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Ethanol

Fundamentals of Production from Renewable Feedstocks and Use as a Transportation Fuel

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ABSTRACT

Ethanol can be directly blended with gasoline, reacted with isobutylene to form the oxygenated fuel additive ethyl tert-butyl ether (ETBE), or burned directly as a neat fuel. Blends of either ethanol or ETBE with gasoline force engines set for gasoline to run lean and can substantially reduce carbon monoxide emissions. ETBE also lowers the overall vapor pressure, thereby cutting back on smog-forming emissions. Neat ethanol further reduces smog formation since it has a low volatility, the photochemical reactivity of ethanol and its combustion products is low, and low levels of smog producing compounds are formed by ethanol combustion. Neat ethanol also offers good engine performance owing to its high heat of vaporization, high octane, and low flame temperature.

Fermentation stoichiometry reveals that many feedstocks are expensive for fuels production even considering coproduct credits and ignoring conversion costs, whereas lignocellulosic feedstocks cost much less than their value. Furthermore, the quantities of lignocellulosics are projected to be ample even for neat ethanol production. Release of carbon dioxide during fermentation concentrates almost all the heat of combustion from the solid carbohydrate portion in liquid ethanol. Since the carbon dioxide released during production and use of ethanol is recycled during growth of biomass, ethanol utilization doesn't contribute to the accumulation of carbon dioxide in the atmosphere and possible global warming.

Index Entries: Fuels; emissions; ethanol; feedstocks; greenhouse effect.

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INTRODUCTION

The production of ethanol has received considerable attention over the years as an octane booster, fuel extender, or neat liquid fuel. Renewable feedstocks have been stressed because they provide a domestic, endless supply of raw materials that could be immune to disruption by foreign suppliers and improve international balance of payments. In fact, major production plants operate in both Brazil and the US for manufacturing ethanol from sugar cane and corn, respectively. However, government tax incentives are used to support the ethanol industries in both countries since the selling price of ethanol exceeds its value compared to gasoline. Up to 90% of new cars in Brazil run on neat ethanol, whereas the remainder operate on a 20% ethanol/80% gasoline blend, and Brazil currently produces over 15 billion liters (4.0 billion gallons) of ethanol annually. In the US, about 8.6 million metric tons (340 million bushels) of corn are used each year to produce about 3.2 billion liters (850 million gallons) of anhydrous ethanol for 10% blends with gasoline. This is enough ethanol to blend with 8% of the 424 billion liter (112 billion gallon) US gasoline market.

Although ethanol has been substituted in commercial fuel markets at an increasing rate since the late 1970s, considerable controversy still exists. Some groups are concerned about underwriting its use and the lack of tax revenues. Others maintain that ethanol economics suffer because carbon dioxide is released during fermentation, feedstock costs are too high, or coproduct credits are required to make ethanol production economically viable. Concern is often voiced that ethanol and its derivatives will hurt automobile performance and emissions. Moreover, with the recent attention to possible global warming via accumulation of carbon dioxide in the atmosphere, many people assume that production of ethanol is undesirable since carbon dioxide is released during combustion and fermentation.

These conclusions are based on partial understanding of the overall processing scheme for conversion of renewable feedstocks into ethanol and limited consideration of its potential as a fuel. A careful analysis of the fundamentals of ethanol use as a transportation fuel and processing would clarify the key technical and economic requirements to produce a viable transportation fuel from renewable feedstocks. Thus, the goal of this paper is to show that through application of rather elementary principles and evidence, much of the confusion surrounding ethanol use can be resolved. Furthermore, provided fundamental needs are properly addressed, ethanol production from renewable feedstocks and use in transportation has tremendous potential for providing an environmentally safe fuel at prices competitive with conventional transportation fuels.

ETHANOL AS AN AUTOMOBILE FUEL

Not all ethanols are equal—ethanol can be used as a fuel in at least four different forms: anhydrous ethanol (''neat'' ethanol or ~100% ethanol),

Table 1
Properties of Ethanol, ETBE, Isooctance and Gasoline

Property	Ethanol	ETBE	Isooctane	Unleaded regular gasoline
Formula	C_2H_5OH	$(CH_3)_3COC_2H_5$	C_8H_{18}	C_4–C_{12}
Molecular weight	46.07	102.18	114	–
Specific gravity @ 15°C	0.79	0.75	0.69	0.72–0.78
Air/Fuel stoichiometry (mol)	14.32	42.9	59.68	57.28
Lower heating value (kJ/kg)	26,860	36,280	44,380	41,800–44,000
Energy: kJ/L of standard stoichiometric mixture	3.53	3.61	3.55	
Octane number				
RON	106	118	100	91–93
MON	89	102	100	82–84
(RON+MON)/2	98	110	100	88
Blending RON[a]	118–141	117–120[b]		
Blending MON[a]	86–97	101–104[b]		
(Average blending RON+MON)/2	111	111		
Latent heat of vaporization (kJ/kg @ 15°C)	840	–	328	~335
Boiling temperature, °C	78	70	125	27–225
Reid vapor pressure, kPa				
pure component	16	30		
blending	83–186	21–34		55–103
Water solubility, %				
fuel in water	100	2.0	negligible	negligible
water in fuel	100	0.6	negligible	negligible

[a] 10% blends.
[b] Assumed 12.7% blend.

hydrous ethanol (95% ethanol and 5% water, as used in Brazil), anhydrous ethanol–gasoline blends (10% ethanol/90% gasoline blends used in the US, known as gasohol, and 20% ethanol/80% gasoline blends used in Brazil), and as a component of the newly proposed fuel additive, ethyl tert-butyl ether (ETBE) (*1*). Some of the important properties of anhydrous ethanol, ETBE, isooctane (a model compound for gasoline), and regular unleaded gasoline are presented in Table 1. The differences in some of these properties account for the differences in automobile performance and emissions among these fuels and blends.

Fundamentals

The combustion of ethanol with a stoichiometric amount of air proceeds as follows

$$C_2H_5OH(g) + 3O_2(g) + 3(\tfrac{79}{21})N_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) + 3(\tfrac{79}{21})N_2(g) \quad (1)$$

This combustion reaction is exothermic and liberates 28 MJ/kg (11,990 BTU/1b) of vaporized ethanol or 1.27 GJ/kg mol (548,000 BTU/mol). Thus, the energy released per standard cubic foot is 3.53 kJ/L (94.7 BTU/ft^3). The volumetric values for the stoichiometric vapors of isooctane, hydrous ethanol, 10% anhydrous ethanol–isooctane blends (a model for gasohol), ETBE, and 22% ETBE–isooctane blends are 3.55 kJ/L (95.2 BTU/ft^3), 3.51 kJ/L (94.2 BTU/ft$_3$), 3.56 kJ/L (95.7 BTU/ft^3), 3.61 kg/L (97.0 BTU/ft^3), and 3.58 kg/L (96.0 BTU/ft^3), respectively. Since each of these fuels, as well as most other hydrocarbon fuels, have nearly the same energy of combustion per unit volume of stoichiometric mixture in the vapor state, each fully vaporized fuel will produce nearly identical power when used in the same engine under stoichiometric conditions at the same initial temperature. Thus, the power of an engine cannot be greatly changed by using different fuels for the charge conditions described, whereas the amount of fuel consumed to generate equal power will be approximately in inverse proportion to the lower heating value of the fuel under these conditions.

The latent heat of vaporization will reduce the temperature of the air/fuel mixture and the degree of vaporization of the fuel as it enters the cylinder from these idealized conditions. Fuels with greater latent heats of vaporization, such as ethanol, will have a more significant effect on lowering the charge temperature and increasing the amount of liquid fuel entering the cylinder, which in turn results in better power and fuel economy (2,3). Consequently, these fuels should provide better power than gasoline when such fuels are burned stoichiometrically, and the fuel economy should be better than predicted from the lower heating values.

The octane value of a fuel also affects engine performance. Fuels with higher octane have less tendency to pre-ignite and burn too quickly. As a result, these fuels can be used in engines with higher compression ratios, which provides for better power and fuel economy. The octane index ((RON+MON)/2) for anhydrous ethanol is about 98, which is significantly better than regular gasoline at about 85–87. The research and motor octane ratings of regular gasoline blended with 10 and 25% ethanol are 90 and 94, respectively (4).

Volatility is another fuel parameter that can affect automobile operation. The complex mixture of components in gasoline has a boiling range from 38–200°C (100–400°F). In contrast, ethanol has a single boiling point at 78°C (172°F) and lacks the light ends that are important for cold weather starting of engines. As will be discussed later, this problem can be dealt with in a variety of ways. On the other hand, the volatility of ethanol blends tends to be higher than gasoline; for example, the Reid vapor pressure of 10% ethanol–gasoline blends is 3.4–6.8 kPa (0.5–1.0 psi) greater than gasoline (5).

The interaction of water with fuels must also be considered. In this regard, relatively small additions of water to the blends will cause separation of the ethanol and gasoline. The ability of the blend to carry water without phase separation is increased by temperature and the ethanol content. At 70°F, the water tolerance of 10 and 20% blends is about 0.3

and 0.8%, respectively (*6*). Agents, such as butanol and ETBE, can be added to blends to increase water tolerance (*1,7*).

Finally, in the US, ethanol blends are often used in engines with carburetors set for gasoline. Ethanol has a lower specific gravity but a higher viscosity than gasoline, and tests on 10% ethanol–gasoline blends gave the same air:fuel mass ratios with the same carburetor as gasoline since flow increases with higher specific gravity but decreases with higher viscosity (*8*). Although the air:fuel mass ratios are the same, the energy content per weight of ethanol is less than for gasoline, and the fuel–air mixture for a blend will contain less energy than a gasoline–air mixture when a carburetor set for gasoline is used. The effect is the same as changing the fuel:air ratio in the lean direction, hence the leaning effect of ethanol–gasoline blends when used in engines set for gasoline.

Engine Performance and Operating Considerations

Hydrous Ethanol

In Brazil, up to 90% of all new automobiles have been designed to burn hydrous ethanol since it appears to be a better fuel than anhydrous ethanol, while sparing the expense of removing the final 5% of water. For example, the addition of 10% water to ethanol increases its octane by about 8 units and increases the latent heat of vaporization (*7*). Volkswagen in Brazil has reported that VW engines designed for operation with hydrous ethanol consume about 22% more fuel than comparable VW gasoline engines (*7*). Ford Motor has reported that hydrous ethanol-fueled Escorts equipped with alcohol engines operate at 85 vol% of the fuel economy of gasoline-fueled Escorts (*7*). Thus, engines designed for ethanol are thermodynamically more efficient (more distance per energy content of fuel) than engines designed to run on gasoline, and 1.19 L ethanol will power a vehicle the same distance as 1.0 L of Brazilian gasoline, much better than would be predicted from heating values (1.5 L ethanol to 1.0 L gasoline). For US gasoline, a ratio of 1.25:1.0 may be more appropriate. This excellent performance of automobiles designed to use hydrous ethanol is undoubtedly a result of the higher latent heat of vaporization and octane number of ethanol compared to gasoline.

The cold weather starting problem noted earlier can be solved by several techniques, including the addition of more volatile fuels to ethanol, use of an auxiliary starting system that operates on another fuel such as gasoline, use of a small electric heater to warm a small amount of fuel, and use of a small catalytic alcohol reformer to produce enough hydrogen to start the engine (*7*). Hydrous ethanol does not present a phase separation problem since water is essentially fully soluble in ethanol.

Hydrous ethanol-fueled cars require special materials of construction in certain areas of the fuel system because of potential corrosion problems. However, none of the material problems encountered with hydrous ethanol fuels are insurmountable (*7*).

Anhydrous Ethanol–Gasoline Blends

In many late model cars, the fuel:air ratio is automatically controlled by an oxygen sensor in the exhaust, together with an adaptive learning device such that the equivalence ratio (equivalence ratio is the actual fuel:air ratio divided by the stoichiometric fuel:air ratio) can be maintained at 1.0 no matter what fuel is used. Since the energy density of a 10% ethanol-gasoline blend and gasoline are essentially the same at the stoichoimetric fuel:air ratio, one would expect the power output and fuel economy to be the same with either gasoline or 10% ethanol blends. For cars set for gasoline use, 10% ethanol blends have a leaning effect and may result in somewhat less power and fuel economy. On the other hand, if the gasoline carburetor is set too rich, the leaning effect may improve power output and fuel economy slightly.

Owing to the higher vapor pressure of ethanol blends, vapor lock and difficult starting may be a problem at high temperatures; however, the results of fleet tests vary widely (*7*). Water contamination can lead to phase separation of ethanol–gasoline blends, which could cause operating and corrosion problems. Yet, the fact that large quantities of ethanol–gasoline fuels are used in the US, Brazil, and Europe without difficulty indicates that the problems are not insolvable. Finally, the fuel systems of newer vehicles are fully compatible with 10% ethanol blends (*7*).

ETBE

ETBE is a relatively new high octane, oxygenated fuel additive made by reacting ethanol with isobutylene. Preliminary tests indicate that it is every bit as good as, and possibly better than, the widely used additive, MTBE (methyl tert-butyl ether), formed by reacting methanol and isobutylene. Although the EPA currently allows 12.7% ETBE blends (*1*), if ETBE were blended at 22%, each gallon of fuel would use the same amount of ethanol as a 10% direct ethanol blend.

The properties of ETBE are close to those of gasoline. For example, the air–fuel stoichiometry, heating values, latent heat of vaporization, and solubility characteristics are similar to gasoline. Since the blending octane number of ETBE is much higher than for gasoline, and about the same as for pure ethanol, automobile performance should be enhanced for ETBE blends, and there should be no operational problems. Because of ETBE's low latent heat of vaporization, one would not anticipate cold start problems. The low blending Reid vapor pressure of ETBE lowers engine vapor lock and allows the addition of more low-cost butanes.

Emissions

Carbon monoxide (CO) emissions result from incomplete combustion of carbon-containing fuels and is regulated for health-related concerns.

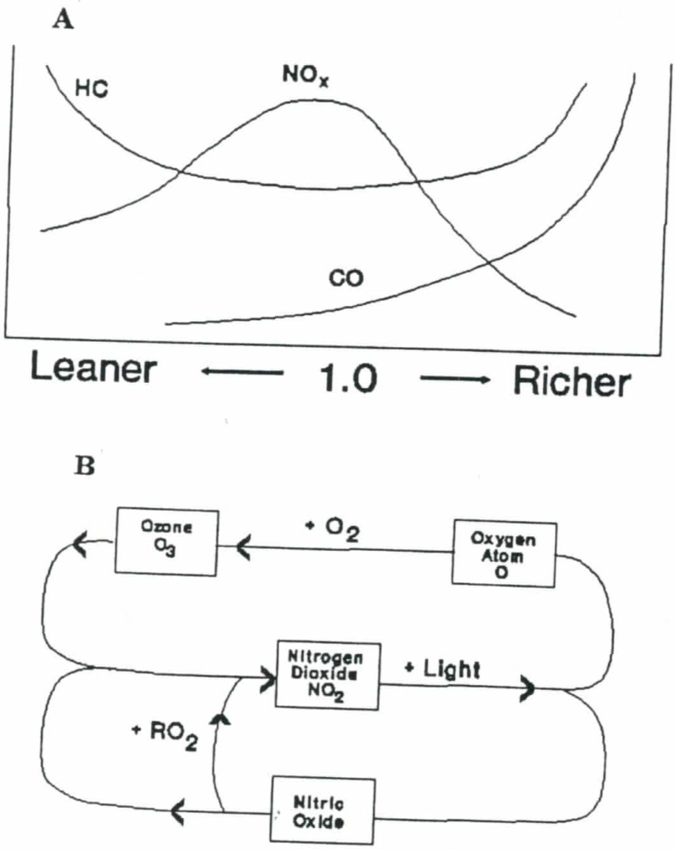

Fig. 1. **(A)** Emissions as a function of equivalence ratio (equivalence ratio is the fuel:air ratio divided by the stoichiometric fuel:air ratio). **(B)** In the absence of hydrocarbons, only a small steady state level of ozone results from the NO–NO_2–O_3 cycle. When hydrocarbons or other reactive contaminants are present, they can form peroxy radicals (RO_2) that oxidize NO, leaving little NO to react with ozone. Thus, ozone levels increase.

Transportation sources account for over two-thirds of US CO emissions, and automobiles account for two-thirds to three-fourths of all vehicle emissions (*5*). Nearly complete combustion takes place at equivalence ratios equal to or somewhat less than 1.0 (Fig. 1A), and under these conditions, no fuel is inherently better than another regarding carbon monoxide emissions. However, older gasoline engines often burn rich and produce excessive CO. The problem is compounded at higher altitudes, where the air density is less than at sea level.

Nitrogen oxides, unburned fuel, and derivatives from vehicle exhaust are involved in the production of tropospheric ozone (ozone closest to the earth), which is the primary component of "smog." Smog has been shown to impair respiratory function and damage vegetation (*5*). Ozone builds up when volatile organic compounds (VOC) and nitrogen oxide react

(Fig. 1B). Transportation sources account for 30–50% of VOC emissions (5), which are difficult to control owing to the number and complexity of sources. VOC are emitted from the tailpipe, through evaporative loss in the fuel system, and as evaporative loss during refueling.

Aldehydes result from partial combustion of ethanol. At low concentrations, aldehydes can cause eye irritation and skin rashes. However, even under conditions of 100% fleet penetration in the US with 10% ethanol/90% gasoline blends, the amounts of aldehydes emitted are considered to be too low to pose a health risk. Catalytic converters could effectively control aldehyde emissions (5). Aldehydes are also formed by photochemical breakdown of hydrocarbons from gasoline-powered vehicles in the atmosphere.

Anhydrous and Hydrous Ethanol

Since the volatility of a fuel is one of the primary factors affecting VOC emissions, anhydrous or hydrous ethanol with low vapor pressures should result in lower concentrations of organic compounds in the air compared to gasoline. In addition, the photochemical reactivity of ethanol is much less than for hydrocarbons. Unlike the relatively high emissions of several types of hydrocarbons that are very reactive in producing ozone, anhydrous and hydrous ethanol combustion produces very low levels of smog-producing compounds (9). Neat ethanol engines are also effective in reducing NO_x emissions, because ethanol burns at a lower temperature than gasoline and NO_x formation decreases as temperature decreases (7). Thus, lower fuel evaporative emissions, photochemical reactivity of ethanol, tailpipe hydrocarbon emissions of reactive hydrocarbons, and NO_x should result in reduced ozone levels for anhydrous and hydrous ethanol fuels.

10% Anhydrous Ethanol–Gasoline Blends

The leaning effect of ethanol blends on engines adjusted for gasoline reduces carbon monoxide. Although the effect depends on the emission control technology (catalytic converter, closed loop, closed loop with adaptive learning, and so on), an EPA study indicates that carbon monoxide emissions are reduced 10–30% for automobiles not equipped with the latest adaptive learning technology (5).

Because blending 10% anhydrous ethanol with 90% gasoline increases the fuel Reid vapor pressure by 3.5–6.8 kPa (0.5–1.0 psi) (5), ethanol-blended fuels have higher evaporative fuel emissions if the volatility of the blending gasoline is not adjusted to a lower value. However, if the gasoline volatility is reduced so that the volatility of the blend is the same as straight gasoline, no increase in VOC would result from blending. Since NO_x emissions peak at equivalence ratios slightly less than 1.0 (Fig. 1B), the leaning effect of ethanol–gasoline blends can either yield higher or lower NO_x emissions than gasoline (7). Ozone is usually not a problem during the winter months, and the use of ethanol blends only during the winter months for carbon monoxide reduction should not impact ozone levels.

As with gasohol, the addition of ETBE to gasoline causes an engine without the latest adaptive learning closed loop technology to run lean, and CO emissions would be expected to be reduced (*8*). The recently completed 1988–89 Colorado Oxygenated Fuel Program dramatically reduced ambient CO concentrations in Denver, CO by mandating the use of oxygenated additives in gasoline. During the program, 90–95% of the fuel sold contained 11% MTBE, and it can be assumed that ETBE would behave similarly. Because ETBE lowers the Reid Vapor Pressure of gasoline significantly, use of ETBE–gasoline blends should lower VOC along with ozone that results from the interaction of hydrocarbons and nitrogen oxide.

THE VALUE OF ETHANOL

The value of ethanol depends on the end use: anhydrous ethanol, hydrous ethanol, anhydrous ethanol–gasoline blends, or a component of ETBE. Based on a lower heating value of 32 MJ/L (115,000 BTU/gal) for gasoline, and a corresponding value of about 21 MJ/L (76,000 BTU/gal) for hydrous ethanol, the value of hydrous ethanol would be ⅔ of gasoline. However, as noted above, the thermodynamic efficiency of hydrous ethanol in automobiles designed to run on this fuel is higher than the lower heating value would predict, and 1.25 L ethanol is equivalent to 1.0 L gasoline on a distance basis (*10*). Thus, the ratio of hydrous ethanol selling price per liter to gasoline selling price per liter should be 0.80 on the open market.

The 10% anhydrous ethanol–gasoline blends currently sold in the US offer higher octane than the blending gasoline, as well as carbon monoxide reduction in older cars. However, because of perceived problems associated with potential phase separation, Reid vapor pressure elevation, and negative publicity, the value of anhydrous ethanol as a blending agent has been determined only by its utility as a fuel extender. Thus, anhydrous ethanol as a blending agent has an open market value determined by its energy content. As a result, the ratio of the value per volume of ethanol to that for gasoline is about 0.67 for 10% ethanol–gasoline blends.

ETBE appears to have fuel additive properties that are better than MTBE (methyl tert-butyl ether). Since the processes for making ETBE and MTBE are essentially the same, the value of ethanol in ETBE is determined by the price of methanol, with adjustments for property differences of ETBE relative to MTBE. Historically, the value of methanol on a volumetric basis has been about 70% of the value of gasoline. However, since the markets for methanol are rapidly changing, it is difficult to predict whether this relationship will hold in the future.

RENEWABLE FEEDSTOCKS

Several carbohydrate containing feedstocks could be used as substrates for biological production of ethanol including sugar crops, starch crops, and lignocellulosic materials. In the US, about 6.2 million metric tons (6.9 million tons) of sugar are produced annually, with prices controlled at about \$0.40/kg (\$0.18/lb). Corn, a starch crop, sells for only \$0.066–0.132/kg (\$1.50–3.00/bushel or \$0.03–0.06/lb), and in recent times, production has varied between a high of 226 million metric tons (8.9 billion bushels) in 1985 to a low of 119 million metric tons (4.7 billion bushels) in 1988, owing to drought. Current consumption including exports is about 178 million metric tons (7 billion bushels) per year.

Lignocellulosic materials are comprised of carbohydrate polymers known as cellulose and hemicellulose plus lignin and smaller amounts of other materials. Agricultural residues, municipal solid waste, and underutilized standing forests are examples of this largely untapped source of renewable feedstocks. Since the major fuel use of lignocellulosic biomass is currently limited to burning of forestry residues for some process heat, significant disagreement exists over the availability and cost of these materials, and the estimates of the resource vary widely. For the US, Lynd (*10*) has compiled a range of estimates of the amount of collectible underutilized wood, a term used to describe traditional, naturally standing forest resources that are in excess of that required by the forest products industry, that varies from 91 to 253 million dry metric tons/yr for wastes and 182 to 909 million dry metric tons/yr of collectible excess production at a price of \$20–36/dry ton (*19*). The range of availability estimates is shown in Table 2. Collectible amounts of agricultural residues in the US, also compiled by Lynd (*10*), range from 75 to 364 million dry metric tons/yr at a price of \$24–49/dry ton (*19*), with the availability estimates presented in Table 3.

The impact of short rotation forestry, in which hardwood plantations are intensively managed to provide high yields per acre over short harvest times, is more difficult to quantify because it is an unproven technology, but it has been estimated that 765 million dry metric tons could be produced in the US each year at a cost of \$34–68/dry ton (*19*). Herbaceous energy crops, terrestrial nonwoody plants grown for their energy content, would probably compete with short rotation crops for land use, thus restricting the total US availability of the two to 765 million dry metric tons/yr, but at a cost of \$27–45/dry ton. The domestic availability of municipal solid waste (MSW), the trash generated by residential, commercial, industrial, and institutional sectors, is estimated to be about 90 million dry metric tons/yr, assuming that only large municipalities with more than 500,000 people are attractive for siting of a capital intensive bioprocessing facility; the estimated cost of MSW ranges from \$24 to a credit of \$14 in tipping fees after paying for processing of the raw feedstock.

In sum, the total amount of underutilized wood, agricultural residues, short rotation energy crops, and MSW is estimated to provide 1200–2380

Table 2
Growth and Production of Underutilized Traditional Wood Resources in the US (millions metric dry tons/year)[a]

Study	Wastes		Excess Production	
	Total	Collectible	Total	Collectible
Young et al. (*11*)		91		
Jeffries (*12*)	348	159	379	182
Ng et al. (*13*)	209	155	409	245
Ferchak and Pye (*14*)		253	2727	909
OTA (*15*)	76		616–1639	280–560
Humphrey et al. (*16*)	55			
Average	172	164	1160	439

[a] Based on Lynd (*10*).

Table 3
Estimates of Agricultural Residue Availability[a]
(millions metric dry tons/yr)

Study	Total	Collectable
Young et al. (*11*)		364
Jeffries (*12*)	350	
Ng et al. (*13*)	736	289
Ferchak and Pye (*14*)	382	253
Goldstein (*17*)	323	
OTA (*15*)	381	75
Vergara and Pimentel (*18*)	430	
Humphrey et al. (*16*)	364	
Average	424	245

[a] Based on Lynd (*10*).

million dry metric tons of lignocellulose/yr in the US at prices from \$20–70/dry ton. This is enough feedstock to generate 490–1000 billion L (130–270 billion gal) of ethanol. Even though these values are subject to significant uncertainty, they indicate that the resource base of renewable feedstocks is substantial.

Stoichiometry and Feedstock Choice

A critical consideration in the choice of renewable feedstocks for ethanol production is the stoichiometry of the reactions. The fermentation of glucose to ethanol proceeds as follows

$$C_6H_{12}O_6 \rightarrow 2\,CO_2 + 2\,C_2H_5OH \qquad (2)$$

Thus, at best, 92 weight units of ethanol are produced for every 180 weight units of glucose consumed, neglecting the need of the fermenting microorganism for 4–10% of the sugar for growth and maintenance. This corresponds to an absolute maximum yield of 51.1%. For utilization of cellulose or starch, the glucose is first obtained by the following hydrolysis reaction

$$\mathrm{n\,C_6H_{10}O_5 + H_2O \rightarrow n\,C_6H_{12}O_6} \quad (3)$$

in which *n* represents the number of anhydrous glucose molecules in the cellulose or starch chain. Thus, 162 weight units of starch or cellulose produce 180 weight units of glucose, a yield of 111.1%. Overall, the conversion of cellulose or starch into ethanol is represented by the sum of reactions 2 and 3, whereas the maximum absolute yield of ethanol from cellulose or starch is the product of the two yields, or 56.8%.

For lignocellulosic biomass, we must also consider the hemicellulose fraction. For hardwoods and other biomass predominantly containing the five carbon sugar xylose in the hemicellulose, the hydrolysis reaction proceeds as

$$\mathrm{n\,C_5H_8O_4 + n\,H_2O \rightarrow n\,C_5H_{10}O_5} \quad (4)$$

whereas the xylose produced is fermented to ethanol with the stoichiometry

$$\mathrm{3C_5H_{10}O_5 \rightarrow 5CO_2 + 5C_2H_5OH} \quad (5)$$

For reaction 4, the absolute maximum yield is 113.6%, whereas for reaction 5, the absolute maximum yield is 51.1%, the same as glucose fermentation. Thus, the overall absolute maximum yield of ethanol from hemicellulose is 58.1% from the coupled hydrolysis and fermentation reactions.

If we simply use the stoichiometry of the reactions, we can determine the maximum price that we are willing to pay for the feedstock, based on the value of the ethanol product. Although this approach neglects the price of conversion, it quickly screens out feedstock choices that are not promising. For a gasoline price of $0.20/L ($0.75/gal) (current price as of April 24, 1989) at the refinery gate, ethanol is worth about $0.14–0.16/L ($0.53–0.60/gal), depending on the end-use for ethanol. Thus, the maximum price that we could afford to pay for glucose is about $90–102/metric ton ($82–93/ton), whereas cellulose or starch is worth $100–114/metric ton ($91–103/ton) and hemicellulose is valued at about $103–116/metric ton ($93–106/ton), neglecting conversion costs. Clearly, the controlled price of sugar in the US at $396/metric ton ($360/ton) exceeds what we would be willing to pay to produce ethanol. Additionally, molasses at a price or $66–110/metric ton ($60–100/ton) for 50% sugars is not a viable feedstock either.

Many of the renewable feedstocks, such as corn and lignocellulosic biomass, are not composed of merely one component, but are a complex mixture of various types of carbohydrates, lignin, oils, and proteins. For such cases, the following equation relates the maximum one would be willing to pay for the feedstock to the value of ethanol neglecting other costs:

$$C_s = (S_E + \Sigma P_j\, z_j)(\Sigma \alpha_i\, x_j\, y_i) \tag{6}$$

where C_s is the maximum feedstock cost in dollars/weight, S_E is the value of ethanol in dollars/weight, P_j is the selling price of any coproducts j produced in the overall process, z_j is the yield of coproducts in weight of coproducts/weight of ethanol, α_i is the fractional yield of ethanol compared to the theoretical maximum, x_i is the fraction of component i (e.g., cellulose) in the feedstock, y_i is the absolute maximum theoretical yield of ethanol from component i, the first summation is taken over each coproduct j, and the second summation is for each component i that is fermentable to ethanol.

Several important conclusions can be reached based on Eq. (6). First, we want to maximize each of the products of $a_i y_i$, the yields of ethanol from the various components of biomass. Second, for a given ethanol value, the price we are willing to pay for the feedstock will increase as the fraction of convertible substrate x_i increases. Finally, the higher the selling price and yield of coproducts, the more that we can afford to pay for the feedstock at a given selling price for ethanol. However, this last conclusion concerning coproducts must be taken with some caution. First, coproducts are derived from the feedstock, and although coproducts from nonfermentable, noncarbohydrate fractions of the feedstock may benefit the economics of ethanol production, use of the fermentable fraction for coproducts decreases ethanol yields and revenues. Thus, the coproducts must be more valuable than ethanol, compared to the conversion costs. In addition, if ethanol is produced in large quantities that meet a substantial portion of the fuel market, it will be difficult to find compatible high volume coproducts with high values since price and volume generally are inversely related. Thus, even though effective short-term strategies may be developed based on high value coproducts, ultimately, fuel coproducts will be needed to support a large ethanol industry.

Corn is composed of about 72% starch, 10% protein, 5% oil, 6% hemicellulose, 3% cellulose, 2% sugars, 1.4% ash, and less than 1% lignin. In corn wet milling, the following products result: 67% starch, 4% oil, 4% germ meal, 11.5% fiber, 5.5% gluten, and 8% steepwater. If the starch is converted to ethanol, 9.5 L (2.5 gal) of ethanol result, plus 6.8 kg (15 lbs) of carbon dioxide per bushel of corn. The germ meal, fiber, and steepwater are normally combined to produce 6.64 kg (14.6 lbs) of corn gluten feed, which is sold at about \$0.13/kg (\$0.06/lb), whereas 0.73 kg (1.6 lbs) of crude oil is sold at \$0.46/kg (\$0.21/lb) and 1.4 kg (3.2 lbs) of corn gluten meal at \$0.31/kg (\$0.14/lb) (all prices April 24, 1989). Thus, for an ethanol selling price of \$0.14–0.16/L (\$0.53–0.60/gal), the most we would be willing to pay for corn is \$117–124/metric ton (\$107–113/ton), while it now sells at about \$98/metric ton (\$89/ton). For whole grain processing of corn to ethanol, about 9.8 L (2.6 gal) of ethanol result per bushel of corn, along with 7.7 kg (17 lbs) of distillers dried grains and solubles (DDGS) valued at \$0.17/kg (\$0.08/lb) and 7.3 kg (16 lbs) of carbon dioxide. Assuming the carbon dioxide has no value (which is often not the case), the corn is worth \$108–115/metric ton (\$98–104/ton).

Thus, corn is far more favorable for ethanol production in the US than sugar. However, the net price of corn is near the high end of its value as a feedstock for production of ethanol that is competitive for fuel use at the plant gate, and higher prices are currently charged for ethanol from corn to cover operating and capital recovery charges. Furthermore, although the protein markets are very large, the high coproduct credits for corn oil, corn gluten feed, and corn gluten meal would not likely be sustained for production of the quantities of ethanol required to make a major penetration into the neat fuel markets, and the value of the feedstock would drop below historical corn price patterns as such credits dropped or disappeared. Although corn could be a significant source of ethanol in the near term, these factors, along with the limited availability of acceptable land, would eventually hinder growth in ethanol production from corn.

For lignocellulosic biomass, the feedstock is primarily made up of the following components, neglecting the generally small amount of extractives and ash: 50% cellulose, 28% hemicellulose, and 22% lignin. If we assume that lignin is burned to provide heat to run the rest of the process, while all the carbohydrate fractions are converted into ethanol with 90% yield, then 0.55 weight units of lignin will be produced per unit of ethanol, with a coproduct value of about \$44/metric ton (\$40/ton) as boiler fuel. Applying Eq. (6) to this case, we find that we could pay \$81–90/metric ton (\$73–82/ton) for the lignocellulosic feedstock and still break even, ignoring conversion costs. On the other hand, if the lignin is transformed into an octane enhancer with a higher value than boiler fuel, the feedstock is worth even more. In any event, the cost of lignocellulosic biomass is clearly far less than what it is worth to make ethanol that is competitive for fuel use on this basis, even for low priced lignin coproducts that are compatible in sales volume with fuel ethanol. Thus, lignocellulosic biomass appears to be a more favorable feedstock for fuel ethanol production than either sugar or starch crops.

Energetics

Based on the stoichiometry of Eqs. (2) and (3), it is tempting to conclude that production of ethanol from biomass is inefficient since almost half the sugar weight is lost as carbon dioxide. However, for use as a transportation fuel, the value of ethanol is set on the basis of its energy utility, and we should be more concerned with how much of the substrate fuel value ends up in the ethanol. The following equation can be used to calculate the standard heats of reaction from heats of combustion:

$$\Delta H^{o}_{rxn} = \Delta H^{o}_{C\ reactants} - \Delta H^{o}_{C\ products} \tag{8}$$

Now, since the standard heats of combustion of gaseous carbon dioxide and liquid water are assigned zero values, the only difference between the heat of combustion of the sugars and ethanol in Eqs. (2) and (5) is the heat of fermentation. Similarly, the only difference between the heat of combustion of cellulose and glucose, starch and glucose, or hemicellulose and xylose in hydrolysis relationships (3) and (4) is the heat of reaction. Since we would expect the heats of reaction to be small in all cases, it is likely that most of the energy of the carbohydrate source will be preserved in the ethanol product.

The heats of combustion of cellulose, glucose, and ethanol are −2.84, −2.82, and −1.37 GJ/kg mol, respectively, at 20°C, and when these are adjusted according to the appropriate stoichiometric coefficients in Eqs. (2) and (3), we see that 99.3% of the heat of combustion of cellulose is preserved in glucose, 97.4% of the heat of combustion of glucose is maintained in ethanol, and 96.6% of the heat of combustion of cellulose is carried over into ethanol. Alternatively, the energy storage density of cellulose, glucose, and ethanol are 17.5 MJ/kg (7530 BTU/lb), 15.9 MJ/kg (6730 BTU/lb), and 29.8 MJ/kg (12,800 BTU/lb), respectively, indicating that by releasing carbon dioxide that has no calorific value, the fermentation process really serves to increase the energy storage density of biomass—an important benefit. Thus, although the laws of thermodynamics that "you never get what you pay for" are proven once again, ethanol comes remarkably close to breaking even on an energy basis, and the energy storage density of biomass is improved substantially.

THE GREENHOUSE EFFECT AND ETHANOL FROM BIOMASS

The threat of global warming is a major concern, with consequences projected to include transformation of huge areas of our country from heavily forested woodlands (the Southeast) into deserts and movement of the corn belt from the Midwest to Canada over the next 40–50 years. The possibility of global warming is attributed to a variety of current practices that include burning of fossil fuels, uses of chlorofluorocarbons, deforestation, and decay of vegetation. However, the biggest single concern remains the release of carbon dioxide from combustion of fossil fuels in boilers, furnaces, and automobile engines, with coal burning making the largest contribution of carbon dioxide per amount of energy released, followed by petroleum and natural gas. Over 1.2 billion metric tons of carbon are released annually in the US alone from burning of fossil fuels. Over the last 30 years, carbon dioxide concentrations have increased more than 10% to over 350 ppm, and carbon dioxide concentrations in the atmosphere continue to rise by over 1.5 ppm each year.

There is significant confusion about the release of carbon dioxide when biomass or its derivatives, such as ethanol, are burned. The critical fact to realize is that carbon dioxide is the primary nutrient for growth of

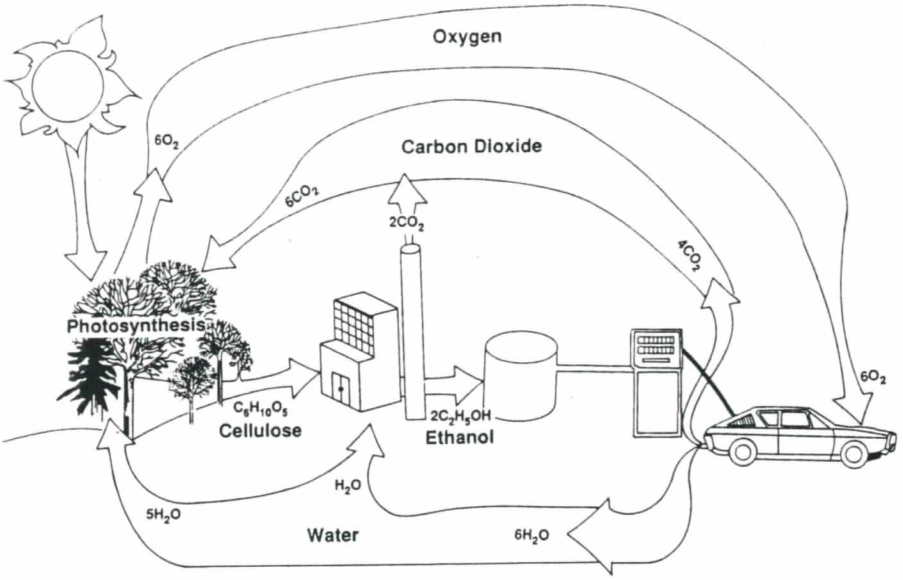

Fig. 2. Carbon dioxide produced during fermentation of sugars to ethanol and combustion of ethanol as fuel is recycled back to replenish the feedstock. Thus, at steady state, use of ethanol as a fuel does not contribute to carbon dioxide accumulation in the atmosphere and the possible consequences of global warming.

trees or other plants in the first place. Figure 2 illustrates the conversion of the cellulose from trees into ethanol and its use to fuel a vehicle. In this example, as in any burning of biomass for fuels, the amount of carbon dioxide released when ethanol is produced from biomass and burned for fuel is exactly the amount required to replenish the plants needed to produce the ethanol. Furthermore, similar balances apply to the consumption and regeneration of oxygen and water in this closed cycle. Of course, we must insure that new trees or other biomass are planted to replace those that we harvest for energy, as practiced in the paper-and-pulp and corn-to-ethanol industries.

Although carbon dioxide will be recycled according to the path in Fig. 2 at steady state, there may be some transient changes in carbon allocation. The exact impact of ethanol production and use on the accumulation of carbon dioxide is difficult to assess since it depends on the feedstock mix employed and the impact of biomass conversion on existing biomass cycles. For instance, if crop residues are used as the substrate, no real change in carbon dioxide levels occurs since the residues decay anyway to form carbon dioxide that supports future year's growth. However, methane also is formed during natural decay of vegetation, and transformation of residues to ethanol would reduce accumulation of this important greenhouse gas. Similar arguments can be made for the use of forestry residues and municipal solid waste as ethanol feedstocks. Thus, the impact on global warming would be neutral to beneficial for any of these waste streams.

Utilization of woody and herbaceous plants for fuel production is more complex. If wood is collected by thinning existing forests, the overall quantity of standing vegetation should remain about the same, and intelligent application of this practice would simply use biomass that would die anyway to provide energy, while minimizing decay to methane. On the other hand, if we plant intensively managed forests for energy farming, the amount of biomass on the site, B, would be determined by the annual growth rate, G, and the growth period between harvests, T

$$B = G\,T/2 \tag{9}$$

assuming that biomass growth rate is constant. If little to no biomass stood on the site prior to energy farming, then a gain in the total amount of carbon fixed results. For example, with a five-year cycle and a growth rate of 6.4 dry metric tons/acre/yr, a gain of about 16 metric tons of biomass results in this case. If 380 billion liters (100 billion gallons) of ethanol were produced in this way, then about an additional 940 million metric tons of carbon would be fixed, owing to ethanol production, while the plantation is being established. On the other hand, if the land was previously heavily forested, with an average density of 32 dry metric tons/acre, than about 940 million metric tons of carbon would be released into the air during the period required to establish a biomass farm to produce 380 billion liters of ethanol/yr. For either case, once the farm is operating at steady state, carbon would be recycled back to grow the short rotation trees, and no further loss or gain in atmospheric carbon would occur.

A much more detailed analysis is required to more accurately predict possible impacts of biomass conversion to fuels on carbon dioxide buildup, and such an analysis is well beyond the scope of this paper. Even in the worse case considered here, the one time release of 940 million metric tons of carbon for a perpetual supply of 380 billion liters of ethanol annually is dwarfed by the annual release of 1.2 billion metric tons of carbon/yr from fossil fuels in the US alone. Thereafter, carbon continually recycles from the air to plants to ethanol and back to the air in the case of ethanol production from biomass. On the other hand, for the use of fossil fuels, carbon is taken from a huge reservoir below the ground and released into the air, leading to continual carbon dioxide buildup and the projected dire consequences of the ''Greenhouse Effect.'' Obviously, there can be no comparison between the consequences of the two options. Finally, by selection of appropriate sites for biomass growth, the production of ethanol from biomass can actually contribute to carbon dioxide removal.

CONCLUSIONS

Ethanol can be used as a neat hydrous fuel, blended with gasoline to boost octane and reduce carbon monoxide emissions, or reacted with isobutylene to form the oxygenated fuel additive ethyl tert-butyl ether (ETBE). Neat hydrous ethanol achieves better mileage than predicted from its energy content alone, apparently owing to its high octane and high latent heat of vaporization. Thus, about 1.25 L of ethanol will power a vehicle as far as 1 L of gasoline. When blended with gasoline, ethanol boosts octane and compensates for rich carburetor settings by the leaning effect to reduce carbon monoxide emissions. ETBE provides an oxygenated fuel additive with properties similar to gasoline and promises to provide good blending compatibility, octane improvement, ozone reduction, and leaning effect. Neat hydrous ethanol can lower emissions of nitrogen oxides and volatile organic compounds, decreasing ozone formation and smog, and is relatively environmentally benign. Aldehyde emissions from vehicles can be addressed and may be less than for gasoline.

The value of ethanol at the refinery gate varies with the intended use, but currently falls in the range of \$0.14–\$0.16/L (\$0.53–0.60/gal) for gasoline at \$0.20/L (\$0.75/gal). At these prices, strictly stoichiometric considerations show that corn is preferred to sugar as a feedstock in the US, but the costs of sugar and corn are both too high to produce ethanol at prices competitive for fuel uses at the plant gate. On the other hand, lignocellulosic biomass, such as agricultural and forestry residues, municipal solid wastes, and short rotation energy crops, are available in sufficient quantity to meet anticipated liquid fuel needs. Furthermore, the value of the latter substrates for ethanol production is greater than their cost. Although nearly half the weight of sugar is lost as carbon dioxide during fermentation to ethanol, about 97% of the fuel value of the carbohydrate substrate is preserved. Thus, the fermentation process concentrates the energy of solid biomass in a liquid form, ethanol, and the economics don't suffer on an energy basis. Although carbon dioxide is released during both fermentation of biomass to ethanol and combustion of ethanol, the growth of new biomass to maintain a supply of feedstock requires carbon dioxide, and other than some transient changes in carbon allocation, no net accumulation of carbon dioxide results. Furthermore, by careful siting of energy plantations, ethanol production can increase carbon fixation.

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