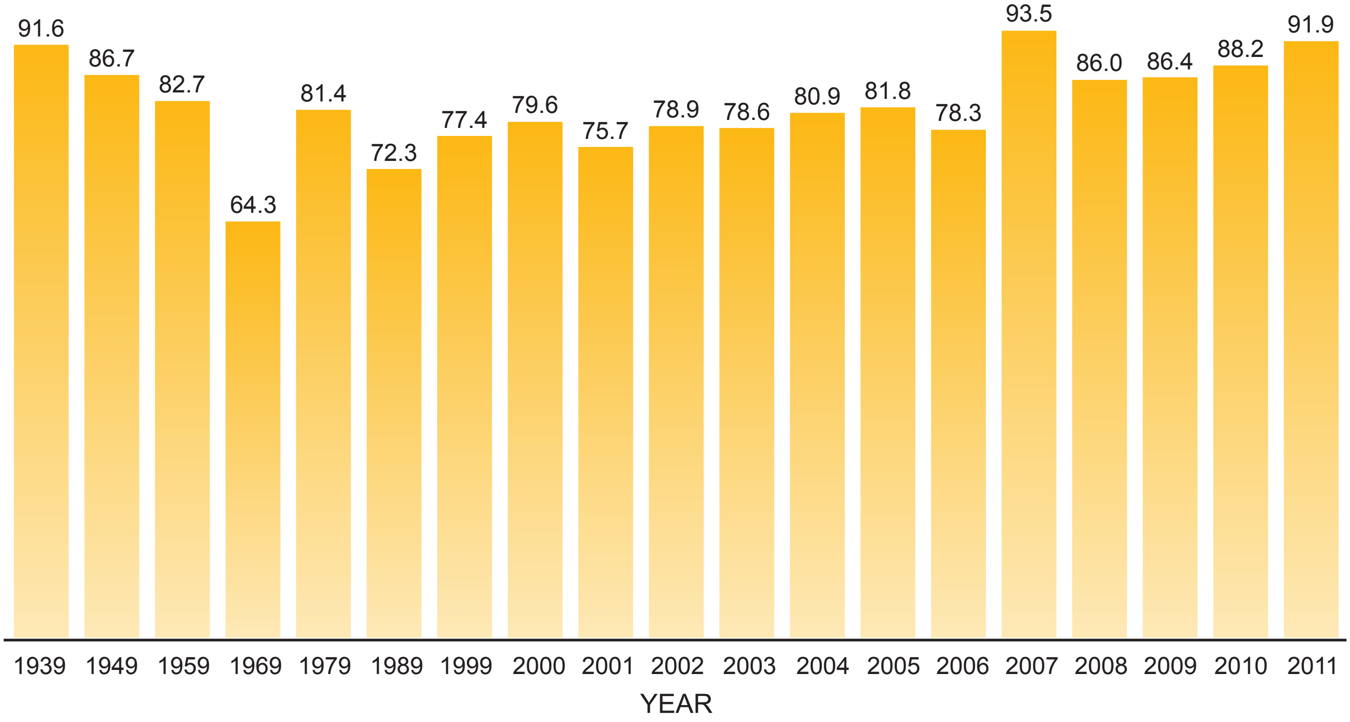
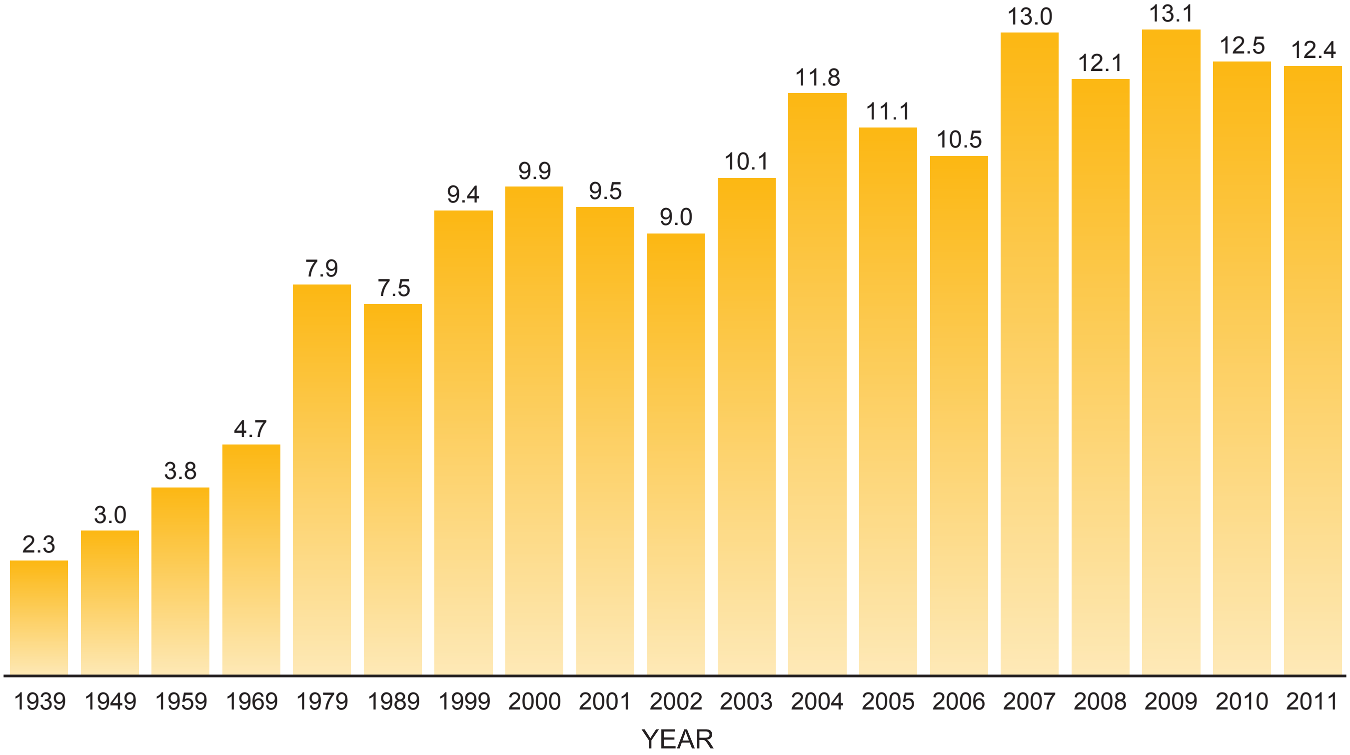
[1] Amani Elobeid et al., *The Long-Run Impact of Corn-Based Ethanol on the Grain, Oilseed, and Livestock Sectors: A Preliminary Assessment,* CARD Briefing Paper 06-BP 49, Center for Agricultural and Rural Development, Iowa State University, November 2006.



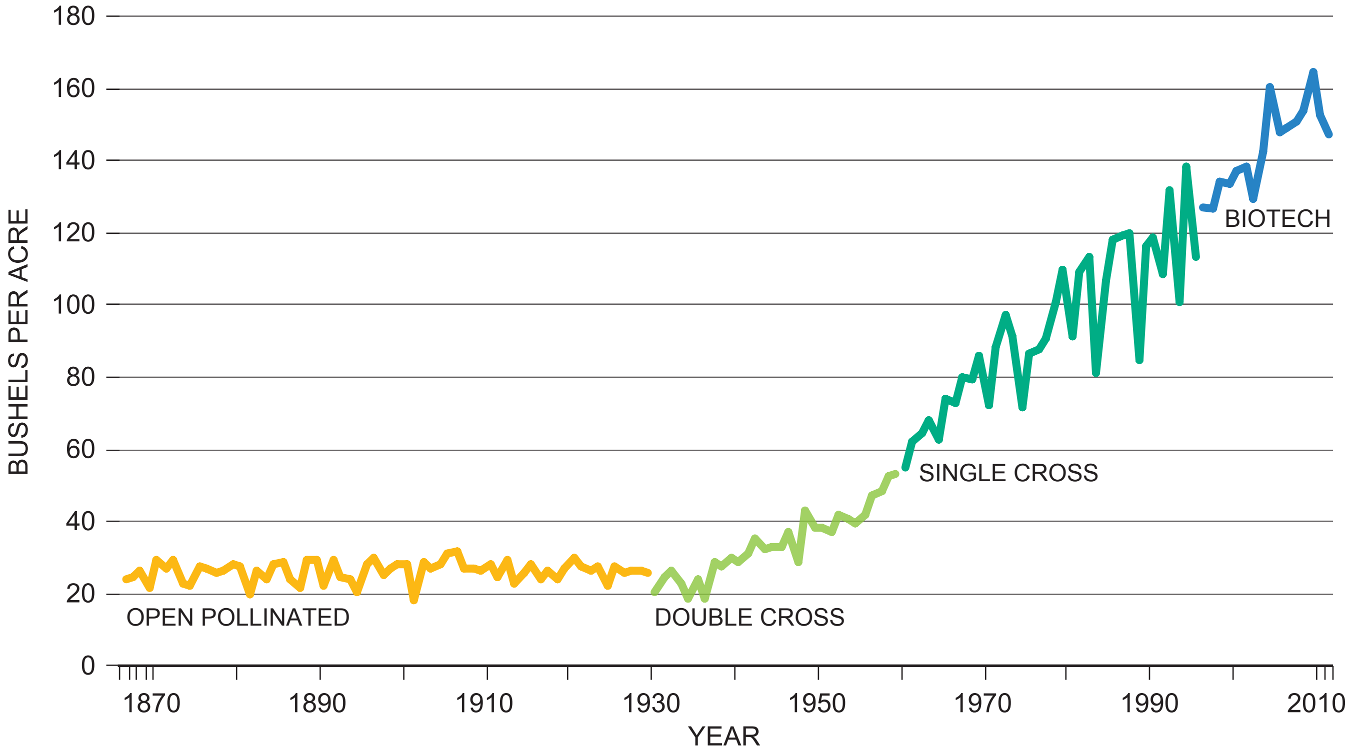
Source: U.S. Department of Agriculture, National Agriculture Statistics Service.

Figure 12-2. *Corn Acres Planted in the United States (Thousands of Acres)*



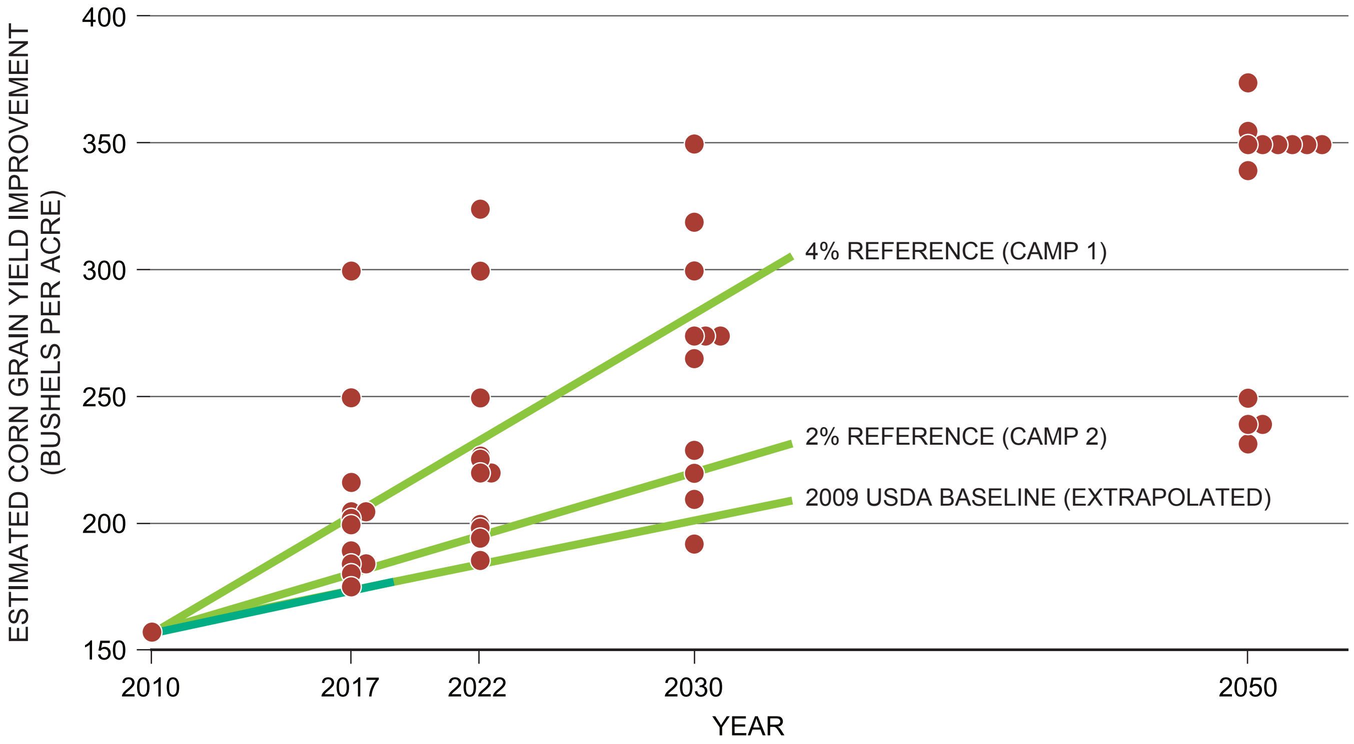
Source: U.S. Department of Agriculture, National Agriculture Statistics Service.

Figure 12-3. *Total Corn Production in the United States (Billions of Bushels)*



Source: U.S. Department of Agriculture, National Agriculture Statistics Service.

Figure 12-4. *Corn Yield Gains, 1865–2010*



Source: Idaho National Laboratory, *High Yield Scenario Workshop Series Report*, December 2009.

Figure 12-5. *Projections for Future Corn Yields* participants believed that genetic development and advanced management concepts would produce a near-term step change in annual yield increase (≥4%) and enable grain yields exceeding 250 bushels per acre by 2030."[2]

The U.S. Department of Agriculture (USDA) yield outlooks are below the expected yields projected by the DOE panel. Plotting actual corn yields against USDA-predicted corn yields, Figure 12-6 shows that USDA projections are relatively conservative. Depending on which future predictions are correct, cornstarch-based ethanol production has the potential to supply up to 35 billion gallons of ethanol or ethanol energy equivalent biofuels by 2030.

Corn-Based Ethanol Production

Corn ethanol is produced by two distinct processes, dry milling and wet milling, shown in Figures 12-7 and 12-8.

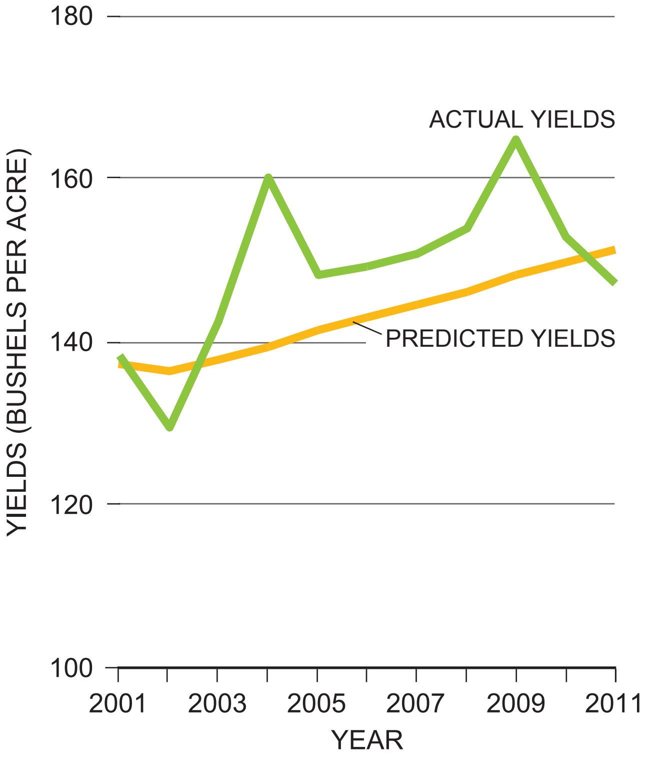


Figure 12-6. *USDA-Predicted Corn Yields, by Year of Prediction, versus Actual Yields*

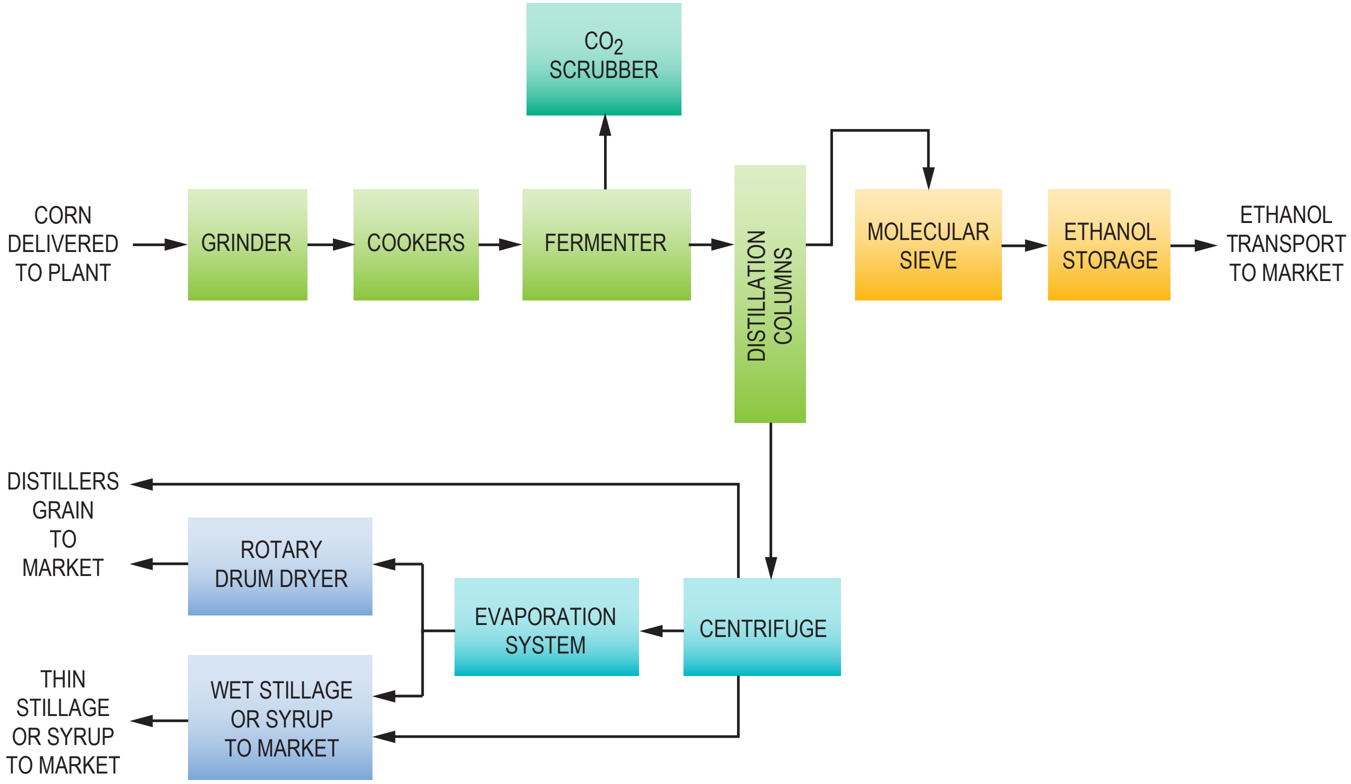


Figure 12-7. *Ethanol Production from Corn Dry Milling*

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[2] Idaho National Laboratory, *The High-Yield Scenario Workshop Series Report,* prepared for the Department of Energy, Energy Efficiency and Renewable Energy Biomass Program, December 2009.

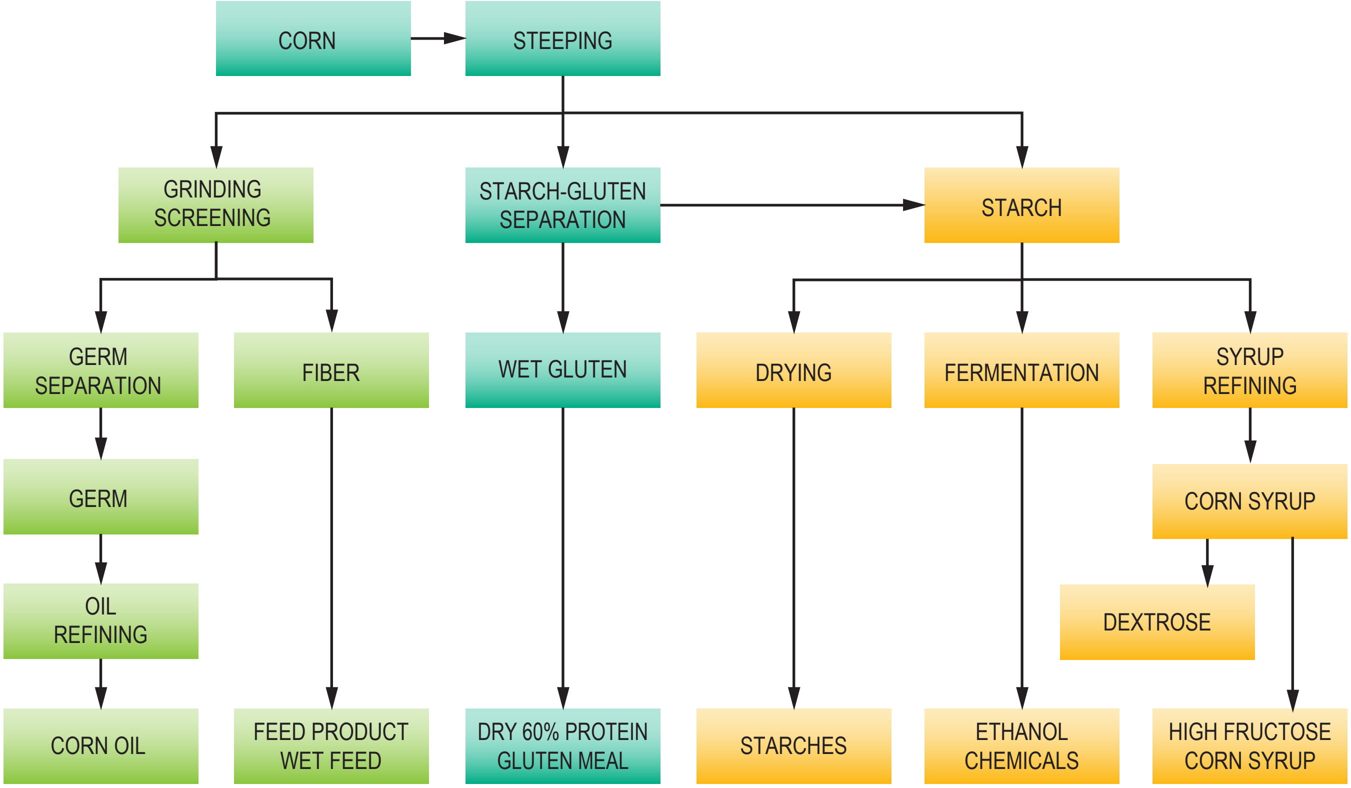


Figure 12-8. *Ethanol Production from Corn Wet Milling*

Ethanol production has grown steadily in the United States since 1980, when the RFS legislation was enacted. The tax incentive for blending ethanol into gasoline was a key to the growth of the industry and the development of infrastructure. The growth of the ethanol industry and ethanol production has by and large kept pace with the Renewable Fuel Standards (RFS and RFS2) mandate. Corn-based ethanol usage has in certain periods exceeded the RFS2 mandate when the economics were favorable for ethanol blending. The maximum single year growth occurred between 2007 and 2008, when over 2 billion gallons of capacity were added to the industry. Figure 12-9 shows the growth of ethanol production since 1998.

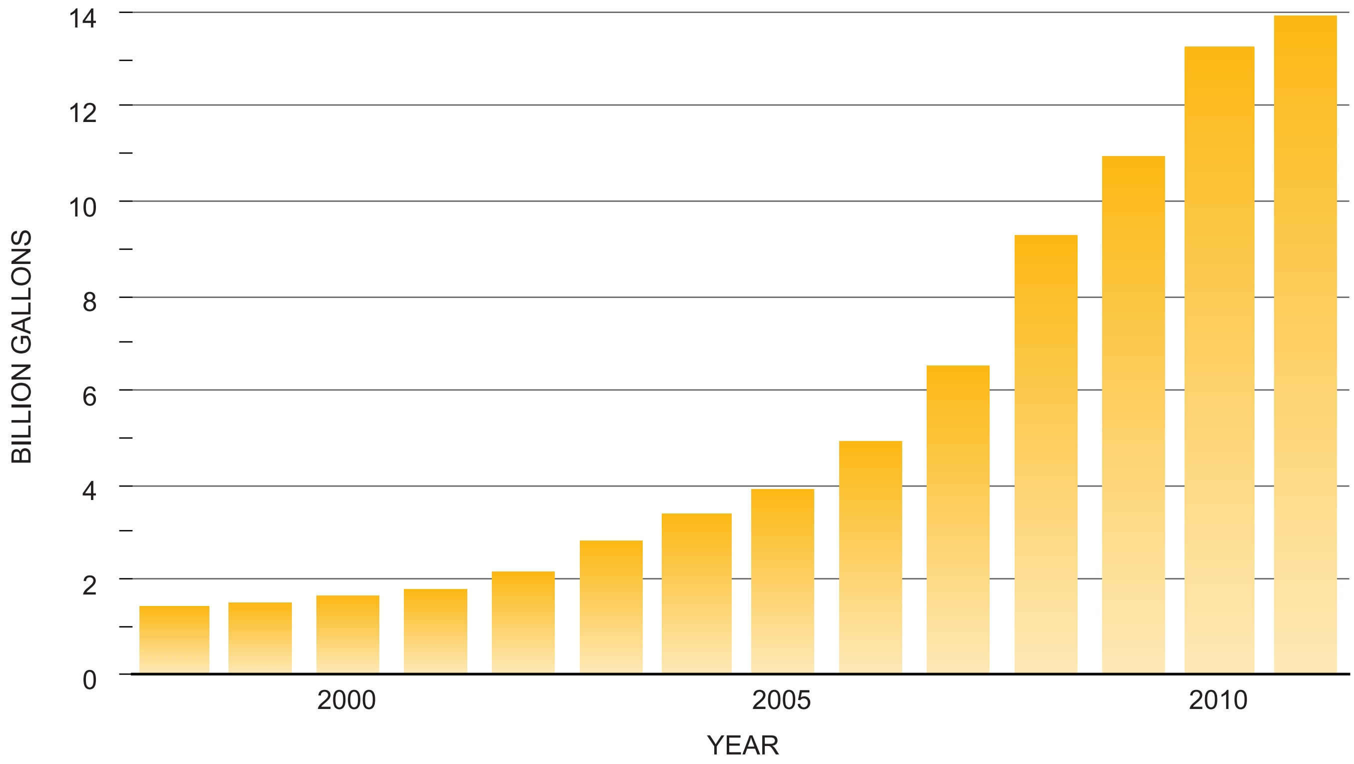
Oilseed Supply Chain

Soybeans are by far the main source of vegetable oil and biodiesel production in the United States, accounting for almost 90% of biodiesel produced from oilseeds. As stated earlier, other crops besides corn have seen yield gains and oilseeds are no exception. Figure 12-10 shows soybean yield increases. Both oilseed and oil extracted from distillers dried grains from ethanol production can be sources of vegetable oil for biodiesel production.

Yield increases in protein crops and the production of distillers dry grains play a particular role in helping to enable additional biofuel to be produced, as protein markets have been more limited than starch markets. As soybean yields increase, the total demand can be met with fewer acres. These acres can then be planted in alternative crops, such as corn or cellulosic biofuel crops.

Oilseed-Based Biodiesel Production

Over 90% of the oilseed-based biodiesel produced in the United States is from soybeans, where the balance is from canola. The yield of biodiesel from soybeans is about 66 gallons per acre and 92 gallons from canola. The production processes for biodiesel are well established. There are three basic routes to biodiesel production from oils and fats: base catalyzed transesterification, direct acid



Source: U.S. Department of Energy, Alternative Fuels Data Center.

Figure 12-9. *U.S. Ethanol Production*

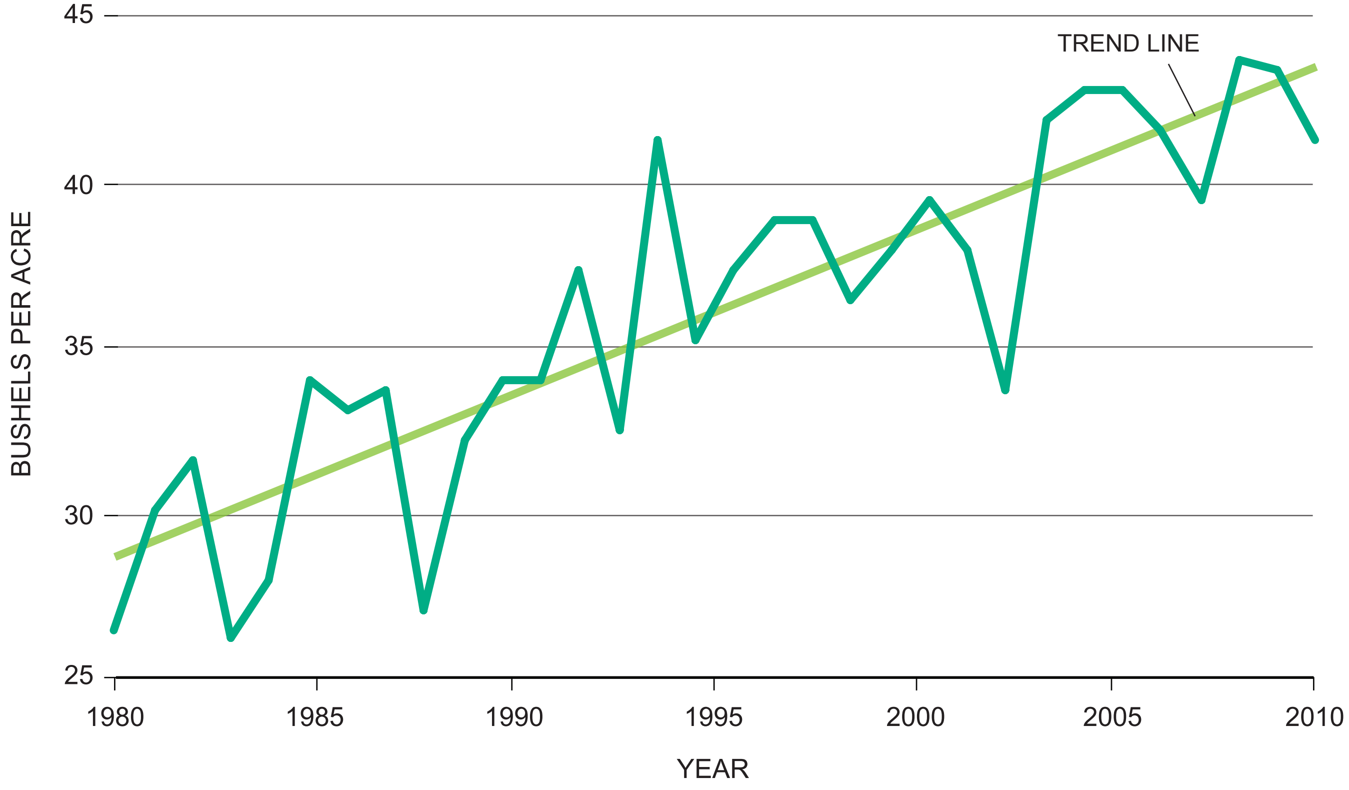


Figure 12-10. *U.S. Soybean Yield, 1980 through 2010*

catalyzed transesterification, and conversion of the oil to fatty acids and then to biodiesel. Figure 12-11 shows a simplified diagram of biodiesel production.

SECOND GENERATION BIOFUELS TECHNOLOGY – CURRENT STATUS AND HURDLES

Biomass Supply

Biomass is a relatively local product and this is especially the case for crop residues and grasses. Long-term storage and transportation to conversion facilities is a problem that has not yet been solved. The disconnect between cost and energy-efficient delivery of the feedstock to centralized plants has placed severe limitations on the economies of scale of biomass conversion plants. Storage of biomass until needed by a processing plant is also a challenge because of dry matter losses up to 15% over a season as well as the footprint required to store a low-density biomass for delivery to a large central plant.

While there are several challenges associated with the collection, storage, and delivery of biomass, the resource itself is substantial. In DOE's *U.S. Billion-Ton Update,* the authors have detailed U.S. biomass feedstock potential nationwide.[3] The 2011 report identified over 1 billion dry tons of biomass resources annually under a high yield case for energy uses without impacting other vital U.S. farm and forest products such as food, feed, and fiber crops. Figure 12-12 shows biomass availability by segment as reported in the DOE report. The DOE report provides a comprehensive review of the biomass supply and should be referenced for additional insights into the availability of biomass.

A 2009 study conducted by the National Academies also reported that biomass supplies could reach 550 million dry tons by 2020.[4] The biomass supply would be adequate to meet the project biofuels production estimated in this study.

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[3] U.S. Department of Energy, *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry,* prepared by Oak Ridge National Laboratory, August 2011.

[4] National Academies, *Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Impacts,* 2009, http://www.nap.edu/catalog/12620.html.

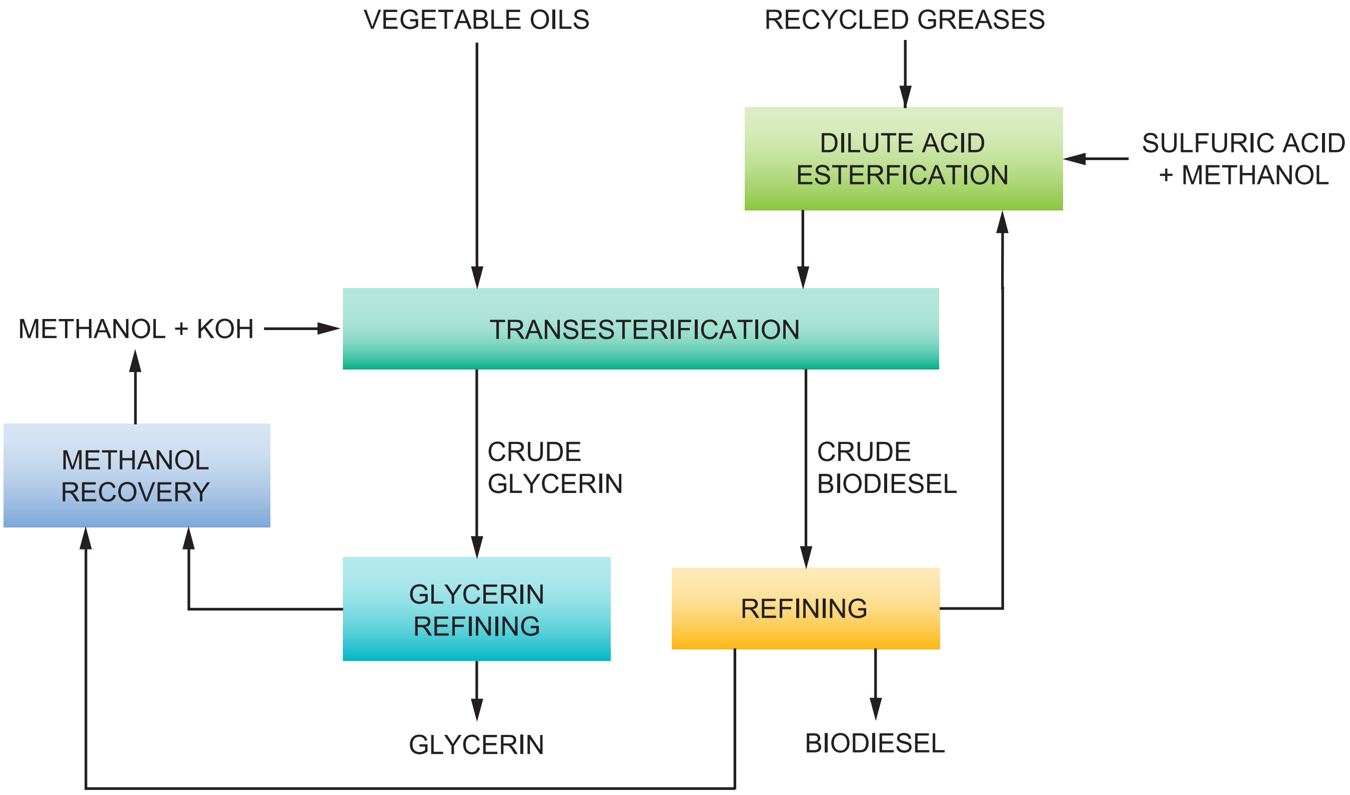
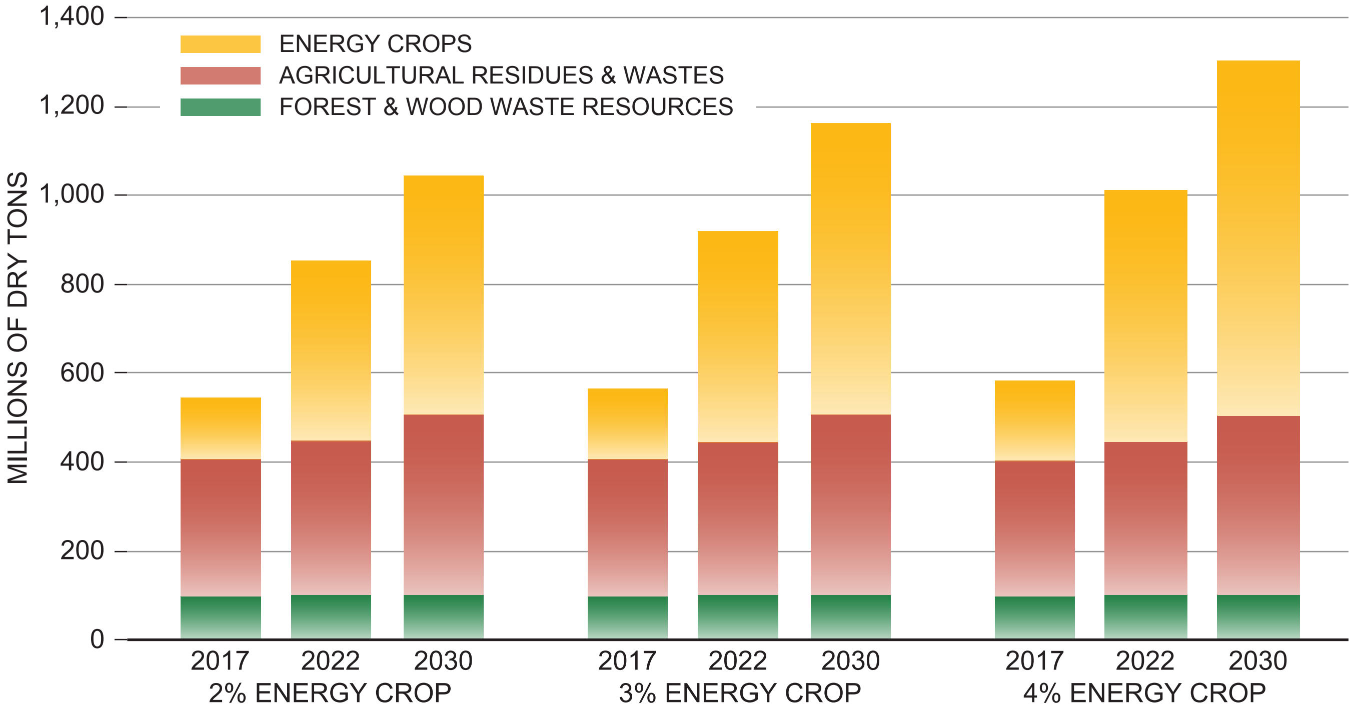


Figure 12-11. *Simplified Process Flow Diagram of Biodiesel Production*



Source: U.S. Department of Energy, *U.S. Billion-Ton Update*, August 2011.

Figure 12-12. *Estimated Forest and Agricultural Biomass Availability at $60 per Dry Ton or Less Under High-Yield Assumptions*

Biomass Hurdles

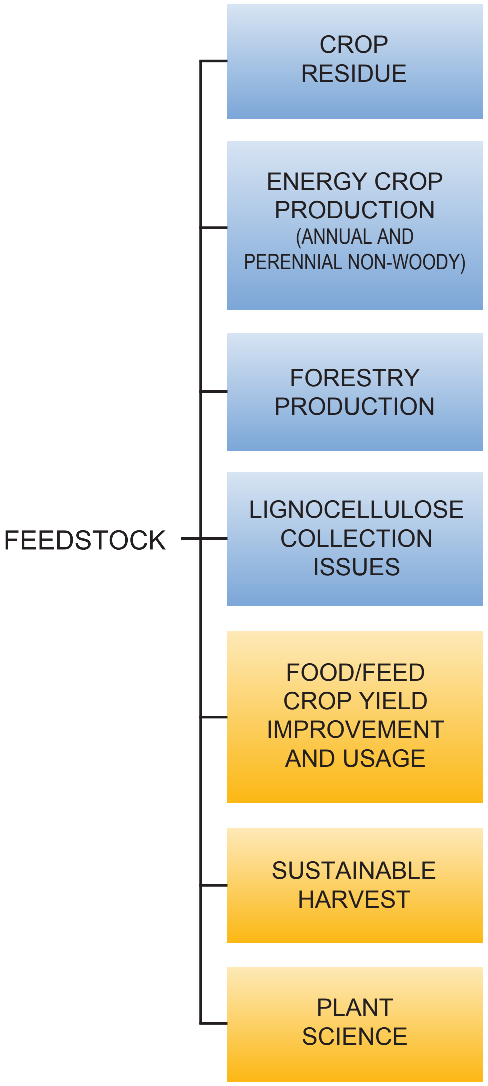
Table 12-1 as well as Figure 12-13 show hurdles that will need to be addressed in order to achieve timely production of the necessary biomass for biofuel production. Developing the knowledge needed for the long-term sustainability of agricultural production to meet food, fiber, and fuel needs will be a priority. Increasing crop yield, developing crops that are more tolerant to the vagaries of nature and can use fertilizer more efficiently will be key developments. Once the crops are produced, getting this new volume collected, stored, and transported will also be new hurdles for this new industry. The columns in Table 12-1 are interdependent; therefore, it becomes difficult to delineate between the columns because the high importance items are closely related to the items identified in the low importance column.

Biotechnology for Cellulosic Ethanol – Current Status

Conversion technologies in which biomass polysaccharides are hydrolyzed into their component sugars, and sugars then fermented to produce biofuels, fall under what is known as the biochemical platform. A typical process configuration for a cellulosic ethanol plant using the biochemical pathway is shown in Figure 12-14. For a biochemical platform biofuel production plant, the key unit processes are typically pretreatment, hydrolysis, fermentation, and distillation. Of these four unit processes, distillation technology will be similar to that used in corn ethanol plants, and is not expected to pose significant technical challenges. Pretreatment, hydrolysis, and fermentation, on the other hand, present significant technical and economic challenges, and are the subject of substantial government and private industry research efforts. One of the overarching objectives of these efforts is to find that combination of pretreatment method, enzyme cocktail/dose, hydrolysis duration, and overall yield (from pretreatment, hydrolysis, and fermentation) that minimizes the biofuel production cost. These efforts have begun to bear fruit; several pilot/demo cellulosic biofuel plants based on the biochemical pathway are in operation and at least one commercial scale plant

High Importance	Medium Importance	Low Importance
Sustainable cropping practices	Regional crop characteristics	Availability of crop residue
Maintaining soil nutrients	Harvest machinery	Energy crop harvest
Collection infrastructure needs	Return of nutrients from biomass processing	Maintaining soil productivity in energy crop production
Breeding and biotechnology development to increase yield improvement rates	Long-term control of weeds, disease, and pests	Development of energy crop traits for end use
Increasing biomass density and stability once harvested	Transportation and storage infrastructure	
Improved photosynthetic efficiency		
Drought tolerance		
Fertilizer efficiency and recycling		

Table 12-1. Key Hurdles and Priorities



MANAGING FOOD, FEED, FIBER, AND FUEL DEMANDS ON A LIMITED LAND SUPPLY

CROP RESIDUE COLLECTION

- Future availability of feedstock will depend on several variables, including crop acreage planted to meet competing demands; continued improvements derived for agricultural biotechnology; cropping practices and soil quality maintenance considerations. There are significant regional differenced in crop characteristics to consider, as well as differences in harvesting mechanics for stover and straw. More corn stover is available than straw, but straw is more readily removed (although in some areas in must be left in the field to retain moisture in the soil). Straw collection infrastructure is generally well developed, while corn stover collection is not. When cereal grain is ready to harvest, straw usually contains ~20% moisture or less, suitable for baling. In contrast, stover contains up to 50% moisture and must remain in the field to dry and be collected later, depending on the weather. A wet harvest season can prevent its collection entirely

ENERGY CROP PRODUCTION (ANNUAL AND PERENNIAL NON-WOODY)

- Selection and breeding of suitable varieties for different regions in the U.S., needed fertilizer rates for sustainable yields, long-term control of invasive varieties, and development of genetic engineering tools for these crops.

FORESTRY PRODUCTION

- Sustainable practices need to be developed for harvesting of woody biomass for energy production while protecting the soil productivity, development of high biomass yielding varieties, development of varieties with more suitable traits for deconstruction to monomers for biological conversion, plant breeding science, and genetic engineering tool developments for high biomass production varieties.

LIGNOCELLULOSE DENSITY ISSUES

- Baled stover has a bulk density 1/6 of corn grain, compacted biomass about 1/4, and briquette about 1/2 that of corn. 15 billion gallons of stover-based fuel will require ~8 times the volume of storage that the current corn required to produce this volume. In terms of the entire U.S. current corn crop, this is about 3.5 times the current storage and logistical capacity. It will also require the road and rail infrastructure to move 3.5 times more volume than our current corn crop. Serious logistical solutions will be needed to address this issue.

🟦 MINIMAL/NO BARRIERS

🟨 WILL TAKE INVESTMENT AND TIME, BUT PATHWAY FOR SUCCESS HAS BEEN IDENTIFIED

Figure 12-13. Detailed Hurdles for Biomass Supply

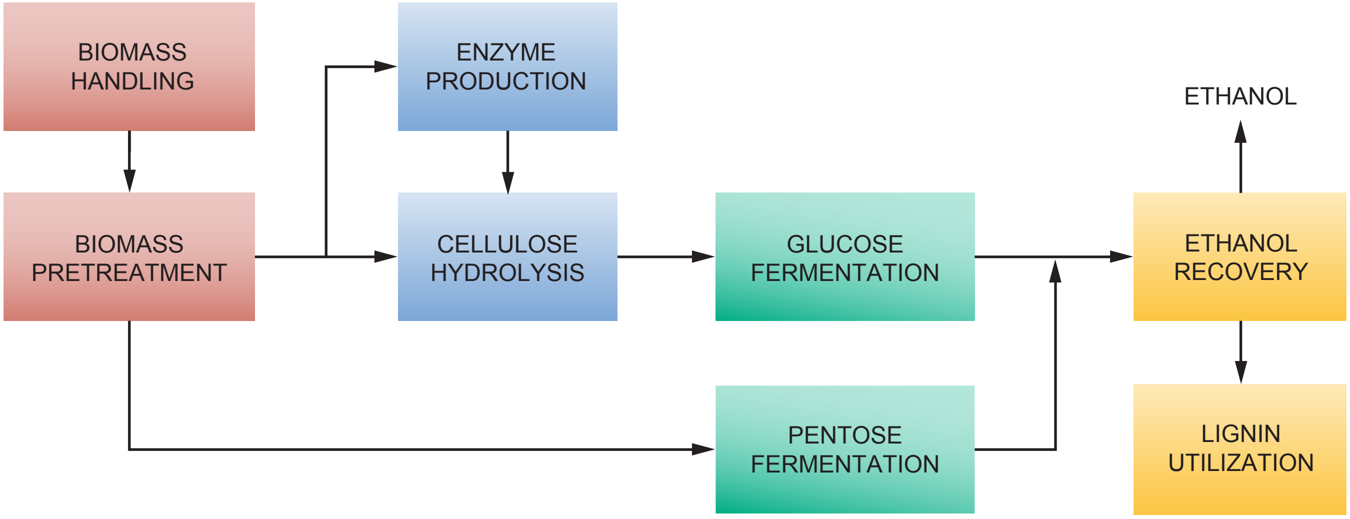


Figure 12-14. *Bioethanol Production Process Diagram*

is under construction. In the United States, plans to build commercial-scale cellulosic biofuel plants have been announced by Abengoa, DuPont, POET, and BP. The current state of technology for the biochemical pathway is discussed below.

Pretreatment

In most currently envisioned biochemical cellulosic biofuel processes, mechanical and chemical processing, known as pretreatment, is a necessary prerequisite to the enzymatic and microbial bioprocessing that forms the fuel. These steps reduce the heterogeneity and recalcitrance of biomass feedstocks and increase the accessible surface area of their constituent carbohydrate polymers, making subsequent processing steps far more effective. Without some form of pretreatment, large chunks of harvested biomass are difficult to convey in a processing plant; sugar yields from enzymatic hydrolysis are often less than 20%.[5] Moreover, pretreatment can serve to decrease natural feedstock variability and, in some cases, fractionates biomass to produce multiple streams enriched in specific components such as cellulose, lignin, or sugars. However, the pretreatment process also produces compounds that are inhibitory to both enzymes and fermentation organisms.[6] The nature and amount of inhibitory chemicals is dependent on pretreatment type, feedstock type, and pretreatment severity.[7]

When feedstock enters the conversion process it is typically first subjected to physical preprocessing. These steps can clean and size-reduce the biomass, providing an interface between harvest and conversion. Like other natural products, biomass can be highly variable depending on its genetic background, growing conditions, and harvest; e.g., moisture content may range from 10–80% by weight. Physical preprocessing must accept this variation and through operations such as dewatering, milling, and physical separations mitigate it for downstream processes. Washing, screening, and other physical separations are vital yet often overlooked components of pretreatment, which prevent grit, large fragments of feedstock, and foreign objects from damaging downstream equipment.

Much of the technology for physical pretreatment already exists in industries such as cane sugar

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[5] N. Mosier et al., "Features of Promising Technologies for Pretreatment of Lignocellulosic Biomass," Bioresource Technology 96, no. 6 (2005): pages 673–686.

[6] H. B. Klinke, A. B. Thomsen, and B. K. Ahring, "Inhibition of Ethanol-producing Yeast and Bacteria by Degradation Products Produced During Pre-treatment of Biomass," *Applied Microbiology and Biotechnology* 66, no. 1 (2004): pages 10-26.

[7] B. Du et al., "Effect of Varying Feedstock-Pretreatment Chemistry Combinations on the Formation and Accumulation of Potentially Inhibitory Degradation Products in Biomass Hydrolysates," *Biotechnology and Bioengineering* 107, no. 3 (2010): pages 430–440.

and forest products. Nonetheless, advances could be made in this area through reductions in capital and energy costs. In two similar studies, the feed handling and mechanical pretreatment section has been estimated to be 6.6% of total installed equipment cost, and approximately 10% of the electricity usage for a relatively simple corn stover conversion process, although finer milling increased electricity demands substantially.[8,9,10]

Thermochemical pretreatment, usually treatment of the biomass with acid, base, or solvents at temperatures from 100–200°C disrupts the interactions between cellulose, hemicellulose, and lignin, and is the critical step for enhancing the accessibility of biomass for biological conversion. A wide range of treatments can achieve this goal, yet few are both effective and economical.[11] Dilute acid pretreatment, typically with 0.5–3% sulfuric acid at temperatures up to 200°C and residence times of minutes, hydrolyzes hemicellulose to sugars, producing a fermentable pentose stream and a solid cellulose/lignin product amenable to enzymatic hydrolysis. Hydrolysis also releases soluble lignin-derived compounds, sugar degradation products (furfural, hydroxymethylfurfural, etc.), and acetic acid along with the hemicellulose-derived sugars, and these species can inhibit fermentation.[12]

Detoxification, usually by treatment with bases such as lime or ammonia, is necessary before the soluble sugar stream can be fermented, but detoxification can lead to sugar losses.[13] Strong alkaline pretreatments, such as treatment with lime at 70–130°C, are slower but remove lignin from biomass analogous to alkaline pulping processes.[14] Alkaline pretreatment can also be performed with aqueous or gaseous ammonia. Aqueous ammonia processes extract the majority of the lignin and some of the hemicellulose from the biomass, leaving behind a more accessible cellulose product.[15,16]

Unlike other pretreatments, treatment with gaseous ammonia, referred to as ammonia fiber expansion (AFEX), produces a solid biomass product following recovery of the ammonia. Instead of converting hemicellulose or lignin into soluble products, AFEX breaks the linkages between carbohydrates and lignin and decreases the carbohydrate polymer size.[17] Ammonia pretreatments also have the advantage of producing fewer inhibitory compounds than acid processes and may even provide nutrient benefits for fermentation.[18,19]

Comparative studies of both acidic and alkaline pretreatment methods in combination with enzymatic hydrolysis have shown that they can achieve similarly high yields of sugars (87–94%) under laboratory conditions.[20] Nevertheless, there may be significant differences in performance upon scale-up and commercialization. Other pretreatment technologies nearing commercialization include organosolv, a delignification method originally developed for pulping that uses acid or base and organic solvents and concentrated acid hydrolysis.[21] In contrast to other processes, concentrated

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[8] A. Aden et al*., Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover,* NREL/TP-510-32438, National Renewable Energy Laboratory, June 2002.

[9] F. K. Kazi et al., "Techno-Economic Comparison of Process Technologies for Biochemical Ethanol Production from Corn Stove," *Fuel* 89, no. 1 (2010): pages S20–S28.

[10] N. Mosier et al., "Features of Promising Technologies for Pretreatment of Lignocellulosic Biomass," *Bioresource Technology* 96, no. 6 (2005): pages 673–686.

[11] R. T. Elander et al., "Summary of Findings from the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI): Corn Stover Pretreatment," *Cellulose* 16, no. 4 (2009): pages 649-659.

[12] H. B. Klinke, A. B. Thomsen, and B. K. Ahring, "Inhibition of Ethanol-producing Yeast and Bacteria by Degradation Products Produced During Pre-treatment of Biomass," *Applied Microbiology and Biotechnology* 66, no. 1 (2004): pages 10-26.

[13] E. W. Jennings and D. J. Schell, *"Conditioning of Dilute-acid Pretreated Corn Stover Hydrolysate Liquors by Treatment With Lime or Ammonium Hydroxide to Improve Conversion of Sugars to Ethanol," Bioresource Technology* 102, no. 2 (2011): pages 1240-1245.

[14] N. Mosier et al., "Features of Promising Technologies for Pretreatment of Lignocellulosic Biomass," *Bioresource Technology* 96, no. 6 (2005): pages 673–686.

[15] P. V. Iyer et al., "Ammonia Recycled Percolation Process for Pretreatment of Herbaceous Biomass," *Applied Biochemistry and Biotechnology* 57-58, no. 1 (1996): pages 121-132.

[16] A. Isci et al., "Aqueous Ammonia Soaking of Switchgrass Followed by Simultaneous Saccharification and Fermentation," *Applied Biochemistry and Biotechnology* 144, no. 1 (2008): pages 69-77.

[17] M. W. Lau, E. E. Dale, and V. Balan, "Ethanolic Fermentation of Hydrolysates from Ammonia Fiber Expansion (AFEX) Treated Corn Stover and Distillers Grain Without Detoxification and External Nutrient Supplementation," *Biotechnology and Bioengineering* 99, no. 3 (2008): pages 529-539.

[18] Ibid.

[19] M. W. Lau and B. E. Dale, "Cellulosic Ethanol Production from AFEX-Treated Corn Stover Using Saccharomyces Cerevisiae 424A(LNH-ST)," *PNAS* 106, no. 5 (2009): pages 1368-1373.

[20] R. T. Elander et al., "Summary of Findings from the Biomass Refining Consortium for Applied Fundamentals and Innovation (CAFI): Corn Stover Pretreatment," *Cellulose* 16, no. 4 (2009): pages 649-659.

[21] X. Pan et al., "Bioconversion of Hybrid Poplar to Ethanol and Co-Products Using an Organosolv Fractionation Process: Optimization of Process Yields," *Biotechnology and Bioengineering* 94, no. 5 (2006): pages 851–861.

acid hydrolysis with sulfuric, hydrochloric, or other acids completely hydrolyzes biomass into its constituent sugars so that enzymatic hydrolysis is unnecessary.[22]

Steam explosion is a promising pretreatment technology because it has the potential to reduce chemical use, thereby lowering initial chemical cost as well as reducing the cost of chemicals for neutralization and the cost of disposition of precipitated salts in the wastewater. A typical steam explosion process involves heating the biomass to temperatures of 200°C in a pressure-containing vessel then allowing an extremely rapid depressurization.[23] During steam explosion, acid side groups in the biomass may assist in the hydrolysis of xylan and opening up of the lignocellulose structure.

For currently proposed biochemical ethanol processes, chemical pretreatment is an essential yet costly component. The elevated temperatures, high pressures, and harsh conditions used in pretreatment lead to high capital costs, estimated to be about 25% of the total installed equipment cost whether dilute acid or ammonia pretreatments are employed.[24,25] In the case of dilute acid, the major capital costs are the pretreatment reactor itself (due to metallurgy constraints imposed by high temperature, acidic conditions) and the additional vessels necessary for detoxification. Ammonia pretreatment can use less expensive materials for the pretreatment reactor but requires equipment to recover ammonia.[26]

Although its impact is much smaller than feedstock and enzymes, pretreatment also contributes to variable operating costs through requirements for steam, consumption of chemicals for both treatment and neutralization, and for disposal of salts generated in the wastewater treatment system resulting from neutralization. In the case of dilute acid pretreatment, the variable operating costs for chemical pretreatment have been estimated to be 13% of the total for the ethanol process.[27] Indirectly, pretreatment also contributes to feedstock costs because lower yields from pretreatment increase the amount of feedstock required per gallon of ethanol. Accordingly, increasing yields, decreasing severity, and lessening requirements for mechanical and thermochemical pretreatment will improve the economics of biochemical ethanol.

The most comprehensive comparative work on pretreatment technology was conducted by the Biomass Refining Consortium for Applied Fundamentals and Innovation. Table 12-2 contains a summary of the conditions used for leading pretreatment technologies. Figure 12-15 compares the results of technoeconomic analysis standpoint using the pretreatment technologies shown in Table 12-2.[28]

Saccharification/Hydrolysis

In cellulosic biofuel plants that will use the biochemical platform, the sugars for fermentation will arise either from: hydrolysate from biomass pretreatment and enzymatic hydrolysis, concentrated acid hydrolysis, and/or cellulolytic enzymes produced by the fermenting organisms themselves.

Sugar production via enzymatic hydrolysis is the most common of the saccharification methods. Enzymes are biological catalysts that can hydrolyze polysaccharides into their component monomeric sugars so that the sugars can then be fermented into ethanol or other biofuels. A suite of enzymes is required to hydrolyze the complex matrix of cellulose, hemicellulose, and lignin (often called lignocellulose) that comprises plant cell walls. At a minimum, three types of cellulolytic enzymes are required: *exoglucanases* (also known as cellobiohydrolases), which attack cellulose chains from the ends; *endoglucanases*, which can hydrolyze cellulose in the middle of a chain; and *beta-glucosidases*, which convert cellobiose, a dimer of glucose

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[22] G. T. Tsao et al., "Production of Ethanol and Chemicals from Cellulosic Materials," *Process Biochemistry* 17, (1982): pages 34-38.

[23] L. Kumar et al., "Can the Same Steam Pretreatment Conditions Be Used for Most Softwoods to Achieve Good, Enzymatic Hydrolysis and Sugar Yields?" *Bioresource Technology* 101, no. 20 (2010): pages 7827-7833.

[24] A. Aden et al., *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover,* NREL/TP-510-32438, National Renewable Energy Laboratory, June 2002.

[25] F. K. Kazi et al., "Techno-Economic Comparison of Process Technologies for Biochemical Ethanol Production from Corn Stove," *Fuel* 89, no. 1 (2010): pages S20–S28.

[26] T. Eggeman and R. T. Elander, "Process and Economic Analysis of Pretreatment Technologies," *Bioresource Technology* 96, no. 18 (2005): pages 2019-2025.

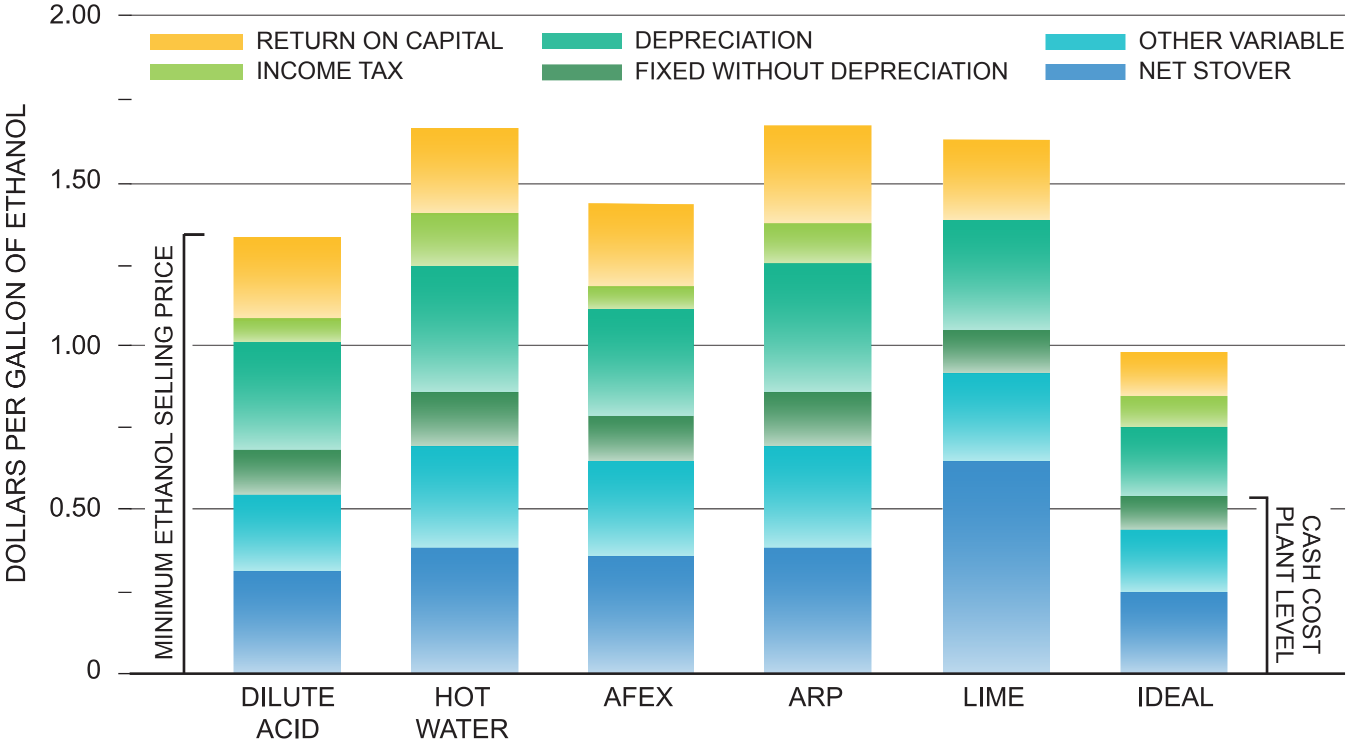
[27] A. Aden et al., *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover,* NREL/TP-510-32438, National Renewable Energy Laboratory, June 2002.

[28] T. Eggeman and R. T. Elander, "Process and Economic Analysis of Pretreatment Technologies," *Bioresource Technology* 96, no. 18 (2005): pages 2019-2025.

Pretreatment Technology	Chemicals Used	Temp., °C	Pressure, atm absolute	Reaction Times, min.	Concentrations of solids, wt.%
Dilute sulfuric acid – concurrent	0.5–3.0% sulfuric acid	130–200	3–15	2–30	10–40
Flowthrough pretreatment	0.0–0.1% sulfuric acid	190–200	20–24	12–24	2–4
pH controlled water pretreatment	Water or stillage	160–190	6–14	10–30	5–30
AFEX/FIBEX	100% (1:1) anhydrous ammonia	70–90	15–20	<5	60–90
ARP	10–15 wt.% ammonia	150–170	9–17	10–20	15–30
Lime	0.05–0.15 g $Ca(OH)_2$/g biomass	70–130	1–6	1–6 h	5–20
Lime + air	0.05–0.15 g $Ca(OH)_2$/g biomass	25–60	1	2 weeks– 2 months	10–20

Source: C. E. Wyman et al., “Coordinated Development of Leading Biomass Pretreatment Technologies,” *Bioresource Technology* 96, no. 18 (2005): pages 1959-1966.

Table 12-2. *Leading Pretreatment Technologies*



Source: National Renewable Energy Laboratory.

Figure 12-15. *Cash Costs and Minimum Ethanol Selling Price Comparison* produced through the action of exo-glucanases, to glucose. Depending on the substrate and pretreatment method, other enzymes may be required for effective saccharification of biomass. In particular, hemicellulolytic enzymes may be required to break down hemicellulose in the fibrils to both provide additional sugars for fermentation and to improve access to cellulose.

The ability of enzymes to effectively access and hydrolyze lignocellulosic substrates is impacted by the type and severity of the pretreatment process that has been applied to the biomass upstream of enzymatic hydrolysis. Pretreatment is required to disrupt the crystalline structure of cellulose and remove other components of the lignocellulose fibrils that interfere with access to the cellulose by the cellulolytic enzymes. As described above, both physical and chemical approaches are used to achieve this goal. As an example, alkaline pretreatment processes remove a portion of the lignin in the biomass, which typically improves hydrolysis performance. Alkaline pretreatments, however, leave in the solid phase most of the xylan and other hemicellulose in the substrate. Therefore, xylanases and other hemicellulolytic enzymes are typically required for hydrolysis of alkaline-pretreated substrates. Acid pretreatments, on the other hand, tend to remove most or all of the xylan, but leave the lignin intact. Thus, careful matching of enzyme cocktail and pretreatment type is an important consideration in enzymatic hydrolysis.

Biomass type will also impact the dosage and type of enzymes used for enzymatic hydrolysis. For example, biomass substrates vary significantly in the amount and type of hemicellulose present. Lignocellulosic substrates with high levels of xylan will require greater use of xylanases for effective conversion. Hardwoods have a variety of hemicellulose types, and may require a broader array of hemicellulase enzymes.

In its simplest configuration, enzymatic hydrolysis is a separate unit operation between pretreatment and fermentation, a configuration known as separate hydrolysis and fermentation (SHF). The major advantage of separating hydrolysis and fermentation is that each process can be run at its respective optimum conditions. Optimal temperatures for hydrolysis are in the 45–50°C range for commercial cellulase preparations, whereas the optimum for most ethanol-producing fermentation organisms is 30–37°C. In SHF, pretreated biomass is dosed with enzymes in a vessel with a mixing device for a period of 3–5 days. Typical conditions are pH 5.0 and 50°C. The resulting hydrolysate would then be transferred to another vessel for fermentation to ethanol or other advanced biofuel. The enzyme dose required to achieve a given cellulose conversion level is a primary determinant in the overall cost of the enzymatic hydrolysis unit process, and in turn the minimum ethanol selling price. The main drawback of SHF is that the concentrations of the products of the hydrolytic enzymes, cellobiose and glucose, build up during the course of the batch process. Cellobiose and glucose inhibit cellulases and thus limit yields.

Hydrolysis does not have to be a separate unit process. In simultaneous saccharification and fermentation (SSF), enzymatic hydrolysis and fermentation is concurrent in a single vessel to which both enzymes and fermentation organisms have been added. With SSF, cellobiose and glucose concentrations remain low because they are consumed immediately by the fermentation organisms present in the fermenter. Removal of these enzyme products is an advantage, since they are inhibitory to further enzymatic degradation. A second advantage is that SSF eliminates the need for an SHF vessel, which should reduce capital costs. However, optimal temperatures for fermentation do not coincide with optimal temperatures for hydrolysis, at least for the fermentation of sugars to ethanol by *Saccharomyces cerevisiae*. Commercial preparations for biomass hydrolysis are most effective at 50°C, which is too high for most commercially relevant fermentation organisms.

Hybrid hydrolysis and fermentation represents a third approach in which hydrolysis is started under optimal conditions for hydrolysis. After a set time period, the temperature is lowered and fermentation organisms are added, but hydrolysis is allowed to continue under these non-optimal conditions.

High solids loading during enzymatic hydrolysis is important because the presence of water as a diluent increases processing costs. In particular, the energy needed to distill ethanol from the fermentation beer is a strong function of ethanol concentration, which in turn is directly related to the sugar concentration in the hydrolysate. However, conversion efficiency decreases almost linearly with solids concentration.[29] Several theories have been proposed for this effect, including: mass transfer limitations due to poor mixing in high solids reactors; mass transfer limitations due to the lower ratio of solvent (water) to enzymes and solids; inhibition of enzymes by the products (cellobiose, glucose) or derivatives of the products of enzymatic reactions; inhibition of enzymes by other compounds released during hydrolysis; non-productive binding of enzymes to lignin or other compounds in the solid or liquid phases; and interference with adsorption of enzymes on solid substrates caused by products. The primary impact of solids loading on conversion results from the interference with enzyme adsorption to solid substrates by products.[30]

With support from DOE, strides have been made in reducing the cost of enzymes used in biomass hydrolysis. These efforts are focused on increasing the specific activity of enzymes, leading to a reduction in the dose required to effect a given cellulose conversion level.

As noted above, enzymatic hydrolysis performance is closely intertwined with the type and severity of pretreatment. A tradeoff often exists between pretreatment cost and enzymatic hydrolysis cost. Pretreatments that are more effective in removing lignin and in opening of the lignocellulosic structure typically use more chemicals, higher temperatures, and higher pressures and are therefore more expensive. But as result of improved pretreatment, lower enzyme doses can be used. When conducting technoeconomic analyses of biorefineries, it is therefore critical to incorporate these tradeoffs into the modeling of the overall process.

Fermentation

The ideal fermentation organism would be a highly robust industrial organism that can tolerate high titers of fermentation products, can tolerate inhibitors present in the hydrolysate such as acetic acid, furfural, hydroxymethylfurfural, and various products of lignin degradation, has a high growth rate, and achieves a high percentage of the theoretical yield. A variety of fermentation organisms are under evaluation by academic, government, and industrial entities to convert biomass sugars into advanced biofuels. A variety of target fuel molecules are also under evaluation, including ethanol, isobutanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, isopentenol, terpenoids, fatty-acid esters, and alkanes.

Ethanol is the primary target for many of the companies proposing to produce cellulosic biofuels. The most widely utilized microorganism for producing ethanol is *Saccharomyces cerevisiae*, a yeast used extensively in industrial fermentation processes, including the production of ethanol from corn. All fermentation organisms are to some extent sensitive to the very products they create. Relatively speaking, yeast are robust and can tolerate high titers of ethanol as well as other inhibitory substances present in the hydrolysate. Another advantage of yeast is that they have the ability to ferment at low pH values, which minimizes the possibility of infection by invading microorganisms. Certainly, the familiarity with yeast in existing corn ethanol plants is another advantage in using this organism for cellulosic ethanol fermentations. The major drawback of *S. cerevisiae* is that it is not naturally capable of fermenting five carbon sugars such as xylose and arabinose. Fermentation of pentose (five carbon) sugars to a fuel product (or other value-added product) is critical to the economic viability of a cellulosic biofuel plant. Several researchers have genetically transformed yeast to allow them to utilize xylose (usually the dominant five-carbon sugar in lignocellulosic substrates).[31,32]

Yeast is not the only microorganism adept at producing ethanol. A gram-negative bacterium, *Zymomonas mobilis*, that has been genetically modified to allow it to utilize pentose sugars as well as hexose (six carbon) sugars.[33] Like yeast, *Z. mobilis* can tolerate high concentrations of ethanol, up to 120 grams per liter. Its growth rate is higher than

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[29] J. B. Kristensen, C. Felby, and H. Jorgensen, "Yield-determining Factors in High-Solids Enzymatic Hydrolysis of Lignocellulose," *Biotechnology for Biofuels* 2, no. 11 (2009): pages 1-10.

[30] Ibid.

[31] M. Sedlak and N. Ho, *"Production of Ethanol from Cellulosic Biomass Hydrolysates Using Genetically Engineered Saccharomyces Yeast Capable of Cofermenting Glucose and Xylose," Applied Biochemistry and Biotechnology* 114, no. 1-3 (2004): pages 403-416.

[32] S. Watanabe et al., *"Ethanol Production from Xylose by Recombinant Saccharomyces Cerevisiae Expressing Protein-engineered NADH-preferring Xylose Reductase from Pichia Stipitis," Microbiology* 153, no. 9 (September 2007): pages 3044-3054.

[33] M. Zhang et al., "Metabolic Engineering of a Pentose Metabolism Pathway in Ethanologenic Zymomonas Mobilis," *Science* 267, no. 5195 (1995): pages 240-243.

that of yeast and it can achieve sugar conversion yields that are 97% of the theoretical maximum.[34]

Several biorefinery companies are pursuing butanol as a fermentation product that is a more infrastructure-compatible fuel that could potentially be pumped in pipelines in blends with petroleum-based fuels. Product toxicity is a key concern in the production of isobutanol. At concentrations greater than 7–8% in an aqueous environment, butanol will form a separate phase, which is easily and economically separated from the fermentation broth. However, the fermentation organisms must be able to tolerate the maximum concentration of butanol that is soluble in the fermentation broth, unless a technique for continuous removal from the aqueous fermentation broth is used.

Three other fuel fermentation pathways are being actively pursued commercially:

- Processes to produce oil from photosynthetic algae or, in at least one case, heterotrophic algae for lipid production. In this case, the algae are fed sugars and the sugars are metabolized into fuel molecules, renewable chemicals or bioproducts.
- Fermentation organisms (yeast) to produce isoprenoids that can be used for fuels or chemicals.
- Fatty acid pathway found in bacteria to produce hydrocarbon chains in the diesel and gasoline ranges.

These pathways currently use relatively pure sugar streams (e.g., from sugar cane) for fermentation. However, there is no major technical obstacle to the utilization of sugars from biomass sources. It may require genetic manipulation of their fermentative organisms to incorporate xylose utilizing metabolic pathways, which has been demonstrated in closely related fermentative organisms.

The production of lipids or other non-water soluble compounds by fermentative organisms will change the nature of the process for separating the biofuel from the fermentation broth. These non-water soluble fuels can be removed by phase separation techniques, which are inherently less energy-intensive than distillation.

These latter three fuel pathways introduce additional economic challenges; in some cases, the organisms that are being used in these processes require some level of aeration for maximum production. Aeration of production vessels will add significant operating costs to the process. On the other hand, the fuel molecules produced are inherently more compatible with existing petrochemical fuels and can, therefore, be considered "drop-in" fuels.

In addition to the three unit processes via the biochemical platform described above, a consolidated bioprocessing (CBP) approach is also under development. With CBP, hydrolysis and fermentation are combined in one vessel. The fermentation organism(s) also produce cellulolytic enzymes, eliminating the need for separate addition of enzymes. Because enzyme cost is still a major component of the overall operating cost of a biochemical pathway biofuels plant, using a consolidated bioprocessing approach, in which the microorganisms (yeast or bacteria) produce cellulolytic enzymes, reduces both capital and operating costs. As envisioned, the CBP process will be able to ferment both the glucose and xylose from the cellulose and hemicellulose in pretreated biomass directly to ethanol (or other biofuels).

The CBP approach removes a major operational expense, i.e., the enzyme cost, and converts cellulose to ethanol in a single fermentation vessel. Due to process simplification, and lower enzyme costs, this approach has the potential of being the low cost biochemical process used to convert lignocellulose to ethanol. This technology applies to a variety of lignocellulosic feedstocks, including wood waste, grasses, corn stover, and sugar cane bagasse. The technology faces substantial technical challenges, however, in that it may prove very difficult to optimize enzyme producing metabolic pathways and ethanol producing metabolic pathways in the same organism.

Fermentation of biomass hydrolysates presents several challenges not encountered in corn mash. These challenges include:

- **C5 Sugar Utilization.** Although substantial research has been invested in identifying or modifying organisms for utilization of pentose sugars, there has been no commercial demonstration of an efficient C5 fermenting organism.

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[34] P. L. Rogers, J. L. Lee, and D. E. Tribe, "Kinetics of Alcohol Production by Zymomonas Mobilis at High Sugar Concentrations," *Biotechnology Letters* 1, no. 4 (1979): pages 165-170.

Technoeconomic models indicate that C5 utilization is necessary for economic viability of biorefineries.

- **Inhibition.** Biomass hydrolysate is more complex chemically than corn mash. Significant quantities of inhibitory substances are produced during pretreatment and hydrolysis. These inhibitors may include soluble lignin fragments, acetic acid, and sulfate.
- **Aeration.** The most well-known microbial-based biofuel production pathways are true fermentations, and therefore do not require oxygen. However, some of the advanced biofuel pathways being proposed are aerobic processes, and will therefore require aeration, which can significantly increase cost and complexity.
- **Product Toxicity.** All fermentation organisms are affected to some extent by the very products they create. Saccharomyces cerevisiae, the species of ethanol-producing yeast used in a variety of industrial applications, is relatively robust and can tolerate high ethanol titers.

Biotechnology Hurdles

Technology for advanced biofuel production will continue to evolve between now and 2050, although it is extremely challenging to predict which of the technologies being explored today will become dominant in 2050. Over such a long time frame, completely new fuel production pathways may be developed and commercially implemented—pathways that are unknown today. Many research efforts that are underway hold promise for improving biomass conversion. Several of these solutions and the barriers they overcome are discussed in the following sections.

Feedstock Development to Reduce Recalcitrance

The development of biomass feedstocks designed specifically for conversion to biofuels is in its infancy. Over the long term, with better understanding of cell wall and lignin synthesis pathways in plants, there is potential for genetically modifying plants to reduce their hydrolytic recalcitrance. Several approaches are being explored for reducing biomass recalcitrance. One approach is to reduce the lignin content of biomass feedstocks. Several academic and industrial laboratories have produced low-lignin varieties of tree species.[35] The obvious challenge is to maintain the structural integrity of the low-lignin trees. Another approach to reducing feedstock recalcitrance is to genetically manipulate lignin synthesis in such a way that enzymatic hydrolysis is improved.[36]

Pretreatment Technology

Integrated optimization of pretreatment and enzymatic hydrolysis is an important enabler for economically viable advanced biofuel production. Effective pretreatment appears to require the addition of acidic or basic chemicals to open up the structure of the biomass and remove lignin and/or hemicellulose to improve access to cellulose. Optimization of pretreatment conditions will continue, but breakthroughs based on the use of standard pretreatment chemicals, such as sulfuric acid and alkaline chemicals, do not seem likely. However, other technologies with technical promise are under development including the evaluation of ionic liquids use for biomass pretreatment.[37,38] In one configuration, the ionic liquids would be used to dissolve the cellulose. When an anti-solvent is added to the mixture, the cellulose can be precipitated in an amorphous form, making it highly susceptible to rapid hydrolysis to high conversion levels. Another approach would be to use a different type of ionic liquid to remove lignin from the biomass, thereby improving enzyme access to the remaining solids. The cost of ionic liquids puts constraints on the percentage of ionic liquids that must be recycled in the overall process, but improvements in production or utilization of ionic liquids can hopefully mitigate this constraint.

Saccharification/Hydrolysis

Despite strides in improving their effectiveness, enzymes continue to be a key operating cost for

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[35] V. L. Chiang, "Monolignol Biosynthesis and Genetic Engineering of Lignin in Trees, a Review," *Environmental Chemistry Letters* 4, no. 3 (2006): pages 143-146.

[36] S. C. Gebhard et al., "Catalytic Conditioning of Synthesis Gas Produced by Biomass Gasification," *Biomass & Bioenergy* 7, no. 1-6 (1994): pages 307-313.

[37] S. Singh, B. A. Simmons, and K. P. Vogel, "Visualization of Biomass Solubilization and Cellulose Regeneration During Ionic Liquid Pretreatment of Switchgrass," *Biotechnology and Bioengineering* 104, no. 1 (2009): pages 68-75.

[38] A. P. Dadi, S. Varanasi, and C. A. Schall, "Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step," *Biotechnology and Bioengineering* 95, no. 5 (2006): pages 904-910.

cellulosic biofuel plants. Projects funded by DOE are currently underway to further increase the specific activity of cellulolytic enzyme cocktails and thereby reduce the cost. In addition, enzyme companies are exploring ways of producing enzymes more cost-effectively, and working with biofuel producers to reduce the cost of enzymes through process modifications. These efforts are expected to continue to produce cost reductions between now and 2050.

Fermentation

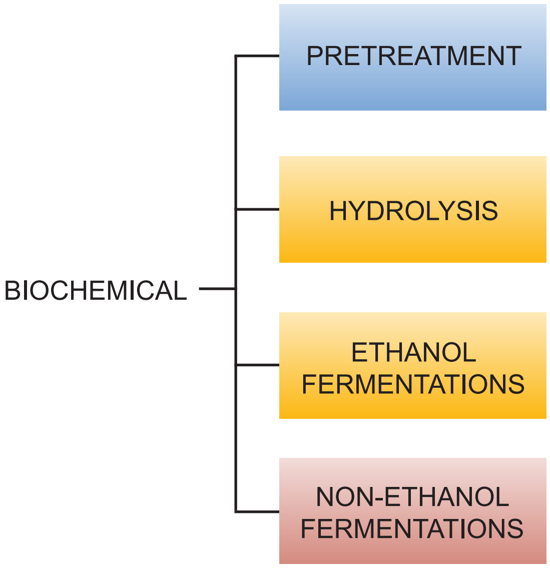
Metabolic engineering of fermentation organisms could yield major advances in biofuel production during the study period. By 2050, metabolic processes may be better known for key fuel producing organisms, allowing researchers to alter the metabolic flux in ways that will greatly increase biofuel yields. By 2050, it is likely that the challenges associated with C5 sugar utilization will have been solved. Genetic manipulation of fuel producing organisms may also improve the tolerance of these organisms to inhibitors in the hydrolysate and to product toxicity.

Distillation

Distillation is the key separation process in the production of cellulosic ethanol via the biochemical platform. Although not expected to present technical challenges, it is critical that biomass is processed at solids concentrations that result in an economically viable ethanol concentration in the beer. The concentration of ethanol in the beer has a strong impact on the energy required for distillation. Figure 12-16 describes the key hurdles in biotechnology for advanced biofuels.

Thermochemical Conversion – Current Status

Biomass thermochemical conversion technologies are receiving renewed attention as concerns about the sustainability and security of domestic energy resources increase, and mounting evidence of global climate change brought about by fossil fuel consumption continues to be a concern. Biomass resources are suited for conversion into liquid transportation fuels, chemicals, and materials.



- With work, economical biomass pretreatment and hydrolysis is attainable (key target is to reduce chemical use while retaining hydrolysis performance).
- Yeast-based ethanol fermentation is comparatively robust (relatively tolerant of ethanol and inhibitory substances); C5 sugar utilization is key.
- Bacterial processes are more problematic from a practical viewpoint (susceptibility to phages and other infections, product toxicity).
- Consolidated bioprocessing presents challenges in metabolic flux partitioning (difficulty to optimize both saccharification and fermentation).
- Modeling will be needed to fully understand the tradeoffs associated with the impact of changes in one unit process on the overall process.

🟦 MINIMAL/NO BARRIERS

🟨 WILL TAKE INVESTMENT AND TIME, BUT PATHWAY FOR SUCCESS HAS BEEN IDENTIFIED

🟥 SIGNIFICANT BARRIER OR HIGH RISK OR HIGH UNCERTAINTY
OR REQUIRES "BREAKTHROUGH OR INVENTION"

Figure 12-16. *Biotechnology Conversion Hurdles*

Gasification and pyrolysis are the thermochemical conversion processes being developed to convert biomass into transportation fuels.[39,40,41] These processes use thermal energy to dehydrate, devolatilize, depolymerize, and oxidize, partially or completely, lignocellulosic materials and enable the development of lignocellulosic biorefineries.

Thermochemical conversion technologies are generally fuel-flexible when it comes to biomass composition. The main biomass fuel properties that impact the long-term technical and economic success of a thermochemical conversion process are moisture content, impurity (sulfur, nitrogen, chloride) concentrations, and ash content. The ash and heteroatom content and composition can be important in choosing gasifier metallurgy and operating conditions. Feedstocks that introduce chloride may lead to corrosion if the gasifier was not constructed of the proper material. Therefore, feedstock analyses are recommended to avoid any issues thus a prudent selection may limit feedstock flexibility of gasifiers.[42]

Low bulk and energy densities of biomass translates into higher costs for feedstock preparation, handling, and transportation, putting biomass conversion technologies at an economic disadvantage in current energy markets. Consequently, biomass utilization is most advantageous when the feedstock is either a high volume waste product of an existing system or is readily available in close proximity to the conversion plant.

Currently, the most technically defined thermochemical route for producing lignocellulosic biofuels involves biomass gasification or reforming followed by syngas cleaning and conditioning (see Figure 12-17) to produce clean syngas (carbon monoxide [CO] + hydrogen [H_2]) for Fischer-Tropsch synthesis with upgrading via hydroprocessing.[43]

Integrated biomass gasification is a flexible process in regard to the feedstock that can be utilized and the biofuels that can be produced. The gasification step transforms the input biomass feedstock into a raw syngas intermediate that requires processing to remove impurities such as particulates, tars, sulfur gases, and chlorine.[44] The composition of the cleaned syngas (CO + H_2) is then catalytically adjusted to provide the fundamental building block for the synthesis of gasoline, diesel, and an ethanol-rich mixture of fuel-grade alcohols.[45,46,47]

Feed Preparation and Handling

Feedstock delivered to the plant gate will require storage and handling on site, which will require additional space and capital equipment. The feedstock may also require additional processing such as size reduction or drying. The technical barriers for feedstock preparation inside the plant gate for thermochemical conversion technologies are low with the primary challenges being cost of the

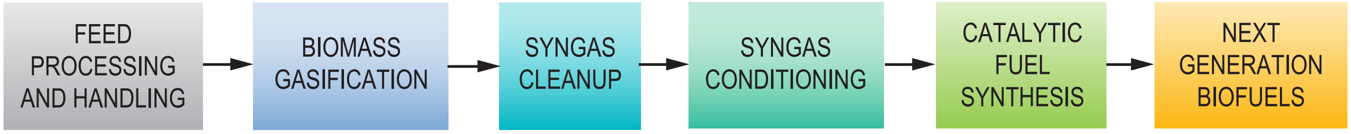


Figure 12-17. *Lignocellulosic Biofuels Production Process*

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[39] G. W. Huber, S. Iborra, and A. Corma, "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chemical Reviews* 106, no. 9 (2006): pages 4044-4098.

[40] H. B. Goyal, D. Seal, and R. Saxena, "Bio-Fuels from Thermochemical Conversion of Renewable Resources: A Review," *Renewable & Sustainable Energy Reviews* 12, no. 2 (2008): pages 504-517.

[41] D. Kubicka, "Future Refining Catalysis – Introduction of Biomass Feedstocks," *Collection of Czechoslovak Chemical Communications* 73, no. 8-9 (2008): pages 1015-1044.

[42] L. Baxter, "Rational Use of Biomass as a Renewable Fuel," Global Climate and Energy Program Symposium, Stanford, CA, June 14, 2005.

[43] E. D. Larson, H. Jin, and F. E. Celik, "Large-scale Gasification-based Coproduction of Fuels and Electricity from Switchgrass," *Biofuels, Bioproducts and Biorefining* 3, no. 2 (2009): pages 174-194.

[44] M. Balat, "Mechanisms of Thermochemical Biomass Conversion Processes. Part 1: Reactions of Pyrolysis," *Energy Sources Part A: Recovery Utilization and Environmental Effects* 30, no. 7 (2008): pages 620-635.

[45] I. Wender, "Reactions of Synthesis Gas," *Fuel Processing Technology* 48, no. 3 (1996): pages 189-297.

[46] P. L. Spath and D. C. Dayton, *Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas,* National Renewable Energy Laboratory, December 2003.

[47] V. Subramani and S. K. Gangwal, "A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol," *Energy & Fuels* 22, no. 2 (2008): pages 814-839.

delivered feedstock, energy for grinding and drying, and potential pretreatment.

Reliable feed system operation has been a significant challenge for all solid feed-based (coal, petroleum coke, and biomass) gasification systems, especially into pressurized reactors. The fibrous nature of many biomass feedstocks can pose an operational challenge for thermochemical biomass conversion processes. Size reduction and inert material (rocks, nails, bailing wire, etc.) removal are required to ensure the operational reliability of the feed system. Heat integration and energy efficiency of feed preparation also needs to be optimized for a given process to maximize efficiency.

Biomass Gasification

The biomass gasification product gas is a low- to medium-energy content gas (depending on the gasifying agent) that consists mainly of CO, H_2, carbon dioxide (CO_2), water (H_2O), nitrogen, and hydrocarbons. Minor components of the product gas include tars, hydrogen sulfide, ammonia, hydrogen cyanide, hydrogen chlorine, alkali metals, and particulates. These minor components of the product gas potentially threaten the successful application of downstream syngas utilization processes. Gas composition and quality are dependent on a wide range of factors including feedstock composition, type of gasification reactor, gasification agents (air, oxygen, or steam), stoichiometry, temperature, pressure, and the presence or lack of catalysts.

Commercial-scale biomass gasification has not been demonstrated and the economics are challenged by limited economies of scale based on feedstock logistics (cost and delivery). Air is typically not used for a biomass gasification catalytic biofuels synthesis process because the size of reactors and compressors need to be larger to accommodate the large volumes of inert nitrogen in the systems.

One technology option is pressurized biomass gasification that typically uses oxygen or a mixture of oxygen and steam as the gasifying agent. Oxygen separation is an expensive option, especially for small-scale biomass gasifiers at 1,000 to 2,000 tons per day. Low-pressure, indirect (steam) biomass gasification is an alternative. Capital costs of direct, pressurized oxygen-blown biomass gasifiers are higher than low pressure, indirect biomass gasifiers primarily because air separation units are not cost effective at projected scales (2,000 tons per day) for biomass gasifiers.[48,49] The capital cost of indirect gasification is lower, but higher tar loadings may lead to higher costs for syngas cleanup. Blending coal and biomass is a means of increasing the scale of syngas production to improve process economics at the expense of GHG emissions profile.[50]

Syngas Cleanup

The heterogeneous nature of feedstocks used in biomass gasification poses a complex and technically challenging situation for comprehensive syngas cleaning and conditioning. This includes removing contaminants (caused by natural variations in feedstock composition or varying gasification process conditions) at significantly different concentrations (parts per billion to percent ranges). Simultaneously removing contaminants to trace levels often requires multiple steps of syngas cleanup where the number and order of these processes is determined by the interaction of impurities on the selected processes and the target cleanliness levels. Various syngas utilization processes (catalytic fuel synthesis, chemical production, fuel cells, combustion turbine, etc.) also tend to have different cleanliness requirements, but catalytic fuel synthesis tends to be the most demanding. Overall process intensification of the gas cleanup and conditioning unit operations will reduce complexity and improve the capital expense and operating expense of biomass gasification processes.

The current commercial basis for syngas cleaning in integrated coal gasification processes involves cooling the syngas for treatment in a liquid scrubbing/absorption system based on either chemical (methyl di-ethanolamine) or physical (Selexol and Rectisol) absorption. These physical removal processes are technically feasible but

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[48] A. Dutta et al., "Techno-Economics for Conversion of Lignocellulosic Biomass to Ethanol by Indirect Gasification and Mixed Alcohol Synthesis. Environmental Progress and Sustainable Energy," *Special Issue: TC-Biomass 2011, The International Conference on Thermochemical Conversion Science* 31, no. 2 (July 2012): pages 182-190; NREL Report No. JA-5100-52266. http://dx.doi.org/10.1002/ep.10625.

[49] S. D. Phillips et al., *Gasoline from Wood via Integrated Gasification, Synthesis, and Methanol-to-Gasoline Technologies*, TP-5100-47594, National Renewable Energy Laboratory, January 2011.

[50] T. J. Tarka, *Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass*, DOE/NETL-2009/1349, National Energy Technology Laboratory, January 14, 2009.

economic viability is challenged by reduced thermal efficiency and high capital and operating costs.

The challenge of tar removal, conversion, or mitigation must be overcome for the successful development of commercial advanced biomass gasification technologies. Tar formation is ubiquitous in biomass. Tars foul heat exchanges, blind filters, deposit on catalysts as coke, and condense in compressors. Tars can be physically removed (quench systems), thermally cracked to carbon and light gases, or catalytically converted (reformed) to syngas. Many tar removal strategies are currently being developed.[51,52,53,54,55] The impact of other impurities, especially sulfur and chlorine, on catalytic processes is a technical challenge. Heat integration of the tar mitigation technology is needed to maximize thermal efficiency.

All current syngas desulfurization systems cool the syngas significantly below its dewpoint, resulting in water condensation. The liquid scrubbing/absorption systems treat the water-free syngas stream to remove the hydrogen sulfide (H_2S) and carbonyl sulfide (COS) species (a COS hydrolysis unit may be necessary to effectively remove COS). The H_2S-rich streams from these absorption systems are sent to a Claus plant for final conversion into elemental sulfur.

Particulate removal with cyclones is proven technology for particles greater than 1 micron. Barrier filters are commercially available (bag houses and candle filters), but mechanical integrity for long-term operation is still an issue. Ash removal is a function of the type of gasifier. High-temperature, oxygen-blown gasifiers tend to produce a molten slag or have a dry ash quench, depending on how the units are operated. Indirect gasifiers tend to produce ash particles that exit the gasifier and are collected downstream or remain as part of the circulating fluidized bed material.

Syngas Conditioning

The syngas ratio (H_2/CO) can be adjusted for the specific downstream catalytic conversion process. Water-gas shift technology (low and high temperature) is commercially available for adjusting the hydrogen concentration. Catalysts and sorbents are also available for removing sulfur, trace metals, ammonia, and chlorine to ultra-low levels (parts per billion) in polishing steps. CO_2 removal may be needed for certain fuel synthesis processes or for improving the overall GHG efficiency of the process. The liquid absorption systems described above will remove CO_2 but alternative solids and liquid absorbents are currently being developed as well as novel membranes systems.

Catalytic Fuel Synthesis

Syngas conversion to fuels and chemicals has been an active area for research and development over the past 100 years. Consequently, considerable literature is available that tracks the scientific and technological advancements in syngas chemistry and many comprehensive reviews are available.[56,57,58] Many catalytic processes are commercially viable (methanol, ammonia, and Fischer-Tropsch) but have not been commercially demonstrated in an integrated biomass gasification process. Pilot demonstrations of many syngas-to-fuels technologies are being built and operated. Improvements in catalyst activity and lifetime are still needed to improve process economics. Higher conversion efficiency (CO utilization) and yields are needed but more challenging.

Catalytic syngas conversion processes are exothermic and generate large excesses of heat. Removing this heat of reaction is required to control reaction temperatures and maintain

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[51] T. A. Milne, R. J. Evans, and N. Abatzoglou, *Biomass Gasifier "Tars": Their Nature, Formation, and Conversion*, National Renewable Energy Laboratory, November 1998.

[52] D. Sutton, B. Kelleher, and J. R. H. Ross, "Review of Literature on Catalysts for Biomass Gasification," *Fuel Processing Technology* 73, no. 3 (2001): pages 155-173.

[53] L. Devi, K. J. Ptasinski, and F. J. J. G. Janssen, "A Review of the Primary Measures for Tar Elimination in Biomass Gasification Processes," *Biomass & Bioenergy* 24, no. 2 (2003): pages 125-140.

[54] Z. Abu El-Rub, E. A. Bramer, and G. Brem, "Review of Catalysts for Tar Elimination in Biomass Gasification Processes," *Industrial & Engineering Chemistry Research* 43, no. 22 (2004): pages 6911-6919.

[55] M. Yung, W. S. Jablonski, and K. A. Magrini-Bair, "Review of Catalytic Conditioning of Biomass-Derived Syngas," *Energy & Fuels* 23, no. 4 (2009): pages 1874-1887.

[56] I. Wender, "Reactions of Synthesis Gas," *Fuel Processing Technology* 48, no. 3 (1996): pages 189-297.

[57] P. L. Spath and D. C. Dayton, *Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas*, National Renewable Energy Laboratory, December 2003.

[58] V. Subramani and S. K. Gangwal, "A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol," *Energy & Fuels* 22, no. 2 (2008): pages 814-839.

optimized process conditions to maximize product yields, minimizing side or competing reactions, and maintaining catalyst integrity. Reactor design and modeling for removal of the exothermic heat of reaction is needed for isothermal operation and process improvements. Moreover, process economics often depend on recovering and utilizing this waste heat, especially when it is produced in high temperature.

The Fischer-Tropsch synthesis (FTS) is the most familiar process that has been utilized for commercial-scale coal to liquids production. FTS using biomass-derived syngas has not been commercially demonstrated. The large economies of scale available with coal gasification systems are not feasible for biomass systems due to the costs associated with feedstock logistics and gas cleanup requirements for high ash and high nitrogen containing feedstocks.

Ethanol from syngas through higher alcohol synthesis or a modified methanol synthesis process is a route for biofuels production that has received a lot of attention. The economic competitiveness of this route, however, is dependent on improving catalyst productivity and selectivity beyond the current state of technology.

Technology advances are needed to reduce overall capital costs for biomass gasification by consolidating or eliminating unit operations. Better FTS catalysts with higher productivity and better long-term performance can increase yields. Improved catalyst reactor designs (slurry bubble column reactors) are being demonstrated with natural gas systems that have the potential for 90% CO conversion efficiency.

Economic Status

World-scale gas-to-liquids (GTL) plants currently under construction provide a basis for reliable capital cost estimates for natural gas reforming for syngas production followed by FTS. The Shell Pearl project (Qatar) has a reported cost of $18–$19 billion for 140,000 barrels per day capacity.[59] That translates into a capital cost of $132,000 per daily barrel. The Chevron/Sasol Escravos project (Nigeria) has a reported cost of $8.4 billion for 34,000 barrels per day.[60] That translates into $247,000 per daily barrel at scales that are closer to unit sizes for biomass-to-liquids plants. Natural gas is an easier feedstock to convert to syngas than biomass via gasification. The capital costs will be higher for a biomass-to-liquids process compared to a GTL process at similar scale. The lower scale of biomass GTL would also increase cost significantly. Considering the complexity of biomass versus natural gas as a feedstock, this value provides a lower limit for capital costs.

A recent study reported that FTS diesel can be produced for $4–$5 per gallon in a plant that processes 2,200 tons of biomass per day.[61] The study describes two gasification options—high temperature (direct) and low temperature (indirect). The yearly output of the high-temperature direct gasification plant is 41.7 million gallons per year at a yield of 55 gallons per ton. The low-temperature process was designed with a capacity of 32.3 million gallons per year at a yield of 43 gallons per ton. The total capital costs were estimated at $222,781 per daily barrel for the high-temperature process and $236,357 for the low-temperature process.

The FTS diesel case presented in the National Academies' report *Liquid Transportation Fuels from Coal and Biomass* takes data from earlier studies that describe the results for a techno-economic analysis of a 3,940 tons per day of switchgrass gasification process that yields 4,410 tons per day of FTS diesel at a yield of 47 gallons per ton. Total plant cost is $144,000 per daily barrel and has $3.05 per gallon of fuel production cost.[62,63] Capital cost estimates based on extrapolating the recent commercial costs experienced in the Shell Pearl or Chevron/Sasal Escravos projects to a smaller scale biomass GTL process would be much higher,

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[59] Shell (website), "Pearl GTL–an overview," http://www.shell.com/home/content/aboutshell/our_strategy/major_projects_2/pearl/overview/.

[60] Hydrocarbons-technology (website), "Escravos Gas-to-Liquids Project, Niger Delta, Nigeria," 2011, http://www.hydrocarbons-technology.com/projects/escravos/.

[61] R. M. Swanson et al., "Techno-economic Analysis of Biomass-to-Liquids Production Based on Gasification," *Fuel* 89, no. 1 (2010): pages S11-S19.

[62] Thomas G. Kreutz et al., "Fischer-Tropsch Fuels from Coal and Biomass," Prepared for the 25th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 29-October 2, 2008.

[63] E. D. Larson, H. Jin, and F. E. Celik, "Large-scale Gasification-based Coproduction of Fuels and Electricity from Switchgrass," *Biofuels, Bioproducts and Biorefining* 3, no. 2 (2009): pages 174-194.

roughly two to three times, than projected in the NAS/NAE/NRC study.[64]

The main challenge with biomass gasification-based biofuels technologies is the high capital cost. This can be partially reduced with economies of scale. The minimum commercial-scale biomass gasification plant will be around 2,000 tons per day. Combining biomass with coal in a co-gasification plant is another strategy for capturing economies of scale on fuel production at reasonable biomass demand.

Pyrolysis Technologies

Pyrolysis is a thermochemical processing option for producing liquid transportation fuels from biomass and creates a product referred to as bio-oil, or bio-crude. Bio-crude will be used in this section to distinguish pyrolysis products from algae-derived oils, which are often referred to as bio-oil. Biomass pyrolysis technology is commercially available but has not been applied to commercial-scale fuel production.

From a fuels perspective, bio-oil is hydrogen deficient because of the high oxygen content (~40 wt.%) so oxygen must be removed by hydrodeoxygenation (H_2O elimination) or decarboxylation (CO_2 elimination). The theoretical gasoline yield from hydrotreating this raw bio-oil is on the order of 100 gallons per ton. Assuming that all oxygen can be removed via hydrotreating with no carbon losses, the theoretical (stoichiometric) hydrogen demand for converting raw bio-oil into gasoline is about 5 kilogram of H_2 per 1 kilogram of dry bio-oil. The current state of technology integrates catalytic fast pyrolysis with conventional hydroprocessing technology as shown in Figure 12-18.

Pyrolysis oil prepared by conventional (non-catalytic) fast pyrolysis is not suitable for integrating into the current fuel infrastructure or into the refinery. Negative properties of conventional pyrolysis oil include thermal instability and high fouling tendency as well as corrosiveness due to high carboxylic acid content (pH 2.2–2.4 typically). The pyrolysis oil is also immiscible with refinery feedstocks and has a high phenolic, metal, and nitrogen content that can foul or deactivate refinery catalysts.

Biomass Pyrolysis

Biomass pyrolysis is the thermal depolymerization of biomass at modest temperatures in the absence of added oxygen.[65,66,67,68,69] The slate of products from biomass pyrolysis depends on the process temperature, pressure, and residence time of the liberated pyrolysis vapors. Charcoal yields of up to 35% can be achieved for slow pyrolysis at low temperatures, high pressures, and long residence times.[70] Flash pyrolysis is used to optimize the liquid products as an oil known as bio-crude or bio-oil. High heating rates and short residence times enable rapid biomass pyrolysis while minimizing vapor cracking to optimize liquid product yields.

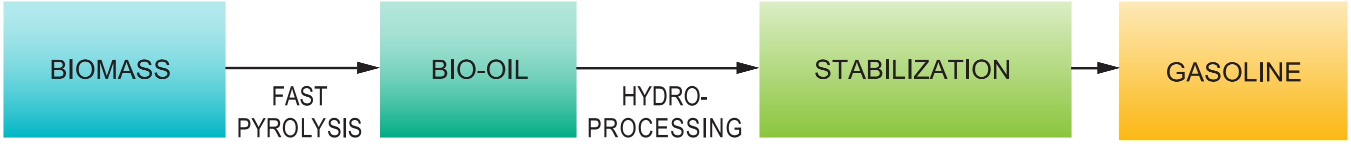

Figure 12-18. *Catalytic Fast Pyrolysis and Hydroprocessing Technology Generic Process Flow Diagram*

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[64] R. M. Swanson et al., "Techno-economic Analysis of Biomass-to-Liquids Production Based on Gasification," *Fuel* 89, no. 1 (2010): pages S11-S19.

[65] S. Czernik and A. V. Bridgwater, "Overview of Applications of Biomass Fast Pyrolysis Oil," *Energy & Fuels* 18, no. 2 (2004): pages 590-598.

[66] G. W. Huber, S. Iborra, and A. Corma, "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chemical Reviews* 106, no. 9 (2006): pages 4044-4098.

[67] D. Mohan, C. U. Pittman Jr., and P. H. Steele, "Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review," *Energy & Fuels* 20, no. 3 (2006): pages 848-889.

[68] A. Oasmaa et al., "Characterization of Hydrotreated Fast Pyrolysis Liquids," *Energy Fuels* 24, (2010): pages 5264–5272.

[69] R. H. Venderbosch and W. Prins, "Fast Pyrolysis Technology Development," *Biofuels Bioproducts and Biorefining* 4, no. 2 (2010): 178-208, doi:10.1002/bbb.205.

[70] M. J. Antal Jr. and M. Grønli, "The Art, Science, and Technology of Charcoal Production," *Industrial & Engineering Chemistry Research* 42, no. 8 (2003): pages 1619-1640.

Traditional biomass flash pyrolysis processes have demonstrated a roughly 70% liquid product yield; however, this pyrolysis oil product has limited use without additional upgrading or refining.[71,72]

Bio-oils are multi-component mixtures comprised of different size molecules derived primarily from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose, and lignin. Therefore, the elemental composition of bio-oil resembles that of biomass rather than that of petroleum oils. The chemical and physical properties of crude bio-oil preclude the application of this material as an intermediate for transportation fuel production. The high oxygen content and low pH of bio-oils limit their long-term storability due to polymerization reactions, which increase bio-oil viscosity over time.[73,74,75]

Catalytic Biomass Pyrolysis

A goal of the catalytic pyrolysis process is to change the chemistry during biomass pyrolysis to make a product more suitable for upgrading and integrating into refinery processing. The most desirable bio-oil property improvement would be to increase thermal stability to the extent that the bio-oil could be distilled to remove metal impurities and high molecular weight components. It then could be processed by hydrotreating or catalytic cracking to remove residual oxygen, including carboxylic acids. Lowering the oxygen and nitrogen content of the bio-oil during catalytic pyrolysis would lower the hydrogen requirements during upgrading, which would lower costs.

Currently available technology, demonstrated at the bench-scale, integrates a two-step hydroprocessing process to stabilize the raw bio-oil with mild hydrotreating and then convert the stabilized intermediate to gasoline and diesel in a more severe hydroprocessing step.[76,77,78,79] Ongoing research and development in catalytic biomass pyrolysis is focused on producing a hydrocarbon-rich intermediate liquid with low oxygen content (< 10%) that is compatible with existing petroleum refining technology, such as hydroprocessing. The objective is to eliminate the stabilization step and improve the overall carbon efficiency of the technology. Research needs include catalyst development, process development and design, pilot-scale demonstration, and scale-up.

Hot Gas Cleanup

Entrained char and catalysts from a biomass pyrolysis process need to be removed prior to condensation of the bio-oil. Alkali and other metals can degrade the stability of the bio-oil and poison downstream hydroprocessing steps. Effective hot gas filtration is needed that avoids condensation of the bio-oil vapors blinding the filter yet minimizes vapor phase cracking that decreases yields.

Bio-oil Upgrading

Bio-oil can be upgraded either at the source prior to full production or after the formation of the liquid product. To date, the two most popular methods in post-production upgrading are adapted from traditional hydrocarbon processing.[80] These processes are bio-oil cracking over solid acid catalysts and hydrotreating in presence of a hydrodesulfurization catalyst and high-pressure hydrogen. Although both these processes have the potential to bring down the oxygen content to desirable level, it should be noted that both cracking and hydrotreating are accompanied by the loss of hydrogen (as H_2O) and carbon (as CO_2 or CO) from the bio-oil. This leads to low ultimate hydrocarbon yields.

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[71] A. Oasmaa et al., "Characterization of Hydrotreated Fast Pyrolysis Liquids," *Energy Fuels* 24, (2010): pages 5264–5272.

[72] R. H. Venderbosch and W. Prins, "Fast Pyrolysis Technology Development," *Biofuels Bioproducts and Biorefining* 4, no. 2 (2010): 178-208, doi:10.1002/bbb.205.

[73] A. Oasmaa and S. Czernik, "Fuel Oil Quality of Biomass Pyrolysis Oils - State of the Art for the End Users," *Energy & Fuels* 13, no. 4 (1999): pages 914-921.

[74] M. F. Demirbas, "Characterization of Bio-oils from Spruce Wood (Picea orientalis L.) via Pyrolysis," *Energy Sources Part A* 32, no. 10 (2010): pages 909-916.

[75] R. H. Venderbosch et al., "Stabilization of Biomass-derived Pyrolysis Oils," *Journal of Chemical Technology and Biotechnology* 85, no. 5 (2010): pages 674-686.

[76] S. B. Jones et al., *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case,* prepared for the U.S. Department of Energy by Pacific Northwest National Laboratory, February 2009.

[77] D. Y. Hong et al., "Hydrodeoxygenation and Coupling of Aqueous Phenolics Over Bifunctional Zeolite-supported Metal Catalysts," *Chemical Communications* 46, no. 7 (2010): pages 1038-1040.

[78] A. Oasmaa et al., "Characterization of Hydrotreated Fast Pyrolysis Liquids," *Energy Fuels* 24, (2010): pages 5264–5272.

[79] F. D. Mercader et al., "Production of Advanced Biofuels: Co-processing of Upgraded Pyrolysis Oil in Standard Refinery Units," *Applied Catalysis B-Environmental* 96, no. 1-2 (2010): pages 57-66.

[80] D. C. Elliott, "Historical Developments in Hydroprocessing Bio-oils," *Energy & Fuels* 21, no. 3 (2007): pages 1792-1815.

Further, the characteristics of bio-oil make it incompatible with conventional refining equipment (i.e., high carboxylic acid content leads to metals corrosion; storage is problematic due to gumming, repolymerization, etc.; high oxygen content and the need to significantly increase hydrogen content lead to poor economics; and the potential for GHG debits for the product). However, catalytic pyrolysis pathways may be attractive, as the low oxygen content of the as-produced oil may overcome many of the deficiencies noted above. Continued R&D is needed.

The impact of bio-oil quality and stability on hydroprocessing catalyst performance needs to be validated at the pilot- and commercial-scales. Raw bio-oil contains potential impurities such as alkali metal, chlorine, nitrogen, and sulfur that could poison hydrotreating catalysts and limit long-term activity, stability, and lifetime. Thermal stability of the bio-oil or bio-crude intermediate will have a major impact on coke formation during upgrading, and hence overall carbon efficiency. Developing catalytic pyrolysis processes may produce intermediates that have better thermal stability. Additionally, any oxygen removed before the upgrading step will lower the hydrogen demand of biofuel production and potentially improve process economics. Bio-oil upgrading is required for biofuel production; however, producing a finished fuel in a stand-alone biorefinery is not as cost effective as developing a biomass (catalytic) pyrolysis process that can be integrated with a petroleum refinery to utilize the existing capital assets and infrastructure.

Pyrolysis oil upgrading is now at the pilot demonstration scale. Hydrotreating raw bio-oil is technically feasible using existing refining technology (catalysts and process conditions). Technology includes a mild hydrotreating step followed hydroprocessing to finished fuel. Yields are low, carbon efficiency is poor because of extensive coke formation, and hydrogen demand is high. All of this challenges the economics of pyrolysis oil to biofuels. Milder pyrolysis conditions lower the capital costs compared to biomass gasification. Processing the hydrocarbon intermediates in an existing petroleum refinery further improves process economics.

Economic Status

In a collaboration between UOP, National Renewable Energy Laboratory, and Pacific Northwest National Laboratory (PNNL), it has been demonstrated that raw bio-oil can be hydroprocessed in a two-step hydrotreating process to produce bio-gasoline and "green" diesel.[81] The first, mild hydrotreating step is to stabilize the bio-oil and remove a fraction of the oxygen. The final hydrotreating step is used to make gasoline and diesel range hydrocarbons.

A technoeconomic analysis of this process was performed by PNNL, which prepared a report for DOE.[82] The design was a 2,200-ton-per-day biomass pyrolysis plant with a mild hydrotreating step for stabilization and hydrotreating for fuel production. Maximum yields from this process were 65 gallons per ton if all hydrogen is produced from the input biomass. The average fuel cost was calculated at $2.04 per gallon ($1.34 on an ethanol equivalent basis). A 2,200-ton-per-day plant yields 66 million gallons per year at a total capital investment of $64,000 per daily barrel. This is for a stand-alone plant that produces hydrogen on site for hydroprocessing. If an external natural gas source is included to provide hydrogen or hydrogen is purchased, then the yield increases to 100 gallons per ton with 95% gasoline range hydrocarbons and 5% diesel.

A biomass pyrolysis case, which is similar to the PNNL Design Case, includes both a stand-alone option and a hydrogen purchase option.[83] The on-site hydrogen production option has a higher capital cost but the operating expenses associated with purchasing hydrogen needs to be evaluated as an alternative. First plants are likely to reduce operating complexity by not integrating the hydrogen production unit operation with the biofuels process and opt for a process that requires hydrogen be purchased. A 2,200-ton-per-day biomass pyrolysis plant with a purchased hydrogen option yields 58 million gallons per year of gasoline and diesel at a cost of $2.11 per gallon. The total capital investment is $47,000 per daily barrel. The cost of production and capital costs increase to $3.09 per gallon and $112,000 per daily barrel, respectively, when on-site hydrogen production is included.

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[81] S. B. Jones et al., *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case*, prepared for the U.S. Department of Energy by Pacific Northwest National Laboratory, February 2009.

[82] Ibid.

[83] W. M. Wright et al., "Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels," *Fuel* 89, no. 1 (2010): pages S2-S10.

Other technologies based on catalytic biomass pyrolysis are being developed to reduce the oxygen content of bio-oil and reduce the overall hydrogen demand of the biofuels process. The goal of this is to improve the thermal stability of bio-oil and improve the carbon efficiency of the hydroprocessing steps. If successful, catalytic pyrolysis could also eliminate the need for the first hydrotreating step to stabilize the bio-oil.

Catalytic biomass pyrolysis provides opportunities to further reduce biofuel costs by potentially eliminating the downstream bio-oil stabilization unit operation. The expectation is that the resulting bio-crude properties can be controlled by combining catalyst and biomass in a high temperature pyrolysis reactor. The goal is to produce lower oxygen containing bio-crude intermediate that is more thermally stable than raw bio-oil so the carbon losses during hydrotreating can be minimized and the hydrogen demand can be reduced.

Another opportunity for cost reduction is using the distributed catalytic pyrolysis approach to feed a centralized processing facility. A 100 million gallons per year bio-gasoline plant that converts upgraded bio-oil into finished fuel would require ~3,000 tons per day of biomass. This could be a single plant or six 500-ton-per-day distributed plants. This scale (~7,000 barrels per day) is still very small in relation to petroleum refineries, the largest of which is greater than 500,000 barrels per day. Depending on the regional biomass availability, the centralized processing facility could be even larger, but even increasing the size by a factor of ten is still small compared to petroleum refining.

Renewable Diesel – Hydrotreating Vegetable Oils

Hydrotreating virgin vegetable oil, used cooking oils, and greases has been technically proven and several partnerships are being developed to commercialize technology for producing green diesel and renewable jet fuel. A primary challenge to the commercial success of this technology hinges on the availability of low-cost feedstocks. Initially, this limits the technology to the used oils and greases and by-products from the animal products industry (fats and tallows).

Long-term performance of hydroprocessing catalysts needs to be demonstrated at the pilot-scale. The impact of potential poisons from the low-cost feedstocks may challenge catalyst activity, stability, and lifetime. As the risk decreases with additional technology development, process economics can be improved by utilizing the existing capital assets in the petroleum refining industry. This will require very tight specifications on any feedstock or processed intermediate that is introduced.

Hydrothermal Liquefaction

This technology is being developed primarily as an option for wet biomass feedstocks. For aqueous feed streams (< 30–50% solids), hydrothermal treatment can provide a technology option that does not require energy intensive feedstock drying. Long-term availability of these resources will be required for commercial processes. Feedstock availability will be a significant challenge for realizing economies of scale to improve process economics.

Hydrothermal liquefaction or upgrading has only been demonstrated at the bench-scale and the long-term performance of the catalysts needs to be demonstrated.[84,85,86,87] The activity, stability, and lifetime of these catalysts need to be proven in real systems. Deactivation (reversible or irreversible) from catalyst poisons is a major technical challenge. Many of the catalysts being developed include platinum-group metals. Long-term activity, regeneration, and recovery of these catalysts are a critical challenge for developing a cost-effective process. Temperature and pressure are key process variables that need optimization.

Sugars to Hydrocarbons – Catalytic Aqueous Phase Reforming

Technical challenges with producing a clean sugar stream from biomass pretreatment is very similar

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[84] D. C. Elliott et al., "Developments in Direct Thermochemical Liquefaction of Biomass: 1983-1990," *Energy & Fuels* 5, no. 3 (1991): pages 399-410.

[85] Y. Solantausta et al., "Assessment of Liquefaction and Pyrolysis Systems," *Biomass & Bioenergy* 2, no. 1-6 (1992): pages 279-297.

[86] M. Balat, "Mechanisms of Thermochemical Biomass Conversion Processes. Part 1: Reactions of Pyrolysis," *Energy Sources Part A: Recovery Utilization and Environmental Effects* 30, no. 7 (2008): pages 620-635.

[87] H. B. Goyal, D. Seal, and R. Saxena, "Bio-Fuels from Thermochemical Conversion of Renewable Resources: A Review," *Renewable & Sustainable Energy Reviews* 12, no. 2 (2008): pages 504-517.

to pretreatment challenges faced in other biofuels technology areas. Commercial-scale separations of fuels from aqueous solution used in aqueous phase reforming will need to be demonstrated, but it should not be vastly different from available separations technologies. Complex reaction schemes for developing aqueous phase reforming processes may require multiple separation steps.

The chemistry and catalysis for converting pretreated biomass into biofuels has been demonstrated at the bench scale and pilot scales with model sugar solution. Demonstration-scale facilities are needed to test long-term catalyst performance. Catalyst deactivation from impurities present in the aqueous feed stream is a technical challenge that has not yet been addressed. Additionally, the impact of multiple sugars feedstocks present in the pretreated biomass hydrolysate may impact yield and selectivity of desired products. Catalyst cost is an economic barrier that needs to be addressed by efficiency catalyst recovery and regeneration or finding lower cost catalysts. Fuels produced by aqueous phase reforming should be compatible with the existing fuel distribution infrastructure and vehicle technology.

Hybrid Technologies

Integrated hybrid technologies have only been tested at the bench scale or in process modeling exercises. No pilot-scale or commercial-scale demonstrations have yet been made. Lignin combustion is not considered a thermochemical fuel technology but is being considered in biochemical conversion processes to provide heat and electricity for internal use. Syngas fermentation is a hybrid technology that has not been tested with biomass-derived syngas, although a pilot-scale demonstration unit is planned. A pilot-scale demonstration to ferment pretreated biomass into acetic acid and combine it in a catalytic process to produce ethanol has been funded but is not operational. The economic viability of these hybrid processes needs to be proven.

A thermobiological hybrid process, which differs from the thermochemical and FTS type processes described above, combines proprietary microorganisms and bioreactor technology with gasification and ethanol separation technologies to produce cellulosic ethanol from non-food feedstocks. This technology has the advantage of combining a feedstock flexible gasification process with an ethanol specific microbe for high yields.

The hybrid approach for the production of cellulosic ethanol incorporates the efficiency of the fermentation process used in the biochemical approach, which selectively produces ethanol rather than a mixture of alcohols and less desirable by-products, with the feedstock flexibility and full feedstock utilization associated with the gasification process used in the thermochemical approach. The yields from this pathway are higher, and the cost targets are lower than both the biochemical and thermochemical approaches.

The thermobiological hybrid approach consists primarily of three steps illustrated in Figure 12-19. The first step is gasification, which is a known commercial technology where a non-food cellulosic feedstock is gasified to produce synthesis gas (syngas), comprised of carbon monoxide and hydrogen. The tolerance of the syngas fermentation allows commercially available gasification technology to be utilized to minimize technological risk while supplying a syngas composition optimized for the fermentation process. The second step is syngas fermentation where proprietary microorganisms ferment the syngas into ethanol in a bioreactor system. This development is adapting commercially available reactor technology to maximize the mass transfer of syngas and capitalize on the high ethanol production rates of microorganisms. Finally, the separation step is where the ethanol is separated from water via commercially available distillation and molecular sieve technology.

This hybrid pathway offers advantages over other approaches. The three-step process combines the front-end flexibility of gasification with biological fermentation designs, which operate at low temperatures and low syngas pressures. The microorganisms consume nearly all of the syngas in the process and selectively produce ethanol, providing high ethanol yields.

Advantages of the pathway include:

- **Feedstock Flexibility.** The process can convert carbon-containing material to syngas, including switchgrass, miscanthus, wood chips, forestry products, corn stover, bagasse and other typical agricultural wastes, and municipal and industrial organic waste.

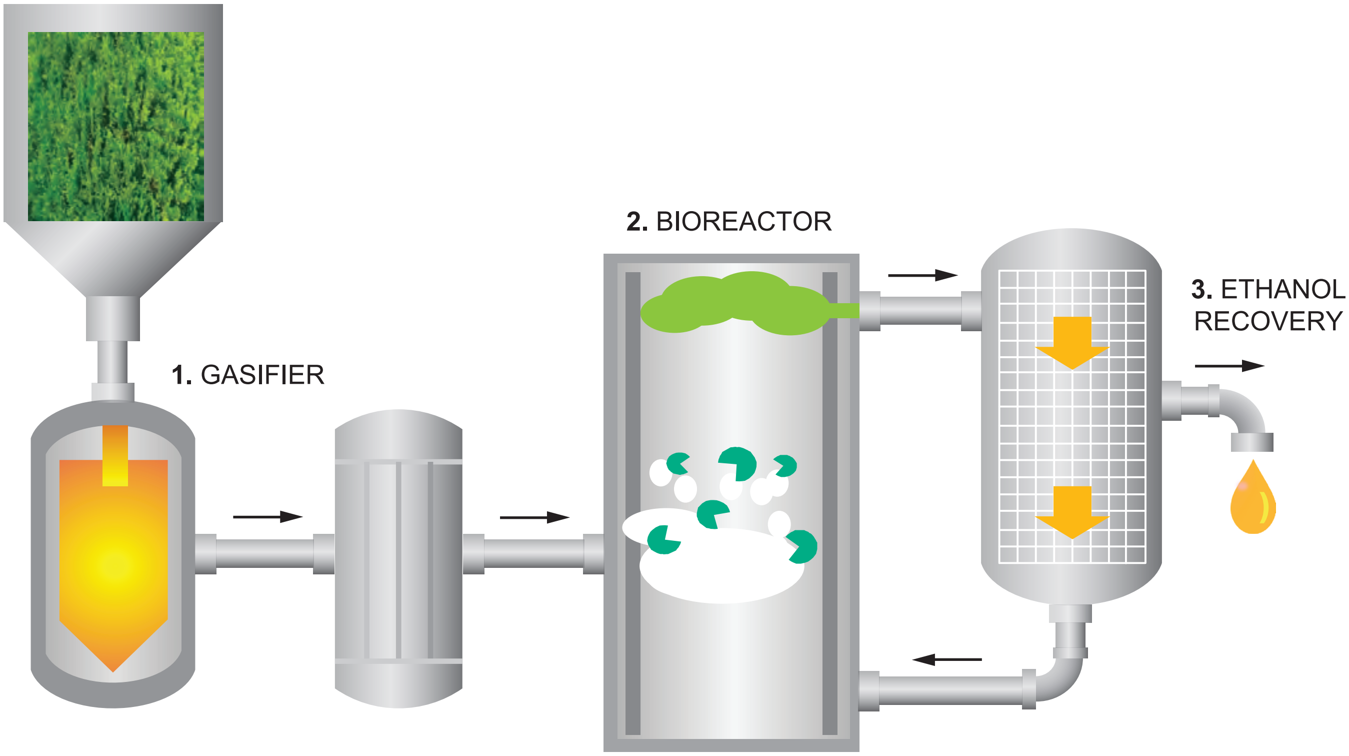

Figure 12-19. *The Hybrid Approach – A Thermobiological Process*

- **Feedstock Utilization.** Gasification allows all of the biomass material to be utilized in the process, not just the cellulosic components.
- **Environmental Profile.** Argonne National Laboratory's GREET 1.8 calculations show a potential reduction of GHG emissions up to 96% compared to gasoline in at least one thermobiological hybrid process. The process also requires less than 2 gallons of net water per gallon of ethanol produced.
- **Selective Ethanol Production.** Proprietary microorganisms produce only fuel-grade ethanol instead of a mixture of alcohols produced in syngas conversion via chemical catalysis.
- **Low Operating and Capital Costs.** The thermobiological hybrid process offers feedstock flexibility as well as plant scalability to address specific regional conditions.

Another hybrid process is being developed to ferment pretreated biomass into acetic acid and combine it in a catalytic process to carbonylate it with CO to produce ethanol. CO is generated from lignin gasification. A pilot-scale demonstration has been funded to demonstrate the process. The economic viability of these hybrid processes needs to be proven.

Thermochemical Conversion Hurdles

One of the biggest challenges for deploying thermochemical conversion technologies for biofuels is the capital investment needed to build out the expected biofuels capacity and reducing operating costs associated with production. Technical challenges involve reducing costs by optimizing thermal integration and process efficiency and maximizing yields while reducing process complexity and severity. In order for thermochemical biofuels technologies to be developed, demonstrated, and deployed at full scale, improvements in feedstock production and logistics will be required to cost-effectively deliver large quantities of biomass to maximize economies of scale to reduce capital costs. This may include densification, pretreatment, or an improved biomass transportation network. An assumption is that there will be enough biomass resources available on a sustainable basis to meet the alternative transportation fuel demand in 2050.

Technical breakthroughs are required on the front end of biomass gasification processes to provide clean syngas for catalytic fuels synthesis. Demonstration and deployment of a commercial-scale (2,000 tons per day) biomass gasifier is a key step for moving this technology forward. Another technical challenge is to improve the efficiency and reduce the complexity of the gas cleanup and conditioning unit operations. Collectively, the gasification and gas cleanup and conditioning operations make up roughly 50% of the capital cost of the overall process. Therefore, integration and consolidation of processes to generate clean syngas to reduce capital and operating costs are important to demonstration of economic viability of this process. A lower risk alternative may be demonstrating this technology for power production or co-processing biomass with coal in more technically advanced coal gasification facilities.

Biomass pyrolysis technologies have the advantage of being lower in severity compared to gasification. The process produces a liquid product that can be collected in a distributed network of pyrolysis facilities and upgraded in a centralized processing facility. Biomass pyrolysis systems tend to be lower capital cost because of lower processing temperatures and pressures. Hydrotreating technology has been developed in the petroleum refining industry and is commercially available for biofuels production. The key technical challenge is producing a hydrocarbon liquid intermediate that has appropriate chemical composition and physical properties for commercial hydrotreating technology. This requires an efficient catalytic process that retains as much carbon in the bio-crude intermediate as possible while rejecting enough oxygen to minimize hydrogen consumption during hydroprocessing. Technical breakthroughs in catalytic biomass pyrolysis process development and hydrotreating catalysts capable of processing bio-crudes are needed.

A near-term deployment strategy to accelerate adoption may be to produce lower quality bio-crudes to optimize the thermal integration and pyrolysis process and co-process very dilute quantities in existing refineries to prove the concept and begin integration of bio-crudes into the existing petroleum infrastructure.

Capital cost of thermochemical biomass conversion processes can be quite high. Economic models of plant biomass gasification processes predict capital costs in the neighborhood of $100 million to $900 million for a 2,000-ton-per-day plant that produces about 50 million gallons per year of biofuels. Biomass pyrolysis technologies of similar scale have comparable capital costs. To meet the thermochemical biofuels demand would require somewhere in the neighborhood of 300 to 500 plants at a projected cost of $50 to $250 billion investment. Key technology hurdles associated with thermochemical conversion are summarized in Figure 12-20.

Algae Technology – Current Status

The photosynthetic cultivation of microalgae for the growth of nutritional products (neutraceuticals) is practiced commercially, with world commercial biomass production estimated at 10,000 tons per year in 2009.[88] Roughly half of the current commercial production is in China, with most of the remainder in Japan, Taiwan, the United States, India, and Australia. Macroalgae (seaweed) may also be cultivated, but will not be covered in this section, as it generally involves fundamentally different technologies (e.g., offshore cultivation).

Several factors make the growth of microalgae for biofuels, and specifically bio-oil production potentially attractive. Algae have the potential to use CO_2-rich streams that are produced from existing power plants, allowing for a better level or scalability. In addition, algae have higher productivity per acre on otherwise non-arable land and use a variety of water qualities (fresh, brackish, seawater, and wastewaters). The by-products of production may have a higher value and the fuel products are directly compatible with existing fuels infrastructure, or convertible to liquid fuels via routes similar to existing commercial processes.

While algae offer attractive features, many technical challenges must be overcome to make the production of microalgal biofuels viable at commercial scale. The large gap between the current state of the technology and that required for biofuels production suggest that relatively long-term

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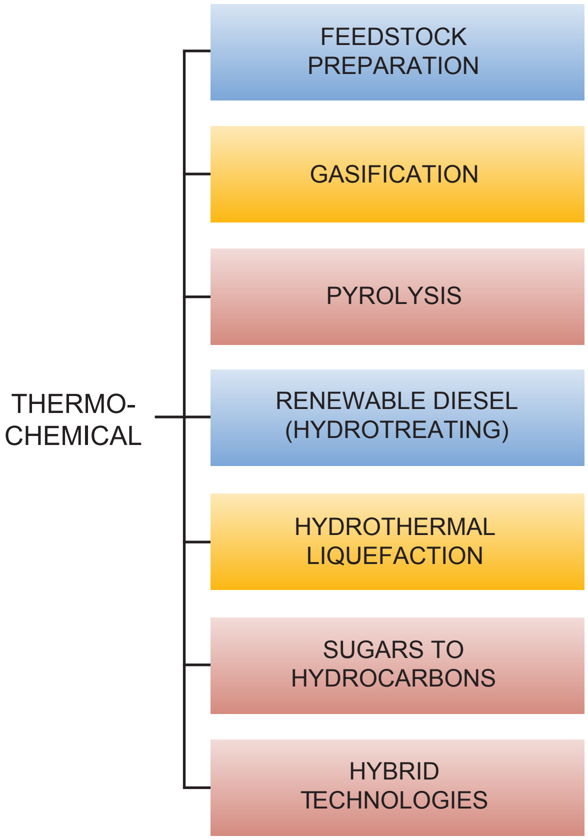
[88] J. R. Benemann and J. W. Oswald, *Systems and Economic Analysis of Microalgae Ponds for Conversion of CO_2 to Biomass*, U.S. Department of Energy, 1994, http://www.osti.gov/bridge/servlets/purl/493389-FXQyZ2/webviewable/493389.pdf.



- Thermochemical conversion technologies can be applied to a wide variety of available feedstocks with a diverse range of physical and chemical properties. Consequently, these technologies can be targeted for lower cost feedstocks but they tend to be lower quality and increase technical risks. Feedstock cost is a major economic hurdle that is not unique to thermochemical conversion technologies.
- Syngas conversion to fuels and chemicals has been commercially practiced with coal and natural gas derived syngas. Biomass gasification processes cannot fully capture the economics of scale realized with fossil fuel conversion to economically feasible clean syngas production from biomass will require process intensification to reduce capital costs.
- Pyrolysis and hydrothermal liquefaction produce a hydrocarbon intermediate that can be integrated into the fuel production and distribution network utilizing existing capital assets to reduce capital costs. These technologies are still developing and need to be demonstrated as commercially relevant scales to validate long-term catalyst performance and consistent intermediate quality to minimize risk to refining infrastructure.
- Developing hybrid thermochemical conversion technologies have been demonstrated in laboratory settings. Pilot-scale demonstrations are needed to test long-term catalyst performance to evaluate catalyst deactivation from impurities and the impact of real biomass feedstock on yield and selectivity of desired products.

🟦 MINIMAL/NO BARRIERS
🟨 WILL TAKE INVESTMENT AND TIME, BUT PATHWAY FOR SUCCESS HAS BEEN IDENTIFIED
🟥 SIGNIFICANT BARRIER OR HIGH RISK OR HIGH UNCERTAINTY OR REQUIRES "BREAKTHROUGH OR INVENTION"

Figure 12-20. *Thermochemical Conversion Hurdles*

research and development will be required. In addition, despite the attractive factors for algal biofuels, their ability to supply in large amounts the long-term transportation fuel has not yet been demonstrated.

Many topical reviews on microalgae for fuels are available. The reviews used extensively for the current discussion include:

1. A 1998 report by the National Renewable Energy Laboratory that details research sponsored over a 20-year period (1976 to 1996) by DOE on microalgal biofuels.[89]
2. A 2010 report by DOE that focuses on a roadmap on technical challenges to meet for commercialization of microalgal biofuels.[90]
3. A 2010 report by UC Berkeley, of a detailed engineering assessment of algal biofuel production.[91]
4. A 2006 report by the Netherlands Organisation for Applied Scientific Research under the auspices of the International Energy Agency and ENI (an Italian oil and gas company), concluding that the global potential of microalgae wastewater (municipal and animal) treatment for CO_2 biofixation is almost 100 million tons annually.[92]

Algae Technology Hurdles

The technology hurdles for microalgal biofuels production, and respective technical challenges, are

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[89] J. Sheehan et al., *A Look Back at the US Department of Energy's Aquatic Species Program: Biodiesel from Algae*, NREL/TP-580-24190, National Renewable Energy Laboratory, 1998.

[90] U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Biomass Program, *National Algal Biofuels Technology Roadmap*, May 2010.

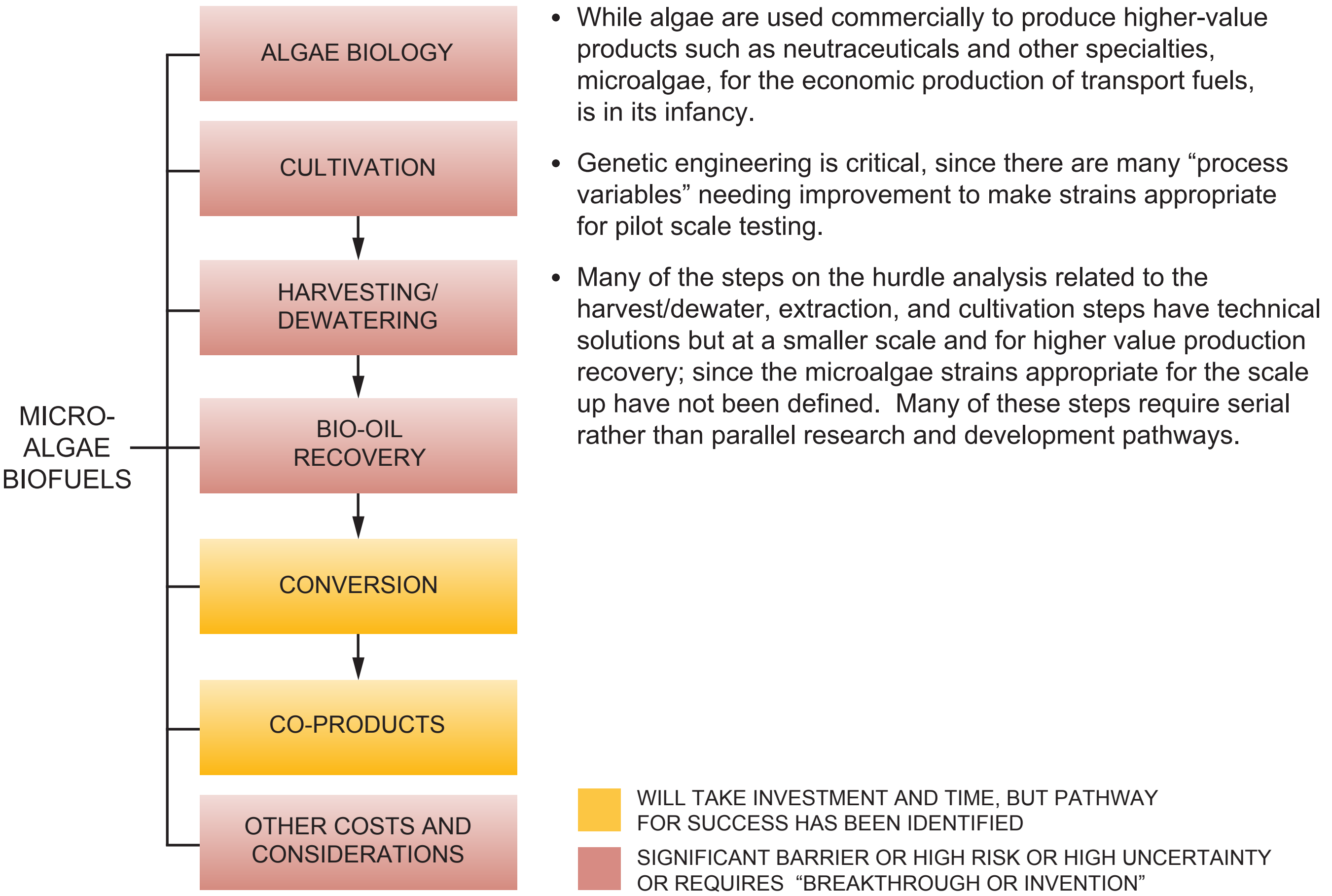
[91] T. J. Lundquist et al., *A Realistic Technology and Engineering Assessment of Algae Biofuel Production,* Energy Biosciences Institute, 2010.

[92] T. Van Harmelen and H. Oonk, *Microalgae Biofixation Processes: Applications and Potential Contributions to Greenhouse Gas Mitigation Options*, International Network on Biofixation of CO_2 and Greenhouse Gas Abatement with Microalgae, 2006.

summarized in Figure 12-21. While most of these steps are commercially practiced for nutraceuticals production, several technical challenges remain for the scalable, economic production of microalgal biofuels, as indicated in the respective sections of this hurdle analysis. Genetic engineering has the potential to produce algal strains that can overcome some of these limitations.

Cultivation

Commercial quantities of higher value products (e.g., β-carotene, nutraceuticals) are cultivated in both open ponds and closed photobioreactors. However, the cost of the open systems can be from 10 to 100 times less expensive, resulting in open ponds being more attractive for fuel production. Continued advances are required to improve cultivation technology and reduce costs. Some of these advances include improved techniques to increase the efficiency of light utilization and effective CO_2 capture, distribution, and use. For example, maximum short-term photosynthetic yields of 2–3% of total sunlight energy have been achieved, with longer term yields in the 1–2% range. This compares to a theoretical maximum utility of about 10% of total solar radiation. One benefit of algae is their ability to grow in media of lower water quality, such as brackish seawater or treated municipal waste sources, which is critical in avoiding competition with food/feed production. For mass cultivation to succeed, the microalgae cultures need to be resistant to predation by grazers, diseases, or invasion by weed algae, in addition to avoiding any interference with and adversely impacting local environments. Although several dozen commercial facilities are producing hundreds of tons of algae biomass sold as high-value nutraceutical products, the production of low-cost transport fuels will require considerable cost reductions, increases in scale, and reduction in energy and other inputs.



- While algae are used commercially to produce higher-value products such as neutraceuticals and other specialties, microalgae, for the economic production of transport fuels, is in its infancy.
- Genetic engineering is critical, since there are many "process variables" needing improvement to make strains appropriate for pilot scale testing.
- Many of the steps on the hurdle analysis related to the harvest/dewater, extraction, and cultivation steps have technical solutions but at a smaller scale and for higher value production recovery; since the microalgae strains appropriate for the scale up have not been defined. Many of these steps require serial rather than parallel research and development pathways.

🟨 WILL TAKE INVESTMENT AND TIME, BUT PATHWAY FOR SUCCESS HAS BEEN IDENTIFIED

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Figure 12-21. *Algae Technology Hurdles*

Harvesting/Dewatering and Biofuel Recovery

Algae concentrations in growth media and concomitant bio-oil or other biofuel are typically low in ponds (on the order of 0.02 to 0.04% dry weight basis). This requires large amounts of energy during processing for recovery of the algae biomass and/or algal biofuels. Although algae concentration in photobioreactors can be about ten-fold higher, as stated earlier, it is much more costly. Effective energy use is critical in the harvesting and oil or biofuel recovery steps, including algae cell disruption and oil extraction. Harvesting via filtration, flocculation, sedimentation, or centrifugation is a major challenge as the algal suspensions need to be concentrated by 1,000-fold in order to recover oil. One alternative to reduce oil recovery and processing steps would be to use genetically engineered microalgae that secrete oil instead of accumulating it within the cells, but such processes are not demonstrated at large scale. Water recovery and recycle is critical for an effective process; although demonstrated in commercial production systems, it remains to be demonstrated for biofuel applications. Oil recovery requires solvent extraction and other purification routes to yield the vegetable oil or hydrocarbon products and current economics of extraction are unclear. Very little work has been carried out on fermentation of algae carbohydrates for biofuel applications, and is not further considered here.

Conversion

While specific algae oil or hydrocarbon products will dictate which conversion processes are needed, it is anticipated that the algae products would be similar to those of higher crops and utilize known process technology (e.g., transesterification for fatty acid methyl esters [FAME], hydrogenation, cracking, etc.). Biochemical conversion routes (e.g., fermentations), or hydrothermal (high pressure) gasification and pyrolysis processes for wet biomass, as discussed earlier in the chapter, may be alternatives to processing and conversion of algal lipids. Conversion technologies must be tailored to the specific product slate, but existing processes can be tailored to process microalgae effectively. Genetic engineering could also be used to produce molecules of choice—products more akin to gasoline or diesel than the vegetable oils and other lipids currently produced by algae. Lower priority is expected for resolution of conversion challenges versus other process steps.

Co-Products

Co-products such as animal feeds, health foods, colorants, lipids, etc., can be of much higher value than transport fuel, and may drive economics for initial applications. However, except for the case of commodity fish and animal feeds, low volume markets for co-products would not provide for significant level of support for transport fuel development. The treatment of municipal and animal waste streams has high value in some areas and may provide co-processing incentives for algae production of transportation fuels. Revenue from higher value co-products, particularly animal protein feeds, or the co-processing of municipal and animal wastewaters support microalgae economics, but the market for most other co-products is insufficient for biofuel applications.

Other Costs and Considerations

Other significant issues for algae-based production of fuels include: net energy use for the process, ability to capture CO_2 at rates sufficient to consider as a carbon capture alternative, land use and siting, environmental and climate factors (i.e., temperature needed for effective cultivation), regulatory issues, and overall process costs.

Economics

Current commercial microalgal products command high values, but are produced at low volume. For example, *Haematococcus pluvalis* is currently grown for the production of astaxanthin as a nutraceuticals product (~$20,000/kg), but is used in low volume (~2 tons/annum). Even production of astaxanthin for salmon aquaculture feeds, with a market about 100 times larger (at one tenth the prices) is small in comparison to transportation fuels markets.

In one study, the capital costs were estimated for a microalgae plant that treats municipal wastewaters, with co-production of algae biofuels, both oil and biomethane, with the latter used to co-generate electricity.[93]

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[93] T. J. Lundquist et al., *A Realistic Technology and Engineering Assessment of Algae Biofuel Production,* Energy Biosciences Institute, 2010).

A flow diagram for the most economic case, in which only electricity is produced, is shown in Figure 12-22. In this case, municipal waste treatment is the driver for the plant, with electricity as a co-product. Economics are projected to be positive, equivalent to a $28 per barrel equivalent oil cost. In contrast, Figure 12-23 illustrated a scenario where bio-oil as the primary product and wastewaters provide the make-up nutrients and water and treatment is incidental to biofuels production. This case is not economically favorable, requiring crude oil prices of $240 per barrel equivalent oil cost. It is concluded that oil production will be expensive, even with the relatively favorable process assumptions they used. However, it should be noted that the algal biomass and oil production rates were well below those projected in this field.

In conclusion, the production of biofuel as a co-product from municipal waste treatment, the production of higher value products, or the production of animal protein, where the biofuel is a co-product, may be more attractive for initial applications of microalgae biofuels production, but have overall relatively modest biofuel outputs.

A 2010 study takes an *a priori* approach to estimating the costs of algal biofuels production. This study does not contain process schematics, yields, or similar details, but provides insight via sensitivity analysis, employing the co-production of a high value product (HVP) (β-carotene), and the sale of biomass as feedstock (soymeal or fishmeal substitute). The analysis points to the critical effect co-production of HVP plays in the economics for potential early production schemes, in this case a 0.1% yield of the HVP yields at 10 times the value of the oil.[94]

Figure 12-24 is a graphical representation of this sensitivity analysis. The project internal rate of return (IRR) is highly dependent on the value derived from the HVP, the biomass yield, and the price of oil. As the state of the technology matures, such sensitivity analyses will help guide the research and development targets.

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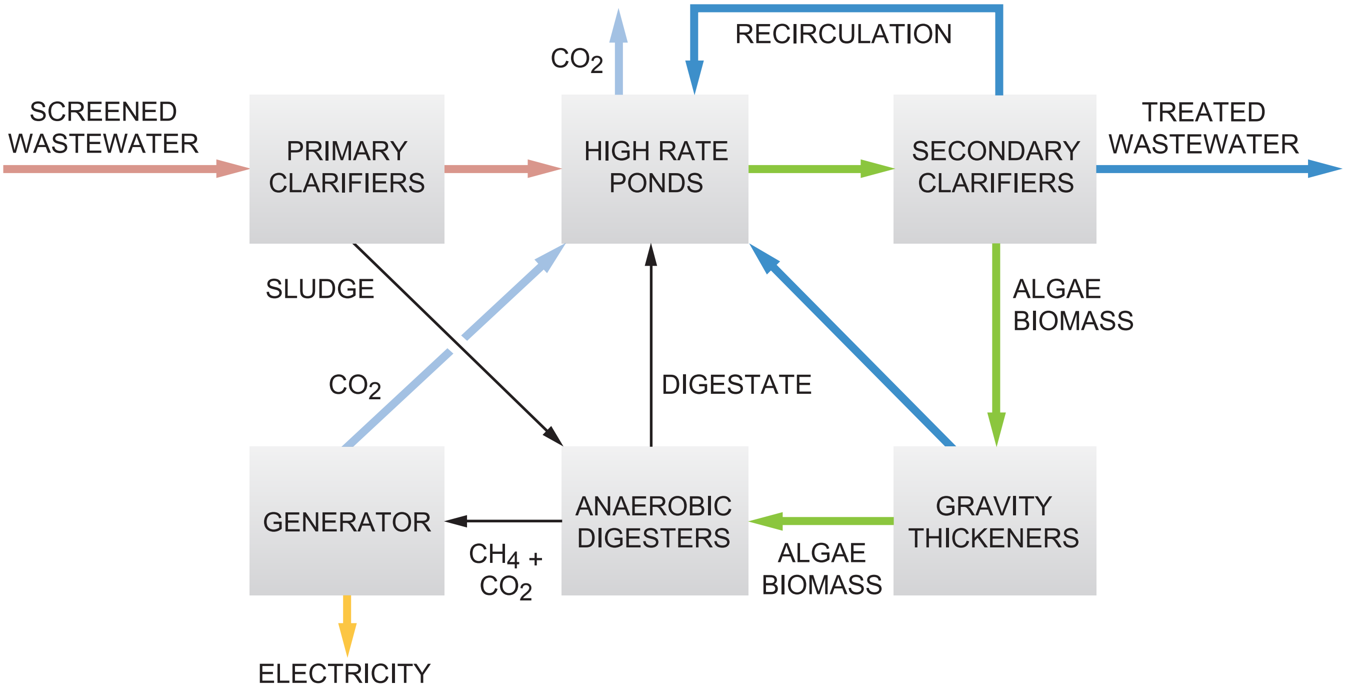
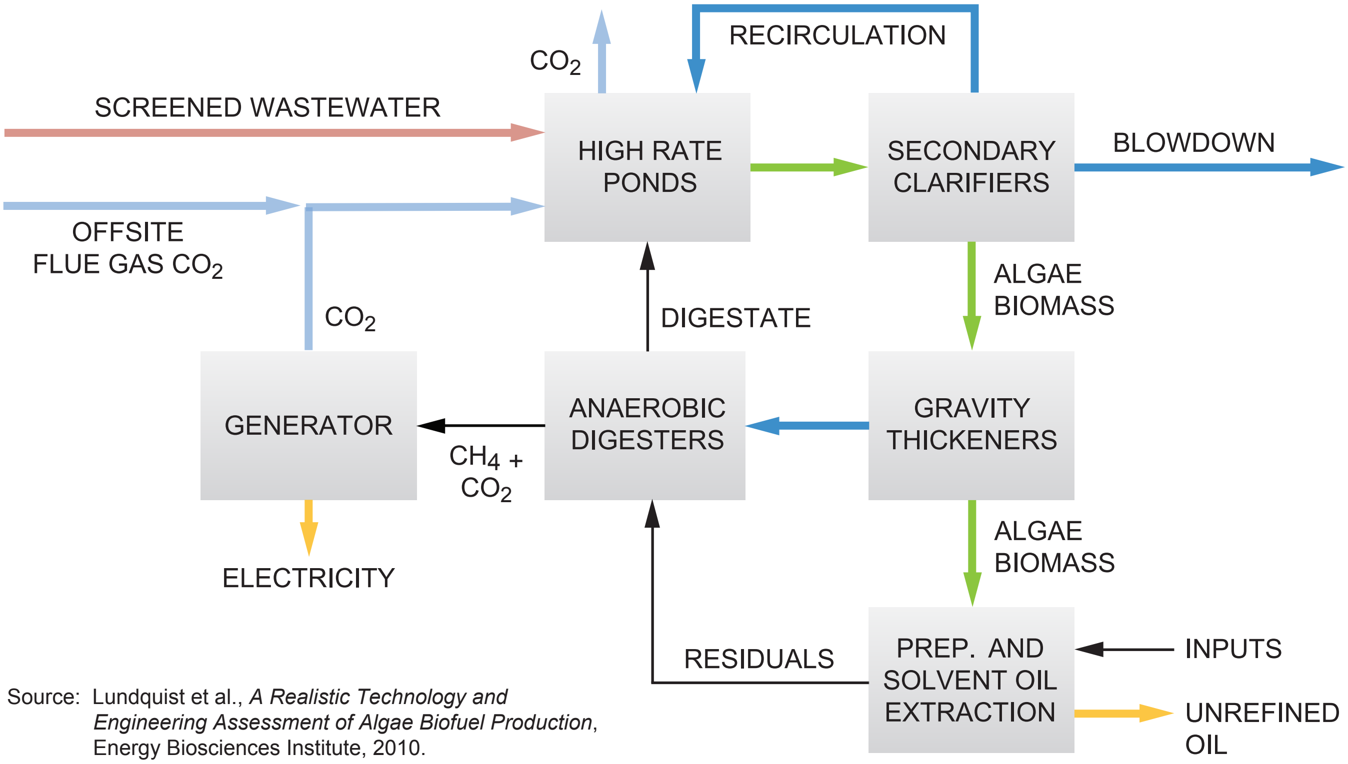
[94] E. Stephens et al., "An Economic and Technical Evaluation of Microalgal Biofuels," *Nature Biotechnology* 28, no. 2 (2010): pages 126-128.



Source: Lundquist et al., *A Realistic Technology and Engineering Assessment of Algae Biofuel Production*, Energy Biosciences Institute, 2010.

Figure 12-22. *Treatment of Municipal Waste, with Biofuels as a By-product*



Source: Lundquist et al., *A Realistic Technology and Engineering Assessment of Algae Biofuel Production*, Energy Biosciences Institute, 2010.

Figure 12-23. *Growth of Algal Biomass, with Some Wastewater Treatment and Biomethane Production*

From the sensitivity analysis, several conclusions can be made. The value of fuel alone is not sufficient for the production of microalgal biofuels for the foreseeable future but high value products may produce small amounts of microalgal biofuels co-products. Likewise, municipal waste treatment, coupled with the production of microalgal biofuels as by-product, may represent a pioneer application. Therefore, continued life-cycle analysis and economic studies are needed to further refine critical variables, energy balances, process schematics, and overall economics. Long-term research and development is required for more productive and lower cost processes to allow stand-alone biofuel applications. In addition, the environmental effects of genetically engineered algae must be evaluated.

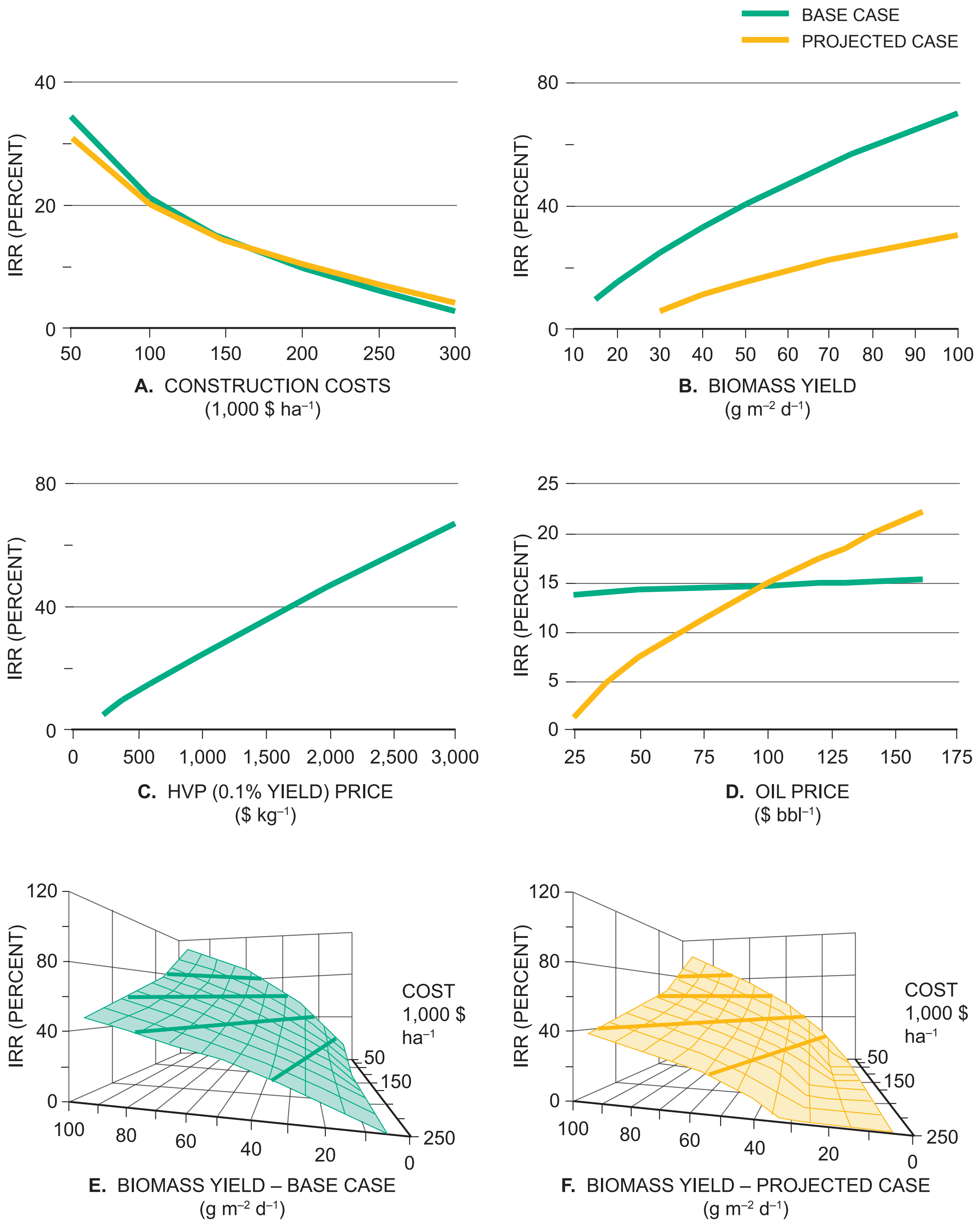
OVERALL IMPACT OF BIOFUELS TECHNOLOGY

Case Studies: Potential Future Supply and Costs

The potential future supply and cost structure of biofuels under two different case studies have been estimated in this section. The first case study is defined as a business-as-usual case and assumes that the level of investment in research and development remains on its current trajectory. Also, it was assumed that current policy would remain in effect and that no significant changes to that policy would occur. The second case study is an aggressive study in which significant increases in technology investment occur and several key technology hurdles are overcome. An additional consideration was to ensure that in both of these case studies biomass supply would be sufficient to meet the requirements for the volume of fuels produced. The costs of these various biofuels as a function of time and volume produced were also estimated.

Biofuel Production and Costs

Table 12-3 represents biofuels production and costs over time that were developed based on two case studies. The first estimate is based on a business-as-usual case, indicated by the red text, while the second estimate represents an aggressive case in which critical technology barriers are overcome, shown in black text. As can be seen in



Source: E. Stephens et al., "An Economic and Technical Evaluation of Microalgal Biofuels," *Nature Biotechnology* 28, no. 2 (2010): pages 126-128.

Figure 12-24. *Sensitivity Analysis*

	2010	2015	2020	2025	2030	2035	2040	2045	2050
Biomass Resource Availability (million tons/year)									
Corn	–	–	–	–	–	–	–	–	–
Imported Sugar Cane	–	–	–	–	–	–	–	–	–
Vegetable oil	–	–	–	–	–	–	–	–	–
Corn Stover	76 | 76	94 | 94	112 | 112	165 | 165	217 | 217	270 | 270	323 | 323	375 | 375	428 | 428
Switchgrass (or energy grasses)	104 | 104	134 | 134	164 | 164	151 | 151	138 | 138	125 | 125	113 | 113	100 | 100	87 | 87
Forest Residues (assume for FT-diesel for acct.)	60 | 60	85 | 85	110 | 110	135 | 135	161 | 161	186 | 186	211 | 211	236 | 236	261 | 261
Woody biomass (assume for pyrolysis for acct.)	110 | 110	117 | 117	124 | 124	121 | 121	118 | 118	115 | 115	113 | 113	110 | 110	107 | 107
Algae	–	–	–	–	–	–	–	–	–
Biofuels Yields per Feedstock (gallons per ton)									
Corn Ethanol	97 | 97	100 | 101	101 | 102	102 | 102	102 | 102	102 | –	103 | 105	105 | 105	105 | 105
Biodiesel (FAME + Hydrotreated veg oil)	20 | 50	50 | 50	52 | 52	55 | 55	55 | 57	55 | 60	57 | 60	57 | 60	57 | 60
Lignocellulosic Ethanol	80 | –	80 | –	80 | –	90 | –	90 | –	90 | –	97 | –	97 | –	97 | –
Bio-gasoline (pyrolysis)	45 | 45	45 | 45	45 | 65	65 | 80	80 | 100	80 | 100	100 | 100	100 | 110	110 | 110
FT – Diesel	40 | 40	50 | 50	50 | 55	55 | 55	55 | 55	55 | 55	55 | 55	55 | 55	55 | 55
Advanced Biofuels	–	–	–	–	–	–	–	–	–
Biofuels Production Costs ($2005/gallon)									
Corn Ethanol	2.17 | 2.17	2.01 | 2.01	2.01 | 2.01	1.98 | 1.95	1.95 | 1.92	1.92 | 1.87	1.87 | 1.87	1.85 | 1.83	1.83 | 1.83
Biodiesel (FAME + Hydrotreated veg oil)	4.05 | 4.05	3.05 | 3.05	3.05 | 2.98	2.98 | 2.98	2.98 | 2.98	3.05 | 3.05	3.05 | 3.05	3.15 | 3.15	3.25 | 3.25
Lignocellulosic Ethanol	5.92 | 5.92	4.65 | 3.38	3.38 | 2.51	2.51 | 2.25	2.25 | 2.25	2.25 | 2.25	2.25 | 2.18	2.18 | 2.18	2.18 | 2.18
Bio-gasoline (pyrolysis)	6.55 | 6.55	3.41 | 3.41	3.41 | 2.11	2.11 | 1.74	2.11 | 1.74	1.74 | 1.74	1.74 | 1.74	1.74 | 1.74	1.74 | 1.74
FT – Diesel	6.45 | 6.45	4.25 | 4.25	4.25 | 4.00	4.00 | 3.05	4.00 | 3.05	3.05 | 3.05	3.05 | 3.05	3.05 | 3.05	3.05 | 3.05
Advanced Biofuels	–	–	–	–	–	–	–	–	–
Biofuels Production Est. (billion gallons per year)									
Corn Ethanol	12.0 | 12.0	15.0 | 15.0	15.0 | 16.0	15.0 | 17.0	15.0 | 18.0	15.0 | 19.0	15.0 | 20.0	15.0 | 21.0	15.0 | 22.0
Biodiesel (FAME + Hydrotreated veg oil)	1.0 | 1.0	1.5 | 1.5	2.6 | 2.6	2.6 | 2.6	2.6 | 2.6	2.6 | 2.6	2.6 | 2.6	2.6 | 2.6	2.6 | 2.6
Lignocellulosic Ethanol	0.0 | 0.0	0.1 | 0.3	0.5 | 4.0	2.0 | 10	7.3 | 16	13.3 | 22.0	19.3 | 28.0	25.3 | 34.0	31.3 | 40.0
Bio-gasoline (pyrolysis)	0.0 | 0.0	0.0 | 0.0	0.1 | 0.2	0.3 | 0.5	1.1 | 1.8	3.2 | 5.4	12.2 | 15.0	12.2 | 16.5	13.4 | 16.5
FT – Diesel	0.0 | 0.0	0.0 | 0.1	0.1 | 0.2	0.2 | 0.3	0.3 | 0.7	0.7 | 1.3	1.3 | 2.8	1.3 | 2.8	1.3 | 2.8
Advanced Biofuels	–	–	–	–	–	–	–	–	–

Table 12-3. *Total Biomass Availability and Biofuels Supply for Business-as-Usual (red) and Aggressive (black) Cases*

Table 12-3, reaching RFS2 in the business-as-usual case will be challenging, while in the aggressive case, RFS2 would be met for advanced biofuels.

In an independent study, the National Research Council (NRC) convened a committee of experts to provide an independent assessment of the economic and environmental benefits and concerns associated with achieving RFS2.[95] The NRC report concluded there are technological and economic challenges for advanced biofuels, and uncertainty about greenhouse gas benefits. Their analysis examined cellulosic biofuels production in the lifetime of RFS2 through 2022, concluding that high oil or carbon prices would be needed to make cellulosic biofuels competitive in that timeframe.

Assumptions for the business-as-usual production estimates for biofuels produced via the biochemical platform include the following:

- Near-term (out to 2015) production estimates were based on publicly announced biofuel projects deemed likely to proceed. In the mid-term (out to 2020), growth is assumed to be driven by "bolt-on" cellulosic ethanol plants that are co-located with corn ethanol plants, in order to take advantage of the significant capital and operating synergies associated with this approach.
- It was assumed that growth would continue to be driven by market pull associated with RFS mandates, but that the maximum growth rate would be on the same order as the maximum growth rate seen in the corn ethanol industry during the years of its most rapid expansion (2005–2008).
- In addition to a maximum percentage growth rate, it was also assumed that there exists a maximum absolute growth rate, beyond which it is unlikely that sufficient capital and resources can be accessed for biorefinery projects. Again, the corn ethanol industry was used as a guide, and that limiting growth rate was set to 1.2 billion gallons per year.

The aggressive scenario was formulated in a similar manner to the business-as-usual scenario, except that: (1) less probable publicly announced projects were included in the near-term production estimates, and (2) the maximum growth rate was assumed to be roughly double that achievable in the most rapid expansion phase of corn ethanol.

Near-term costs for the production of cellulosic ethanol are taken into account with regard to the production costs for biochemical platform biofuels.[96] In future years, these costs are assumed to be reduced by several factors, including: reduction in enzyme costs proposed by leading enzyme manufacturers, increased xylose yields, and improved fermentation of arabinose. There are also assumptions related to the improvements of pryloysis oil upgrading, gasification, and gas cleanup for biofuels produced from thermochemical routes. In the longer term, genetic improvements in energy crops could substantially increase biomass yields per acre and thereby reduce feedstock costs for biorefineries, since some production costs are driven by land area and not by biomass tonnage. Improvements in biofuel yield estimates per ton of biomass are based on technology improvement assumptions.

Greenhouse Gas

Biomass is attractive for use in reducing GHG emissions in the transportation sector because the CO_2 consumed in growing the biomass is assumed to be equivalent to the CO_2 generated by combusting the biomass. Thus as long as the CO_2 emitted during the remainder of the biomass life cycle is less than the total CO_2 emitted during the life cycle of the fuel that the biomass is replacing, which is typically petroleum based, the substitution of biomass provides a GHG reduction. In this study, the life-cycle GHG estimates that were built into the VISION model were developed from Argonne National Laboratory's GREET model. As a result, the fermentation of farmed trees, corn stover, and lignocellulosic biomass are the processes that provide the largest GHG reduction benefit. These processes are closely followed by forest residue gasification and herbaceous biomass fermentation. The GHG reduction values for these processes do not include any indirect land use effects, since GREET does not have indirect land use impacts in its calculations. The results of the GHG modeling activities are detailed in Chapter Six, "Greenhouse Gases and Other Environmental Considerations."

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[95] National Research Council of the National Academies, *Renewable Fuel Standard: Potential Economic and Environmental Effects of U.S. Biofuel Policy,* 2011.

[96] F. K. Kazi et al., "Techno-Economic Comparison of Process Technologies for Biochemical Ethanol Production from Corn Stover," *Fuel* 89, no. 1 (2010): pages S20–S28.

Water Related to Biofuels

The *U.S. Billion-Ton Update* by DOE found over 1.3 billion dry tons per year of biomass potential, which is enough to produce biofuels to meet more than one third of the current demand for transportation fuels.[97] In order to achieve this stated amount, the focus of water use and consumption of many of the feedstocks become points for consideration.

The water requirements of corn ethanol vary considerably across the United States. Primarily focusing on the corn crop, the majority of the water resource used for the corn production of ethanol is rain fed. Eighty-five percent of the corn acres are rain fed. The focus on irrigation water use has provided a misconception about the sustainability of the water balance for corn ethanol, especially in a year with a great amount of rainfall. In areas where water demand exceeds that available from soil moisture and precipitation, irrigation must be applied.

Ninety-five percent of ethanol is produced in three regions: Corn Belt Region 3 (OH, IA, MO, IN, and IL), Lake States Region 2 (MN, WI, and MI) and Northern Plains Region 4 (ND, SD, NE, and KS). The precipitation varies greatly for USDA Region 3, Region 2, and Region 4, with average annual precipitation of 37.83, 29.49, and 21.67 inches respectively.[98] See Figure 12-25 for the annual precipitation in 2010.

The total irrigated acreage for corn is 15% using published data from 2007, as shown in Table 12-4

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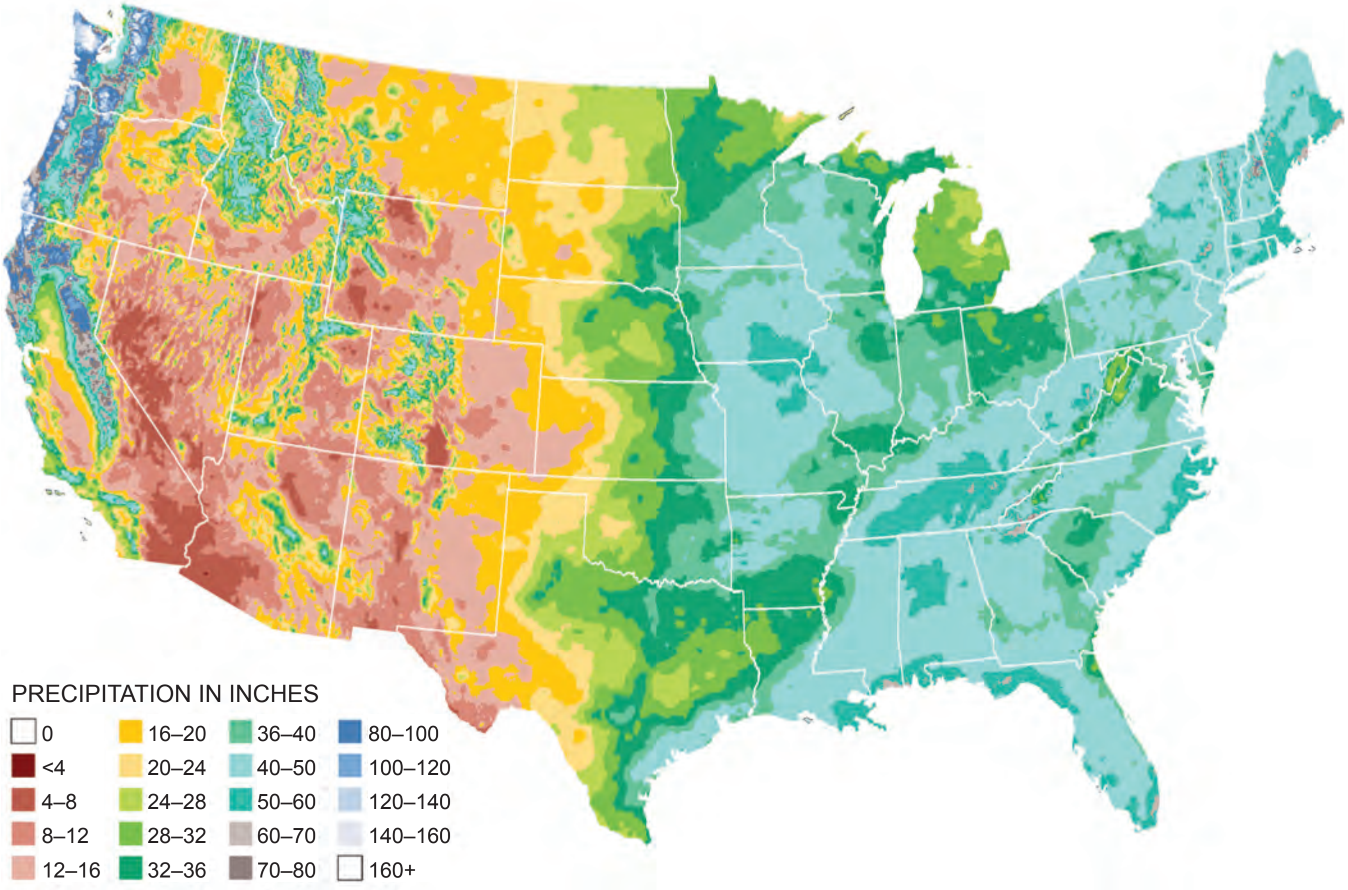
[97] U.S. Department of Energy, *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry,* prepared by Oak Ridge National Laboratory, August 2011.

[98] M. Wu and Y. Chiu, *Consumptive Water Use in the Production of Ethanol and Petroleum Gasoline,* Center for Transportation Research Energy Systems Division, Argonne National Laboratory, January 2011.



Copyright © 2011, PRISM Climate Group, Oregon State University, http://prism.oregonstate.edu. Map created April 8, 2011.

Figure 12-25. *Annual Precipitation for 2010*

Crop	Entire Crop Irrigated			Part of Crop Irrigated			
	Farms	Acres	Ave. Yield per Acre	Farms	Acres Irrigated	Acres Not Irrigated	Ave. Yield per Acre
Corn for grain (bushels)	17,927	6,103,769	180	20,984	7,053,000	6,425,486	150
Corn for silage or greenchop (tons)	8,173	1,369,278	24.8	1,491	128,010	164,203	17

	None of Crop Irrigated			Totals		
	Farms	Acres	Ave. Yield per Acre	Total Acres	Total Irrigated	% Total acres Irrigated
Corn for grain (bushels)	308,849	66,656,287	144.3	86,248,542	13,156,769	15%
Corn for silage or greenchop (tons)	74,653	4,318,170	15.1	5,979,661	1,497,288	25%

Source: U.S. Department of Agriculture, National Agricultural Statistics Services, 2007 Census of Agriculture: United States Summary and State Data, Volume 1, Chapter 1, December 2009.

Table 12-4. *Corn Production on Irrigated and Non-Irrigated Land*

and Figure 12-26. In these regions, most of the water used for irrigation is withdrawn from groundwater aquifers. In the United States, 77% of the irrigation water used for corn is from such aquifers; the remaining 23% comes from surface water.

To understand how water relates to biofuels production, knowledge of the source of the water used to grow the feed crops is necessary throughout the entire process. The feedstock crops have different water requirements as grown in different regions throughout the United States. Importantly, even as yields have increased, the amount of water applied per acre has decreased from 25 inches in the 1970s to 20 inches in the past decade.[99] Further improvements in water use efficiency of crops are envisioned for the future, due to advances in fields such as biotechnology, plant breeding, the increased use of water conserving irrigation practices and permits limiting withdrawals in areas with deficits.

Furthermore, improvements in production efficiency in both crop production as well as ethanol production reduce water usage. Average consumptive water use in ethanol plants has decreased from 5.8 gallons of water per gallon of ethanol to 2.7 gallons of water per gallon of ethanol over a period of a decade.[100,101]

The water requirements for cellulosic biomass, whether rain fed or irrigated, depends largely on the type of feedstock and origin of the feedstock. Other feedstocks within the water use consideration include forest wood, agricultural residues, and a variety of switchgrasses. Typically forest wood doesn't require irrigation. Agricultural residues share the water requirements with crops, which vary from region to region. Switchgrasses are deep rooted and efficient in the use of water and tend to be relatively drought tolerant.

Emerging Biofuels Technologies

New technologies for the production of biofuels from biomass resources are being developed and commercialized. The products range from ethanol to drop-in replacement fuels and utilize a variety

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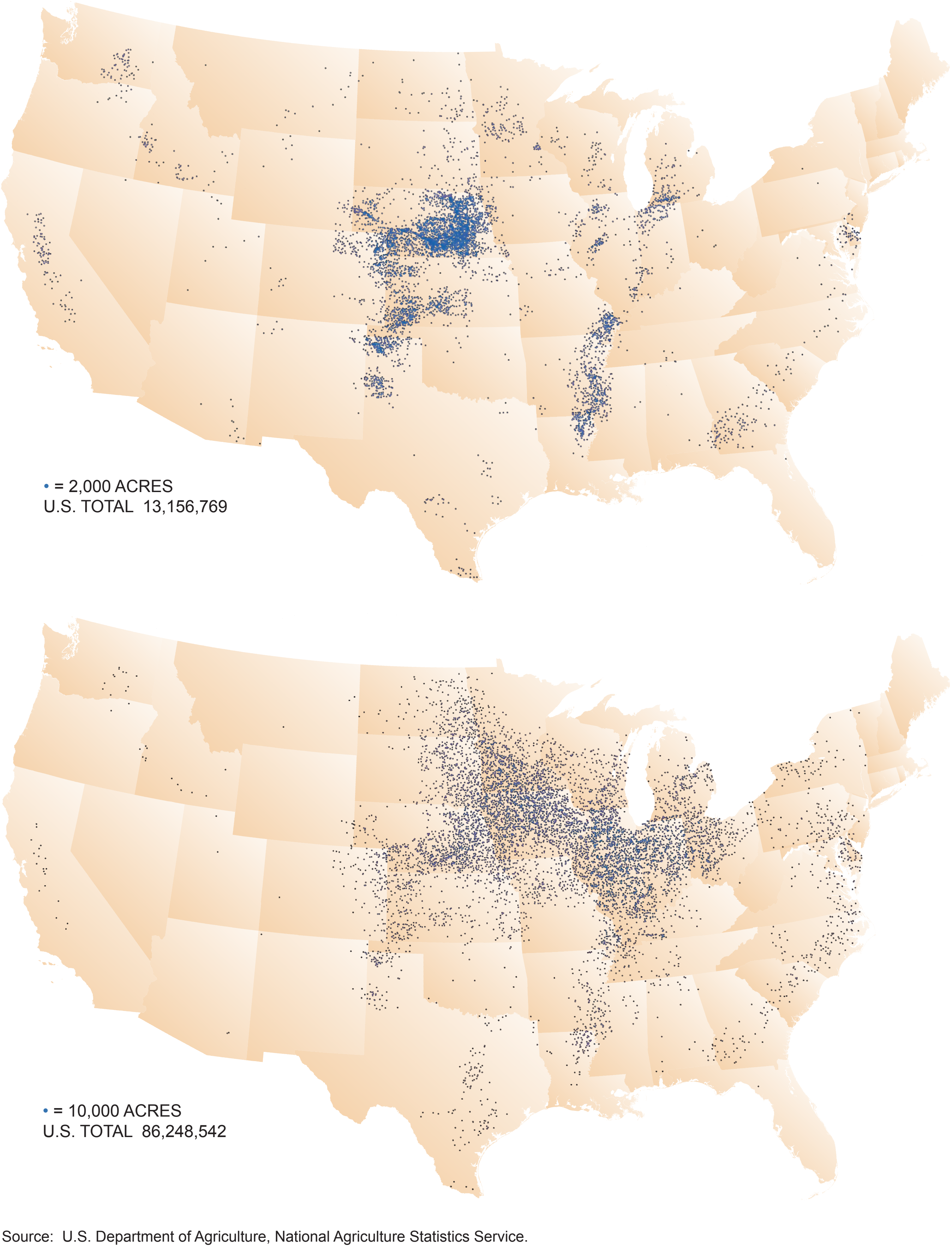
[99] N. Gollehon and V. Breneman, *Resources To Grow Biofuel: An Overview With an Irrigation Perspective,* Presented at the Colloquium on Water Implications of Biofuel Production in the United States, Water, Science & Technology Board, National Academy of Sciences, July 2007.

[100] S. Mueller, "2008 National Dry Mill Corn Ethanol Survey," *Biotechnology Letters* 32, no. 9 (2010): pages 1261-1264.

[101] M. Wu and Y. Chiu, *Consumptive Water Use in the Production of Ethanol and Petroleum Gasoline,* Center for Transportation Research Energy Systems Division, Argonne National Laboratory, January 2011.



Source: U.S. Department of Agriculture, National Agriculture Statistics Service.

Figure 12-26. *Harvested Acres of Irrigated Corn (top) and Total Corn (bottom) in 2007* of technology platforms. The NPC believes in the importance of recognizing these technology platforms, but the likelihood of commercial success or the claimed economics cannot be commented on. Interested readers should consult the industry literature for summaries of technologies at various stages of development and commercialization. A high level overview of the companies that are currently in various stages of development is available from the advanced biofuels database maintained by Biofuels Digest.[102]

Infrastructure Development for Advanced Biofuels

American consumers are provided with gasoline and diesel fuel through an efficient supply chain from the refineries where fuels are produced to local service stations. This supply chain is more fully discussed in Chapter Five, "Infrastructure," and Chapter Eleven, "Hydrocarbon Liquids."

The Distribution System for Biofuels from Biorefineries to Distribution Terminals

Biofuels, ethanol in particular, are usually transported separately from gasoline and diesel fuel and blended together with gasoline or diesel fuel at distribution terminals. The physical characteristics of biofuels play a key role in how they are transported. As an alcohol, ethanol is polar, and therefore miscible with water.[103] This creates challenges for the transportation of ethanol since ethanol will absorb residual water in the distribution system (75 Fed. Reg. 14669, March 26, 2010—hereafter referred to as "RFS2"—at 14757). This is particularly a concern when transporting a blend of ethanol and gasoline because the ethanol can separate from the gasoline and disperse into the water phase resulting in off-specification gasoline and a waste ethanol water mix. For this reason, ethanol is blended into gasoline at the distribution terminal as the fuel enters the tanker truck for delivery to retail.

A similar situation exists with biodiesel, which is an ester. One of the favorable qualities of biodiesel fuel is that it increases fuel lubricity because it clings to metal (the favorable characteristic of lubricating the flow of fuel through the fuel system). However, this trait also causes a tendency for biodiesel to cling to pipeline walls and can be picked up by other following products being transported in a multi-product pipeline. This "trailback" is particularly a concern with regard to jet fuel since product specifications for jet fuel do not allow the presence of any biodiesel (RFS2 at 14757). Because of this, biodiesel is not currently transported in multi-product pipelines that carry jet fuel.

In contrast to ethanol and biodiesel, renewable diesel, which is a non-polar hydrocarbon, can be transported with diesel fuel (RFS2 at 14756). There is, however, a limitation on the transport of renewable diesel via pipeline that was created by the Energy Independence and Security Act (EISA) and the Federal Trade Commission (76 Fed. Reg. 19684, April 8, 2011, at 19687-19689). The law requires labeling of biomass-based diesel, including renewable diesel, above 5% by volume. Because there is no practical way to distinguish renewable diesel from conventional petroleum diesel in the distribution system, renewable diesel is not currently allowed in pipelines above this limit. This places a practical limitation on renewable diesel logistics and usage.

As of 2009, there were 187 operating ethanol and 191 biodiesel production facilities in the United States (RFS2 at 14755).[104] According to the final RFS2 rule, EIA reports that approximately 12 billion gallons of ethanol were produced in the United States in 2011 and approximately 500 million gallons of biodiesel were produced in the United States in 2009 (the last year for which full year data are available) (RFS2 at 14755).

The product flows of biofuels are different from petroleum fuels. For the most part, biofuel refineries are located near their agricultural feedstocks. Given that most biofuel in the United States is currently made from corn or soybeans (i.e., corn-based ethanol and soy-based biodiesel), the predominate flow of biofuels is from Petroleum Administration for Defense District (PADD) 2 in the Midwest outward to the other PADDs. In contrast, the major flow of gasoline and diesel is from PADD 3 outward to other PADDs.

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[102] The Biofuels Digest database can be downloaded from http://www.biofuelsdigest.com/bdigest/2011/11/16/free-database-download-207-advanced-biofuels-chems-projects/.

[103] Solubility of Things (website), "Solubility of Alcohols (eg. ethanol)," 2009, http://www.solubilityofthings.com/water/alcohols.

[104] Renewable Fuels Association (website), www.ethanolrfa.org.

The majority of ethanol is transported via rail (60%), while lesser amounts are transported via truck (30%) and barge (10%).[105] Approximately 1% of ethanol is currently delivered by a pipeline in Florida. The modes of transportation for biofuels are primarily due to the physical characteristics of the biofuels and the fact that the petroleum pipelines generally flow from the Gulf north and east while the biofuels produced in the Midwest need to flow to the coasts in the opposite direction.

A particularly efficient way to transport biofuels by rail is through the use of unit trains (RFS2 at 14757), which enable the shipment of larger volumes and more efficient loading and unloading at terminals. However, not all distribution terminals have the ability to accept unit trains. Only 12 of the 19 ethanol receiving terminals that currently exist or are under construction have the capability to accept unit trains (RFS2 at 14757).[106] As the volumes of biofuels transported by rail increase in response to the RFS2 requirements, industry will be challenged to add unit train capabilities at additional terminals (RFS2 at 14757). This may prove difficult, however, due to proximity of terminals to rail lines, and space limitations at terminals (RFS2 at 14757).

Blending Biofuels at Terminals and Marketing at Retail

Gasoline and diesel are typically transported separately from biofuels from their production facilities to distribution terminals. It is at the distribution terminal that the biofuels are blended with the gasoline or diesel to make the finished blend, which is then transported to retail locations by tanker truck. As a result of the RFS2 program, almost all of the gasoline sold at retail contains 10% by volume ethanol. When biodiesel production reaches 1 billion gallons mandated by RFS2 requirements, biodiesel will make up approximately 2% of the entire diesel fuel pool. Where diesel does contain biodiesel, it typically contains up to 5% by volume. The 5% level represents the level at which biodiesel is compatible with today's engines and vehicles. In practice, this means that some diesel contains biodiesel whereas other diesel does not.

The use of ethanol fuel in the form of E85 is very limited (RFS2 at 14759). The biggest hurdles to the wider use of E85 are economic, not technical (RFS2 at 14759). At present, E85 is only offered at approximately 2,600 (1.5%) of 162,000 retail gasoline stations (RFS2 at 14759). There are several reasons for this.

First, virtually all gasoline stations are independently owned and operated. It is that independent owner/operator—often a small business—that makes the decision whether or not to offer E85 fuel (RFS2 at 14759). Several factors influence that decision. First, less than 4% of the vehicles on the road today are flexible-fuel vehicles (FFVs). However, the number of FFVs should begin to increase rapidly as more FFVs are being produced, in accordance with the commitment of major auto manufacturers to substantially increase their production of FFVs.

Second, the costs of installing E85 storage tanks and dispensers can be substantial. In the final RFS2 rule, the U.S. Environmental Protection Agency (EPA) estimated capital costs of approximately $2,863 million if 19,765 additional stations offered E85 to meet the RFS2 requirements (RFS2 at 14827).

Third, consumers will experience a 25–30% decrease in mileage when using E85 compared to gasoline, due to the lower energy content of ethanol (RFS2 at 14762). This decrease is dependent on the vehicle and the technology used. Some technologies that utilize turbocharging and high-compression engine technology show substantially less mileage degradation. While the mileage is less on E85 than gasoline, ethanol is a very efficient fuel on a BTU basis.

EPA recently announced partial waivers allowing the use of gasoline containing up to 15% ethanol in model year 2001 and newer light- and medium-duty cars and trucks (e.g., passenger cars, pickups, SUVs) (76 Fed. Reg. 4662, 2011). However, no auto manufacturer currently certifies greater than 10% ethanol to be used in its vehicles. At retail locations, the situation with regard to E15 is similar to the situation for E85 in that there are a limited number of vehicles compatible with the fuel, and substantial investments are likely needed for new storage tanks and dispensers for the fuel. The vast majority of storage tanks and dispensers in use today are not

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[105] S. Das, B. Peterson, and S. Chin, "Analysis of Fuel Ethanol Transportation Activity and Potential Distribution Constraints," *Transportation Research Record: Journal of the Transportation Research Board* no. 2168 (2010): pages 136-145.

[106] Ibid.

certified as compatible with E15.[107] As explained by EPA in the final RFS2 rule, various federal, state, and local laws require that storage tanks and dispensers be certified as compatible with the fuel that is stored/dispensed (RFS2 at 14759).

Given the EPA waiver, FFVs remain critical to future ethanol distribution. One concern around the continued rollout of FFVs is the effect of new emissions standards and loss of incentives to the manufactures for the production of FFVs. More stringent air emission standards may make it progressively more difficult to certify FFVs while the loss of incentives may reduce the production of FFVs.

The Capabilities of the Distribution System to Transport 36 Billion Gallons of Biofuels Per Year by 2022 as Required by EISA

As part of its analysis for the RFS2, EPA commissioned a study by the Oak Ridge National Laboratory (ORNL) to analyze fuel ethanol transportation activity and potential distribution constraints associated with implementation of the 36 billion gallon per year renewable fuel requirement of EISA.[108] The objective of the study was to conduct an analysis of ethanol transport by domestic truck, marine, and rail distribution systems from ethanol refineries to blending terminals using ORNL's North American Transportation Infrastructure Network Model.

The ORNL study estimates that the majority of long-distance ethanol movements will continue to be by rail (91% by ton-mile movement). Waterway ton-mile movements are estimated to be only approximately 6.9%. The study further estimated that the national average ethanol distribution cost would be in the range of 6.80–9.63 cents per gallon. Lower distribution costs are expected in the Midwest closer to production facilities, and higher in locales further away from the production locations.

The increase in ethanol demand resulting from the RFS2 program is expected to increase the demand for rail tank cars by up to 41,301. The ORNL study indicates that there continues to be a backlog between new orders for rail tank cars and deliveries, and the availability of rail cars may become an issue under the RFS2 program. It is estimated that 170 barges would be needed to meet the RFS2 demand, which is only about 4% of total barges used in 2007. Finally, it is estimated that about 1,643 more tanker trucks will be on the road distributing ethanol from production facilities to terminals to meet the RFS2 demand. The additional truck demand amounts to less than 0.02% of the total registered trucks in 2005.

Overall, the ORNL study concludes that although distributing the RFS2 volumes would result in a significant increase in the level of ton-mile activity, the increase in rail, barge, and truck traffic is likely to minimally stress the systems to meet the RFS2 ethanol demand. The ORNL study estimates that 17% of rail miles, 2% of highways, and 0.1% of waterway miles would be affected. The percentage increase in ton-mile movements by rail, waterways, and highways are estimated to be 2.8%, 0.6%, and 0.13% respectively, compared to the corresponding 2005 total domestic flows by the various modes.

The Potential for Transporting Biofuels Via Pipeline

The ORNL study discussed above did not consider the possibility of movements of ethanol by pipeline. In response to a requirement under EISA, DOE conducted a study that considered the possibility of a dedicated ethanol pipeline from the Midwest ethanol production center to the Northeastern United States.[109]

The DOE study concluded that based on current consumption projections to meet the RFS2 requirements, "the ethanol volume likely to be transported by a dedicated pipeline from the Midwest to the East Coast was determined to be approximately 2.8 billion gallons per year over the asset's 40-year lifespan…. Based on the assumed ethanol demand volume and a project construction cost of $4.25 billion, the pipeline would need to charge an average tariff of 28 cents per gallon, substantially more than the current average rate for ethanol transport across current modes (rail, barge, and truck) along the same corridor (19 cents per gallon)." Even at a lower pipeline construction cost ($3.75 billion), significant financial incentives would be required

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[107] UL website, 2012.

[108] S. Das, B. Peterson, and S. Chin, "Analysis of Fuel Ethanol Transportation Activity and Potential Distribution Constraints," *Transportation Research Record: Journal of the Transportation Research Board* no. 2168 (2010): pages 136-145.

[109] U.S. Department of Energy, Report to Congress, *Dedicated Ethanol Pipeline Feasibility Study: Energy Independence and Security Act of 2007,* Section 243, March 2010.

to make the pipeline profitable if ethanol blends remain capped at 10% and E85 demand is not significantly expanded.

The study went on to explain that for "the pipeline to be economically viable without major financial incentives, it would need to transport approximately 4.1 billion gallons of ethanol per year—a volume that exceeds projected demand in the target East Coast service area by 1.3 billion gallons per year. This level could be achieved in this region with a significant increase in demand for E85 and/or the widespread use of ethanol blends greater than 10% of an increase in the percent ethanol allowed for blending in motor gasoline is approved by EPA." However, as explained above, there are at present considerable obstacles to the increased use of E85 or E15 when one considers the limited number of compatible vehicles, the significant investments required at the retail levels by small businesses, and consumer demand for the fuel linked to the 25–30% reduction in mileage compared to gasoline.

In addition to the economic challenges for a dedicated ethanol pipeline, there are also technical challenges associated with transporting ethanol by pipeline as explained in the DOE study: "Technical challenges associated with a dedicated ethanol pipeline involve pipeline integrity as well as fuel delivery and consumption issues. Addressing these issues will require continued study of stress corrosion cracking (SCC) to improve pipeline integrity and development of an internal SCC diagnostic tool for pipeline maintenance. The U.S. Department of Transportation is addressing pipeline safety and integrity threats through a comprehensive research program that will drive new knowledge into industry best practices and consensus standards. Compatibility associated with the potential use of the ethanol pipeline for a variety of non-ethanol biofuels including green gasoline and diesel should also be evaluated as a potential source for additional fuel volumes for transport. In an effort to remove technical barriers to increased market demand, existing fleet vehicle studies are examining system compatibility with blends above E10." Despite the challenges associated with transporting ethanol by pipeline, the DOE study concluded that: "the results of this analysis suggest that a profitable dedicated ethanol pipeline is feasible under certain scenarios. A pipeline would enhance the fuels delivery infrastructure and reduce congestion on rail, truck, and barge and would reduce GHG emissions when compared to current delivery methods. The faster product delivery cycles, more reliable delivery schedules, and increased safety will enhance the flexibility to accommodate any significant expansions in ethanol production and demand in the future."

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