

Alternative Fuels from Biomass and Their Impact on Carbon Dioxide Accumulation

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ABSTRACT

A number of transportation fuels can be produced from renewable resources. The major fractions of lignocellulosic biomass, cellulose and hemicellulose, can be broken down into sugars that can be fermented into ethanol. Biomass can also be gasified to a mixture of carbon monoxide and hydrogen for catalytic conversion into methanol. Algae could consume carbon dioxide from power plants and other sources to produce lipid oil that can be converted into a diesel fuel substitute. Through anaerobic digestion, a consortium of bacteria can break down lignocellulosic biomass to generate a medium-energy-content gas that can be cleaned up for pipeline-quality methane. Catalytic processing of pyrolytic oils from biomass produces a mixture of olefins that can be reacted with alcohols to form ethers, such as methyl tertiary butyl ether (MTBE), for use in reformulated gasoline to reduce emissions. Each of these technologies is briefly described. The costs have been reduced significantly for biofuels, and the potential exists for them to be competitive with conventional fuels. An analysis of energy flows is presented for ethanol production as an example of these technologies, and a carbon dioxide balance is provided for the fossil fuels used. This analysis includes consideration of fuel utilization performance and assignment of carbon dioxide to coproducts. Biofuels technologies are shown to require little, if any, fossil fuel inputs. As a result, most or all of the carbon is recycled through their use, reducing substantially the net release of carbon dioxide to the atmosphere.

Index Entries: Carbon dioxide; energy balance; biofuels, biomass; conversion.

INTRODUCTION

The United States contributes about 25% of the carbon dioxide (CO₂) released from fossil fuels to the atmosphere, with transportation fuels accounting for about 27% of that amount (1). Carbon dioxide is believed to be the most important greenhouse gas, trapping nearly 50% of the radiation that could lead to global climate change (2), and significant benefit would be gained from developing fuels that do not contribute to the buildup of CO₂ in the atmosphere.

The US economy depends heavily on unstable sources of imported petroleum. As a result, the nation experienced several oil price shocks as foreign producers controlled supplies of oil in the 1970s. In 1990, the price of oil and gasoline increased again because of the Iraqi invasion of Kuwait, reminding us that oil represents the weakest link in the US energy supply. The United States imports about half of the petroleum it uses annually. Furthermore, petroleum imports are responsible for a large fraction of the trade deficit of the United States, accounting for about 40% in 1990 (3). About 97% of the energy consumed by the transportation sector is derived from petroleum, making this important segment of our economy particularly vulnerable to disruptions in unstable sources of oil.

Fuels known as biofuels can be produced from many plant materials and waste products, such as agricultural wastes and municipal solid waste (MSW), that together are called lignocellulosic biomass. Several oxygenated biofuels, such as ethanol, reduce carbon monoxide emissions when blended with gasoline. A number of biofuels can be substituted directly for conventional transportation fuels to reduce urban air pollution. Biofuels can also be used in the residential, industrial, and utility sectors. Substantial improvements have been made in the technology for producing the liquid and gaseous biofuels that this nation needs most, and these fuels now have the opportunity to make a strong impact on our fuel use and environmental quality.

In evaluating biofuels production as an alternative source of transportation fuels, the overall energy balance has been applied as something of a litmus test to determine the merits of the technology for reducing oil imports. In addition to offering a useful perspective of the merits of the process, energy balance considerations are closely related to a second key issue in evaluating alternative fuels: greenhouse gas emissions. Considerable controversy and confusion exist about the amount of fossil energy required to produce biofuels and the interpretation of this information. It is important to recognize that the use of lignocellulosic biomass for biofuels production strongly influences the fossil energy inputs to the process, and the analyses for other feedstocks do not necessarily apply. Energy inputs must be properly accounted for to arrive at a realistic assessment of the energy used. The type of energy used should be taken into consideration if conclusions are to be reached about the impact on economics

and strategic security: some energy forms, such as coal, are abundant and inexpensive in this country; others, such as petroleum, are largely imported and more expensive. The different fuels used must also be accounted for if the energy requirements are to be used to judge the impact of biofuels use on carbon dioxide release and the possibility of global climate change. Finally, the performance of biofuels must be properly considered if comparisons are to be made to existing options.

This article focuses on the progress of and prospects for biofuels produced by both biological and thermal reactions. First, the possible contribution of biofuels to our energy supply will be presented. Then, selected promising technologies for producing biofuels will be summarized, and some of their important characteristics will be discussed. A comprehensive examination of energy flows and carbon dioxide emissions associated with fuel ethanol production under a variety of scenarios is then presented as an example of biofuels. In this analysis, the fossil fuels used for production of ethanol from lignocellulosic biomass are accounted for and used to determine the implications on carbon dioxide release from the process.

BIOFUELS PRODUCTION TECHNOLOGIES

Biomass Availability and Cost

Plants use the sun's energy to convert CO₂ and water into simple sugars through photosynthesis. These sugars can be stored directly in plants, such as sugar cane, or combined to form starch for plants, such as corn. All plants join sugars together to form the structural carbohydrate polymers cellulose and hemicellulose, which together with lignin support the plant. The cellulose, hemicellulose, and lignin components represent the largest fractions of plant matter, and can be termed lignocellulosic biomass or just biomass. When we burn biomass, the stored energy from the sun is released. Alternatively, the energy content of biomass can also be thermally or biologically transformed to liquid or gaseous fuels that integrate well with our existing fuel distribution and use infrastructure.

Although the outward appearance of the various forms of lignocellulosic biomass, such as wood, grasses, MSW, and agricultural residues, is different, all of these materials are quite similar in composition. Cellulose is generally the dominant fraction, representing about 40–50% of the material by weight, whereas the hemicellulose portion represents about 20–40% of the material. The remaining fraction is predominately lignin with lesser amounts of ash and substances called extractives. The cellulose polymer is composed of glucose sugar, whereas arabinose, mannose, xylose, glucose, and other sugars make up hemicellulose. Although most forms of lignocellulosic biomass are low in cost, the historical costs of conversion to liquid and gaseous biofuels have been too high to allow economic application of these technologies on a large scale.

It is estimated that about 77 million hectares (190 million acres) of land could be used to grow energy crops dedicated for the production of biofuels. For an average productivity of 20 tonnes/ha/yr (9 t/acre/yr), about 1.5 Gtonnes (1.7 billion t) of lignocellulosic biomass could be harvested each year (4). If accessible underutilized wood, agricultural residues, and MSW were included, about 2.3 Gtonnes (2.5 billion dry t) per year of lignocellulosic biomass could be produced at prices from \$20 to \$72/dry tonne (\$18–\$65/dry t) (1,5,6). As a perspective on the size of this resource, about 950 GL (250 billion gallons) of liquid fuels could be produced annually from this quantity of biomass compared to the approx 435 GL (115 billion gallons) of gasoline used in the United States.

Fuel Ethanol from Lignocellulosic Biomass

More than 11 GL (3 billion gallons) of ethanol produced from sugar cane is used in Brazil each year. However, US sugar prices are controlled at about \$0.44/kg (\$0.20/lb), a price that is too high for fuel production. Instead, about 4 GL (1 billion gallons) of ethanol are made from corn in the United States each year. Ethanol from corn currently sells for about \$0.32 to \$0.34/L (\$1.20 to \$1.30/gal), and is competitive because of state and federal tax incentives. Ethanol blends from starch and sugar crops comprised as much as 8% of the US gasoline market in 1987, up from < 1% in 1981. There are about 50 US fuel ethanol manufacturing facilities that use corn and other grains as feedstocks.

Over the years, several processes have been studied for conversion of lignocellulosic biomass to ethanol catalyzed by dilute acid, concentrated acid, or enzymes known as cellulases. In each option, the feedstock is pretreated to reduce its size and open up the structure. Acids or enzymes hydrolyze the cellulose fraction to produce glucose sugar, which is subsequently fermented to ethanol. The soluble xylose sugars derived from hemicellulose are fermented to ethanol as well, whereas the lignin fraction can be burned as fuel to power the rest of the process, converted into octane boosters, or used as a feedstock for production of chemicals.

Dilute acid systems typically have low ethanol yields of 50–70%. Concentrated sulfuric or halogen acid options achieve the high yields required, but the acids must be recovered at a cost substantially lower than the cost at which these inexpensive materials are produced in the first place, a difficult requirement. Enzyme-catalyzed options provide the high yields of ethanol necessary for economic viability, under mild conditions, with low concentrations of enzyme. In addition, enzyme-catalyzed processes have tremendous potential for technology improvements that could bring the selling price of ethanol down to levels competitive with those of existing fuels. Enzymes are also biodegradable and environmentally benign. At this time, the simultaneous saccharification and fermentation (SSF) enzyme-

based process has emerged as a favored route to achieve low-cost fuel ethanol production within a reasonable time frame (7).

In the SSF process, lignocellulosic biomass is first pretreated to open up the biomass structure and facilitate subsequent processing. Several options have been considered for biomass pretreatment, including steam explosion, acid-catalyzed steam explosion, ammonia fiber explosion, and organosolv, and the dilute acid option has good near-term potential. In this process, about 0.5% sulfuric acid is added to the feedstock, and the mixture is heated to around 140–160°C (280–320°F) for 5–20 min. Under these conditions, most of the hemicellulose is broken down to form xylose and other sugars, leaving behind a porous material of primarily cellulose and lignin that is more accessible to enzymatic attack.

Following pretreatment, a portion of the pretreated biomass is used in an enzyme production vessel to support growth of a fungus that produces cellulase enzyme. Then, the cellulase enzyme is added to the bulk of the pretreated substrate along with yeast or other fermentative microorganisms. The enzymes catalyze the breakdown of the cellulose by the so-called hydrolysis reaction to form glucose sugar; the yeast or other suitable microbe ferments the glucose to ethanol. The presence of yeast along with the enzymes minimizes sugar accumulation in the vessel, and since the glucose produced during breakdown of the cellulose slows down the action of the cellulase enzymes, higher rates, yields, and concentrations are possible by consuming the sugar as it is released. Additional benefits are that this process reduces the number of fermentation vessels to about half that for separate hydrolysis and fermentation steps, and that the presence of ethanol makes the fermentation mixture less likely to be invaded by unwanted microorganisms. Finally, the ethanol is separated from the rest of the fermentation broth in a purification step.

The xylose and other sugars released from the hemicellulose polymers are often predominantly five-carbon sugars that are not as readily converted to ethanol as glucose, and until recently, these sugars had to be disposed of. However, several options have been developed for using xylose. At this time, promising options appear to be the use of genetically engineered bacteria (8–11) or some new yeast strains (12,13) for ethanol production.

Because lignin represents a significant fraction of lignocellulosic biomass, it is important to derive value from lignin. Lignin has a high energy content and can be used as a boiler fuel. Generally, the amount of lignin in most feedstocks is more than sufficient to supply all the heat and electricity required for the overall ethanol production process, and to generate excess heat or electricity. Thus, additional revenue can be derived from electricity exports from the plant (14). The electricity sold for current plant designs is equivalent to about 8–10% of the energy content of the ethanol product, and greater revenues are likely as the technology is improved to

require less process heat and electricity. Alternatively, lignin could be converted into chemicals or octane boosters, such as methyl aryl ethers.

Progress on the enzyme-catalyzed processes to convert lignocellulose biomass into fuel ethanol has been substantial over the last 10 yr, with projected selling prices dropping from about \$0.95/L (\$3.60/gal) in 1980 (15) to only about \$0.32/L (\$1.22/gal) (16). This selling price reduction is because of improvements in enzymes to achieve higher rates, yields, and concentrations with lower loadings, proper selection of fermentative microbes, and advances in xylose fermentations through genetic engineering.

Significant opportunities still exist to lower the selling price of ethanol from lignocellulosic biomass at the plant gate to \$0.18/L (\$0.67/gal), a price competitive with gasoline from oil at \$25/barrel. Key target areas include improved glucose and xylose yields from pretreatment, increased ethanol yields to 90% or greater from cellulose and xylose fermentations, decreased stirring and pretreatment power requirements, better productivities through continuous processing, low-cost production of octane enhancers or chemicals from lignin, increased ethanol concentrations, and reduction of fermentation times. Feedstock costs are a significant fraction of the final product selling price, so improvements in feedstock production, collection, and genetics could provide additional cost reductions through economies of scale for larger ethanol plants, decreased feedstock costs, and less non-fermentable feedstock. Many of these goals have been met individually, and the evidence that the rest can be achieved is strong; the primary need is to meet them simultaneously. In addition, multiple additional paths for ethanol production provide other options for lowering the selling price of ethanol.

Biodiesel from Microalgae

Microalgae are single-celled plants that contain photosynthetic machinery driven by the sun's energy to combine CO₂ and water to form a variety of products. Algae are particularly unique in their ability to produce a high fraction of their total weight (about 60% or more) as lipid oils or triglycerides. Lipids are hydrocarbons with a higher energy density than that of the carbohydrates plants typically produce. Although these algal oils can be used directly in diesel engines, they can also be readily converted into esters that more closely match diesel fuel properties and burn more cleanly (17). Diesel fuel currently supplies about 17% of the energy used for transportation in the United States. Production of diesel fuel from algae complements ethanol manufacture from lignocellulosic biomass in that, as ethanol displaces the fraction of petroleum converted into gasoline, substitutes must be found for the fraction now used to manufacture diesel fuel.

Microalgae grow well over a wide range of temperatures in high-salinity water that is unsuitable for other purposes. Therefore, the abundant high-salinity water in aquifers may be used in conjunction with inex-

pensive flat land available in the desert Southwest to grow microalgae to produce biodiesel. Shallow, uncovered ponds or raceways could be created to produce algae with slowly rotating paddle wheels circulating the water and providing mixing. Carbon dioxide from power plant flue gas would be injected into the ponds to promote algal growth. The rapidly growing microalgae would be harvested, and the lipid oils would be extracted for conversion into ester fuels (17).

Microalgal ponds are very efficient in their uptake of CO_2 , recovering about 90% of the gas injected into a pond. Thus, they provide an effective means of CO_2 recovery from power plants. When ester fuels are burned, the CO_2 captured by the algae is released to the atmosphere, but almost twice as much energy is produced for a given amount of CO_2 released as would be possible without the use of algal ponds. As a result, a coal-burning power plant coupled to an algal pond would contribute far less CO_2 to the atmosphere than a conventional gas-fired plant on a total energy released basis (18). Of course, similar benefits could be provided to a gas-fired power plant. If the lipid oils were converted to a chemical for production of durable goods, the carbon could be sequestered for a longer term, further reducing the impact of fossil fuel use on CO_2 accumulation. Use of biodiesel also has a low-sulfur impact on the environment.

Progress on technology for producing oil from microalgae has been considerable. A number of strains have been collected that are tolerant to high salinity, high light intensity, wide temperature variations, and extreme temperatures. Many of these strains grow rapidly and produce about 60% of their weight as lipids when they are deprived of key nutrients, such as silicon for diatoms or nitrogen for green algae (19). The enzyme acetyl Co-A carboxylase (ACC) has been identified as a key catalyst in lipid oil synthesis (19,20), and research is now focused on developing techniques to enhance lipid oil synthesis genetically by controlling the genes responsible for ACC production.

The projected price of biodiesel production from algae has dropped from approx \$4.80/L (\$18/gal) in the early 1980s to around \$0.92/L (\$3.50/gal) now. Opportunities have been identified to reduce the price to about \$0.26/L (\$1.00/gal). The primary need is to enhance the growth rate of algae while achieving high lipid oil concentrations. However, these estimates are based on commercial prices for CO_2 , which represents a major share of the oil production cost. If fines were levied for CO_2 releases from fossil fuels into the atmosphere to reduce CO_2 accumulation, CO_2 prices would drop drastically, and algal oil production could be cost-competitive much sooner.

Biogas

Natural gas, which is primarily methane, is considered an environmentally clean and economically attractive fuel with a high energy content. It is widely used for industrial, residential, and utility applications. It also

has potential merit for transportation markets, but it is nonrenewable. Biogas, a mixture of approximately equal volumes of methane and CO_2 , is a medium-energy-content gas formed by a biological process called anaerobic digestion, in which complex organic compounds are decomposed by microorganisms. Anaerobic digestion has been used in the United States since early in the 20th century to stabilize and reduce the volume of municipal sludge before disposal. In typical installations, the biogas produced in the process was flared rather than recovered as an energy source. Anaerobic digestion is also used to remove soluble wastes from chemical plant effluents. However, although the anaerobic digestion processes now operating are effective in meeting waste disposal requirements, current systems were not designed for cost-competitive energy production and are not well suited to utilization of solid lignocellulosic biomass. In sanitary landfills, naturally occurring anaerobic bacteria break down the biodegradable fraction of the MSW buried there to form biogas, although the gas production rates and yields vary widely. Only a small percentage of that gas is now being economically recovered.

In the anaerobic digestion process, one group of bacteria enzymatically breaks down cellulose and other complex molecules into simple sugars and other monomers. Then, other types of bacteria digest these products, producing organic acids that are in turn broken down to form still smaller molecules of acetate, formate, hydrogen, and CO_2 . Finally, specialized bacteria, called methanogens, use these compounds to produce methane and CO_2 . When CO_2 is removed from biogas, the methane-rich product is a high-energy-content gas that can be directly substituted for natural gas. Thus, this biological pathway directly converts organic matter into a gas that can be used directly in a boiler or processed to be compatible with the existing distribution infrastructure.

If MSW is employed as the substrate, anaerobic digestion also provides an environmentally sound disposal method. In the anaerobic digestion of MSW, the solid waste is shredded, and ferrous materials are removed. Generally, it is also necessary to separate the extrafine and oversized materials for landfill disposal. The mixture is fed into digesters, and the microbial process converts about half the solid waste into biogas. The solids left after digestion is complete are dewatered for disposal. For a tipping fee of \$22/tonne (\$20/t) for the MSW processed, a methane selling price of about \$4.30/GJ (\$4.50/MBtu) is estimated for established technology.

Several improvements have been made in the anaerobic digestion process. Stratified operation of the digester can result in higher solids concentrations and achieve 10% higher methane yield than a conventional vessel. Technology has also been demonstrated to enrich the methane content of the product gas from an anaerobic digester to near pipeline quality by recirculating a leachate stream from the digester through an air-stripping unit or other CO_2 desorption process. Novel anaerobic digestion units have been operated at 35–40% solids concentrations with gas

generation rates of seven to nine times those possible with conventional devices, which are limited to 6–10% solid levels (21). Such devices reduce the volume of the contaminant vessel and thus decrease vessel costs per amount of methane generated.

Continued research could result in further reductions in methane cost to approx \$1.90/GJ (\$2.00/MBtu) (22). Research is needed to identify the organisms present in anaerobic digesters and clarify their complex interactions. Specific organisms can then be selected for genetic breeding and manipulation to allow operation of anaerobic digesters at optimal conditions. Feedback and control mechanisms should be developed to maintain stable operation of digesters (23). Engineering efforts should be undertaken to develop large-scale reactor designs that can process high concentrations of solids to decrease the cost of biogas production. Work is also needed on landfill gas recovery to understand the effect of atmospheric conditions on gas flow, evaluate microbial populations that produce landfill gas, and improve gas generation and capture methods.

Methanol from Biomass

Biomass can be thermally gasified to produce synthesis gas (syngas) rich in carbon monoxide and hydrogen; syngas can then be catalytically converted to methanol. Methanol production includes steps for feed preparation, thermal gasification, methanol synthesis, and gas conditioning and clean-up. Feed preparation typically employs well-developed equipment for biomass drying, size reduction, and feeding. Methanol synthesis from carbon monoxide and hydrogen is a well-established technology. In order to achieve commercial application of methanol production from biomass, low-cost technology is needed for thermally gasifying the biomass to carbon monoxide and hydrogen, and preparing the gas stream for catalytic formation of methanol.

The gasification step can be carried out by controlled direct addition of air or oxygen to the gasifier to produce heat and drive the breakdown of biomass to form carbon monoxide and hydrogen. In such processes, part of the biomass is burned to provide the heat required to drive the formation of the target gases. Alternatively, indirectly heated gasifiers rely on transfer of heat from an external source through a heat-exchange device to break down biomass (24,25). Indirect gasifiers may have some cost advantages relative to units that are directly fed air or oxygen. However, further engineering evaluations and economic studies are needed to establish the relative merits of the alternative processes.

Although the raw syngas is rich in carbon monoxide and hydrogen, it cannot be directly processed in the catalytic synthesis unit because it contains significant amounts of impurities, including particulate matter, methane, tar, and various light hydrocarbons. In addition, the ratio of carbon monoxide to hydrogen must be adjusted to that required for methanol

synthesis. Research has shown that the gas can be cleaned up and the composition adjusted for methanol synthesis. However, further work is required to determine the fate of organic impurities and methane; establish the effect of hydrogen, carbon monoxide, and CO₂ on tar and methane removal; estimate useful catalyst life; and demonstrate the ability of catalysts to destroy tars and reduce methane under realistic operating conditions with various feedstocks.

Currently, methanol is estimated to cost about \$0.22/L (\$0.85/gal) from biomass feedstocks costing about \$46/tonne (\$42/t). Several opportunities have been identified that would make methanol from biomass competitive with gasoline as a neat fuel. Direct syngas conditioning in one step would replace expensive quenching and scrubbing operations to remove tars, and subsequent reheating and steam reforming to reduce excessive levels of methane. We need to develop catalysts that meet lifetime requirements and better gas clean-up systems. Concepts must also be tested at a reasonable scale to establish operational parameters and commercial potential. Improvements in feedstock costs, as discussed for ethanol production, would also benefit methanol economics. Successful demonstration of these improvements could drop the cost of methanol to a price competitive with gasoline from oil at \$25/barrel.

Reformulated Gasoline Components (RGCs)

Concerns about urban air pollution led to enactment of legislation, such as the Clean Air Act Amendments of 1990. Use of neat fuels, such as ethanol and methanol, is one way to reduce emissions of unburned hydrocarbons, which contribute to smog formation, and carbon monoxide. In addition, gasoline compositions are being changed or "reformulated" to reduce their contribution to air pollution. Oxygenates, such as ethanol and ethers, are added to gasoline to improve fuel combustion and reduce the release of smog-forming compounds as well as carbon monoxide. The Clean Air Act Amendments mandate the use of oxygen in fuels for several ozone and carbon monoxide nonattainment regions, thus causing a large demand for oxygenates, such as ethanol and methyl tertiary butyl ether (MTBE). Ethers, such as MTBE and ethyl tertiary butyl ether (ETBE), are made by reacting the appropriate alcohol (i.e., methanol or ethanol, respectively) with isobutylene.

Currently, isobutylene is derived from fossil sources, but this compound and other olefins can also be made by fast pyrolysis of biomass. Fast pyrolysis rapidly heats the biomass to temperatures at which the predominant pyrolysis reactions form oxygenated crude oil vapors, rather than char, water, or gases. A vortex reactor forces biomass particles to slide along the externally heated reactor wall, and the close contact between the particles and the wall produces high rates of heat transfer. As a result, the surface of the biomass particle is pyrolyzed and removed, but the bulk of the particle is still unheated through an ablative pyrolysis phenomenon (26,27).

The oxygenated crude pyrolysis oil vapors produced in the vortex reactor are converted into olefins and other products through a thermal cracking operation. Extensive studies of these reactions have typically shown that some olefins and other hydrocarbons of interest result in yields that are not high enough to be economically interesting. However, zeolite catalysts, such as HZSM-5, used to convert methanol to gasoline, crack the pyrolysis oil vapors with dramatically higher olefins production. Researchers have identified operating conditions with this zeolite catalyst in a slipstream reactor. Low coke yields and relatively high yields of high-octane alkylated aromatics and gaseous olefins were achieved. The olefins in turn can be reacted with alcohols to form RGCs, such as ETBE and MTBE. These products give a very high-octane blending stock for use with reformulated gasoline (27,28).

The offgas from the catalytic cracking reactor contains a considerable amount of gaseous olefins. Catalytic conversion of these olefins to larger hydrocarbon molecules in a secondary catalytic reactor has been studied to facilitate condensation and recovery of these materials. A compressor pressurizes the gases that enter the secondary catalytic reactor. Primarily isoparaffins boiling in the gasoline range have been generated from the gaseous olefins. Changes in the catalysts, coreactants, temperatures, and pressures selected could change the products from the secondary reactor.

Preliminary evaluations of the economics of the combined pyrolysis and catalytic conversion process are encouraging, especially for refuse-derived fuel (RDF), a low-cost feedstock derived from MSW that gives enhanced yields of olefins compared to those from wood. Research on novel catalysts will increase both the olefin yields and the selectivity toward olefins vs aromatics. Initial catalyst screening in the laboratory has already identified some promising candidates, and the results suggest that yields could be improved substantially.

Preliminary process evaluations of the advanced catalytic process suggest that mixed ethers could be produced for \$0.18/L (\$0.67/gal), whereas they would cost about \$0.25/L (\$0.96/gal) based on existing technology (29). However, the vortex reactor represents a new technology that carries a considerable risk because of the lack of current industrial experience. Therefore, further research is required in areas, such as selectivity and catalyst life. In addition, the ability to scale up the fast pyrolysis of biomass to produce condensable pyrolysis vapors must be demonstrated.

IMPACT OF BIOFUELS ON CARBON DIOXIDE ACCUMULATION

In this section, the impact of using biofuels on CO₂ accumulation and the potential for global climate change will be discussed. An example will be presented that is based on ethanol production from lignocellulosic biomass, but the concepts are applicable to any of the biofuels that have been presented here.

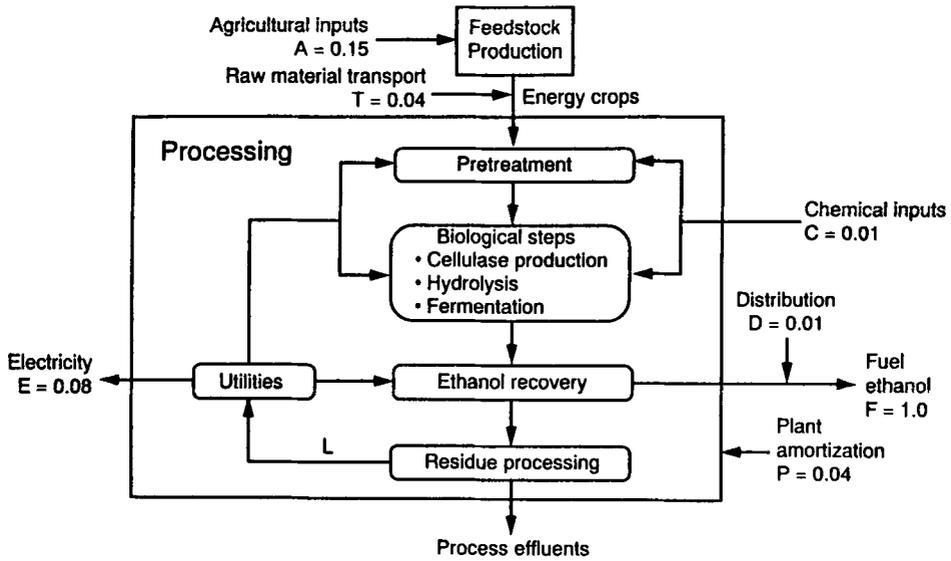


Fig. 1. Energy requirements and outputs for production of ethanol from lignocellulosic biomass based on 1 unit of ethanol energy output.

Carbon dioxide released during fermentation, lignin combustion, and ethanol combustion is recycled back to grow new biomass, provided new trees or other biomass are planted to replace those that are harvested. Thus, CO_2 provides the key link between the fuel and the biomass resource, and CO_2 does not accumulate in the atmosphere. Fossil fuels used in the production and transport of biomass and ethanol are the only sources that can lead to CO_2 accumulation.

Energy Use

Figure 1 summarizes energy flows for the production of ethanol from lignocellulosic biomass (1). Modest energy inputs are required to produce lignocellulosic biomass because cultivation and fertilizer needs are not large. Excess electricity is also generated beyond process requirements (14).

If we add the total amount of fossil energy inputs, about 5.3 MJ/L of ethanol (19,000 BTU/gal) are required for ethanol production from lignocellulosic biomass. Alternatively, three times the electricity exported could be subtracted from the fossil fuel requirements to account for the fossil fuel that would be used in any event for producing that quantity of electricity (1,30). In this case, the net amount of fossil fuel used, as shown in Table 1, is only about 0.22 MJ/L (800 BTU/gal) of ethanol. For comparison, production of gasoline requires about 3.9 MJ/L (14,000 BTU/gal) of gasoline produced. Gasoline has a lower heating value of about 32 MJ/L (115,000 BTU/gal), compared to ethanol at 21 MJ/L (76,000 BTU/gal).

Table 1
Fossil Fuel Use and Carbon Dioxide Released for Ethanol Production from Lignocellulosic Biomass

Process	Feedstock production		Raw material transport	Chemical inputs	Process energy	Plant amortization	Fuel distribution	Total fossil used	Coproduct displacement	Net fossil use
	Natural gas	Petroleum	Petroleum	Natural gas	None	Natural gas	Petroleum			
Assumed fossil fuel Energy used MJ/L ethanol (BTU/gal ethanol)	3.18 (11,400)	0.84 (3000)	0.84 (3000)	0.22 (800)	—	0.84 (3000)	0.22 (800)	5.30 (19,000)	-5.07 (-18,200)	0.22 (800)
Carbon dioxide released kg/L (lb/gal)	0.18 (1.5)	0.06 (0.5)	0.06 (0.5)	0.01 (0.1)	—	0.05 (0.4)	0.01 (0.1)	0.31 (2.6)	-0.55 (-4.6)	-0.24 (-2.0)

Calculated on the basis of the exported electricity displacing coal-generated electricity at 33% efficiency.

Carbon Dioxide Released

An estimate of the contribution of ethanol production to CO₂ accumulation in the atmosphere can be performed by weighing the quantities of fossil fuels used according to the amount of CO₂ released by each. For the purposes of this discussion and with reference to Fig. 1, natural gas is assumed to be the fuel source for agricultural (A), chemical (C), and plant amortization (P) inputs; petroleum is assumed for transportation (T) and distribution (D). Combining CO₂ release data for these sources with the energy requirements presented in Fig. 1 gives the results presented in Table 1 for ethanol derived from lignocellulosic biomass. Only CO₂ that is produced by combustion of fossil fuels is included, because CO₂ generated during fermentation of cellulose and hemicellulose and combustion of lignin and ethanol can be recycled to grow new biomass.

It is interesting to note that if the fossil equivalent for production of electricity is subtracted from the fossil fuel sources for ethanol production from lignocellulosic biomass, a negative CO₂ contribution results (Table 1). This outcome is caused by the low usage of fossil fuels for conversion of lignocellulosic biomass to ethanol and the displacement of electricity produced by coal in the grid. To produce an equivalent amount of electricity from fossil resources would actually produce more CO₂ than the total released during ethanol production, and subtracting the amount of CO₂ that would have been released anyway for generation of that quantity of electricity gives a net credit of 0.24 kg of CO₂/L (2 lb of CO₂/gal) of ethanol produced.

From the data in Table 1, it appears that production of ethanol from lignocellulosic biomass would be a minor contributor of CO₂ to the atmosphere. This is because all of the process heat is produced by combustion of lignin, a renewable feedstock, and few fossil fuel inputs are needed. Biomass sources of fuels and fertilizers could be substituted for the fossil fuels assumed in this analysis, resulting in no net CO₂ release for ethanol from lignocellulosic biomass. By way of comparison, gasoline use releases a total of 82 kg/GJ (190 lb of CO₂/MBTU) or 2.61 kg/L (21.8 lb/gal) of gasoline.

Fuel Utilization

In the United States, ethanol is currently blended with gasoline at 10% concentrations. As mentioned earlier, the energy content of ethanol is 21 MJ/L (76,000 BTU/gal); gasoline contains about 50% more energy at 32 MJ/L (115,000 BTU/gal). By accounting for each of these components, the energy content of the blend is about 31 MJ/L (111,000 BTU/gal). If we assume that the range of a vehicle is proportional to the energy density of the fuel, then 1.036 L of blend would be required to travel the same distance as 1 L of gasoline. On the other hand, data from Southwest Research Institute (31) show that there is no statistically significant difference in the mileage for a 10% blend vs that of regular gasoline. In effect, this evidence

suggests that the ethanol blended with gasoline has an energy density equivalent to 32 MJ/L (115,000 BTU/gal).

Use of neat ethanol can also be considered in at least two different ways. First, the amount of one fuel needed to travel the same distance as another fuel can be determined by the ratio of the lower heating values of the two fuels. Thus, about 50% more ethanol would be required than gasoline to give the same service. For an engine designed for gasoline use with only modifications in timing and air:fuel ratio to allow combustion of ethanol, ethanol fuel would give such a range. However, because ethanol has more favorable fuel properties, such as a higher octane and heat of vaporization than gasoline, an engine optimized for ethanol can be 20–30% more efficient than a gasoline engine (1,6), resulting in an ethanol driving range of about 80% of that of gasoline.

Comparisons of Fossil Fuel Use and Carbon Dioxide Release

Table 2 presents a comparison of the fossil fuel requirements for ethanol from lignocellulosic biomass and gasoline. Consideration is given to both blends and neat fuel use, and to comparison of the amount of ethanol required based on lower heating value and performance. The lower end of the range shown is with credit given for fossil fuel displacement for electricity production, whereas the higher end does not account for excess electricity production. Blends of ethanol from lignocellulosic biomass with gasoline always yield lower fossil fuel use than gasoline. Furthermore, for neat fuel markets, ethanol production from biomass requires one-fifth or less fossil fuel input than gasoline, depending on the accounting given for electricity production and the assumed efficiency of ethanol utilization.

Also presented in Table 2 is the amount of CO₂ released when a vehicle is propelled the same distance by ethanol as gasoline. Again, based on the low use of fossil fuels in production of ethanol from biomass, this fuel scores very well in minimizing CO₂ emissions that could contribute to global climate change. If we subtract the CO₂ emissions that would have resulted from coal to generate the amount of electrical energy produced in the ethanol plant, the net effect is that ethanol removes CO₂. It may be more appropriate to assign the CO₂ released to both electricity and ethanol based on the relative energy contributions and compare each to the alternative, but the benefits would still be substantial.

CONCLUSIONS

A wide range of fuel products that can reduce our vulnerability to disruptions in fuel supplies and improve our balance of trade deficit can be produced from renewable, domestically available resources. These products include the biofuels discussed in this article: ethanol, methanol, methane gas, biodiesel, and olefins for production of RGCs. These biofuels can

Table 2
Fossil Fuel Use and CO₂ Released for Ethanol Production from Lignocellulosic Biomass

Form of fuel use	Fossil fuel used MJ/L of gasoline equivalent (BTU/gal)	CO ₂ Released kg CO ₂ /L of gasoline equivalent (lb CO ₂ /gal)
Blends based on lower heating value	33.56-34.0 (120,400-122,200)	2.41-2.47 (20.1-20.6)
Blends at same range as gasoline	32.39-32.89 (116,200-118,000)	2.32-2.38 (19.4-19.9)
Neat fuel based on lower heating value	0.33-8.00 (1200-28,700)	-0.36-0.38 (-3.0-3.9)
Neat fuel based on improved efficiency	0.28-6.63 (1000-23,800)	-0.30-0.38 (-2.5-3.2)
Gasoline	36.00 (129,000)	2.61 (21.8)

be used in the transportation sector as gasoline additives to reduce emissions of carbon monoxide and smog-forming compounds, and as low-emission substitutes for fossil fuels. Some can also be employed for residential, utility, and industrial applications. Substantial progress has been made in improving the technology for production of biofuels, thereby reducing the price of biofuels production, and goals have been defined to achieve economic competitiveness with existing fuels. Many biofuels are now ready for introduction into our energy sector.

The amount of fossil fuels required to produce biofuels from lignocellulosic biomass is typically quite small. For example, about four times more energy is contained in ethanol fuel than is needed as fossil fuel inputs for the total ethanol production process encompassing all steps from biomass production through fuel distribution. Furthermore, if the export of excess electricity from the process is included, this ratio increases to about 6, if the electricity is considered in terms of its thermal equivalent for export, or to about 100, if credit is taken for displacement of fossil fuels for electricity production. All of these ratios would be even greater if materials derived from renewable resources (e.g., fertilizer derived from methane made via anaerobic digestion of biomass) were substituted for those made from fossil sources.

Accounting for fossil fuel use in biofuels production provides a good indication of the impact of biofuels on carbon dioxide accumulation. However, because fossil fuels differ in the amount of carbon dioxide released per amount of energy delivered, the impact will vary somewhat from a simple examination of energy flows, depending on the mix of fossil fuels used. Furthermore, the manner in which coproducts, such as electricity exports, are accounted for in the carbon dioxide balance impacts the overall outcome. Because low levels of fossil fuels are used for the example of ethanol production from lignocellulosic biomass, the net release of carbon dioxide is much lower than for use of conventional fuels, such as gasoline. If exported electricity is assumed to replace electricity produced by coal-fired systems, ethanol production could be viewed as removing carbon dioxide from the atmosphere. Other approaches could also be employed to assign coproduct impacts, but the overall conclusion remains the same: biofuels, such as ethanol, derived from lignocellulosic biomass contribute substantially less carbon dioxide accumulation to the atmosphere than conventional options. Furthermore, as indicated previously, substitution of renewably derived resources for the fossil fuel inputs assumed in this analysis would reduce the net carbon dioxide impact even further.

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