

Fuel Ethanol from Cellulosic Biomass

LEE R. LYND, JANET H. CUSHMAN, ROBERTA J. NICHOLS, CHARLES E. WYMAN

Ethanol produced from cellulosic biomass is examined as a large-scale transportation fuel. Desirable features include ethanol's fuel properties as well as benefits with respect to urban air quality, global climate change, balance of trade, and energy security. Energy balance, feedstock supply, and environmental impact considerations are not seen as significant barriers to the widespread use of fuel ethanol derived from cellulosic biomass. Conversion economics is the key obstacle to be overcome. In light of past progress and future prospects for research-driven improvements, a cost-competitive process appears possible in a decade.

ALTHOUGH FUEL ETHANOL IS CURRENTLY PRODUCED from sugar cane in Brazil and from corn and other starch-rich grains in the United States, ethanol also can be made from cellulosic materials such as wood, grass, and wastes. The technology for ethanol production from cellulosic materials is fundamentally different from that for production from food crops. Failure to appreciate this difference has resulted in misconceptions about the potential of ethanol as a large-scale transportation fuel in the United States. This article reviews the current state and future potential of technology for producing ethanol from cellulosic biomass. The focus is on the use of ethanol as the primary fuel component on a scale exceeding that possible with low-level ethanol-gasoline blends.

Of the four major energy sources in the United States, petroleum supplies the largest share of total energy used and has the highest fraction imported, both by significant margins (Table 1). The domestic supply of conventional petroleum is also the most limited of our major energy sources. Imported oil accounted for about 44% of the 1989 foreign trade deficit (1), and total petroleum expenditures were equal to about 2% of the gross national product (2, 3). This already prominent role for petroleum in the national economy is expected to increase as domestic oil exploration and production become more expensive and as the cost and volume of imports increase (4). Energy use by the transportation sector totaled 22 quad (1 quad = 10^{15} Btu) in 1989 and accounted for more than 60% of total petroleum consumption (2). Furthermore, the transportation sector, with its nearly total dependence on petroleum, has virtually no capacity to switch to other fuels in the event of a supply disruption (5).

Air pollution is an important factor motivating interest in alter-

native fuels. At the local level, about 100 areas in the United States exceed national ambient air quality standards (NAAQS) for ozone (6), affecting more than half the population (7). Limits set by the NAAQS for carbon monoxide are exceeded in more than 40 areas (6). At the global level, carbon dioxide (CO_2) is responsible for more than half the projected anthropically mediated climate change (8). Transportation fuels account for 27% of the 3.3 billion metric tons of CO_2 released annually in the United States from combustion of fossil fuels (9). Vehicles account for 4.7% of total worldwide anthropic CO_2 emissions, with U.S. vehicles being responsible for 2.5% of total emissions (10).

Ethanol as a Fuel

Production and utilization. Fuel ethanol production by fermentation of starch crops is about 0.8 billion gallons (~ 0.06 quad) (11) in the United States, with ethanol selling for about \$1.20 per gallon (12). The effective price to the blender is lowered by more than \$0.50 per gallon by federal and state tax incentives (13, 14), without which fuel ethanol would not now be cost competitive.

Low-level ethanol-gasoline blends, consisting predominantly of gasoline, may use ethanol directly or indirectly, the latter in the form of ethyl *tert*-butyl ether (11, 15). About 7% of all gasoline sold in the United States currently contains fermentation-derived ethanol, and 10% blends are covered by the warranty of all U.S. automobile manufacturers. Both direct and indirect blends increase octane and also increase fuel oxygen content, facilitating more complete combustion in older cars.

Ethanol may be used as a primary fuel either in neat (unblended) form or with small amounts of gasoline. E_{100} and E_{85} refer to neat ethanol and an 85% ethanol-15% gasoline blend, respectively; similar terms are used for methanol. About 3 billion gallons of ethanol are used annually in Brazil, primarily as a neat fuel (14). Ethanol was used sporadically as a primary fuel in the first half of the 20th century in both the United States and Europe (16). Fiat, Ford, General Motors, and Volkswagen have marketed automobiles designed for use of hydrous (water-containing) ethanol in Brazil (17).

Alcohols are in many respects superior to gasoline as fuels for spark-ignited engines (18-20). Ethanol has fuel properties similar to those of methanol; differences between the alcohols and gasoline are much greater than differences among the alcohols (20-22). Combustion of ethanol in internal combustion engines designed for alcohols will give higher thermal efficiency and power than combustion of gasoline in conventional engines (19, 20, 22). Ford has concluded that cold-starting problems have been solved for E_{85} and M_{85} for some applications, but not for E_{100} or M_{100} . A significant development for the use of alcohol fuels is the flexible fuel vehicle, which has the potential to operate on any mix of ethanol, methanol, and gasoline (5, 20).

Ford's experience, as well as estimates and data from others (23,

L. R. Lynd is with the Thayer School of Engineering, Dartmouth College, Hanover, NH 03755. J. H. Cushman manages the Biofuels Feedstock Development Program Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831. R. J. Nichols is with the Environmental and Safety Engineering Staff, Ford Motor Company, Dearborn, MI 48121. C. E. Wyman manages the Biotechnology Research Branch, Solar Energy Research Institute, Golden, CO 80401.

Table 1. Selected data for U.S. energy utilization. Consumption, dependence, and import data are from (2) for 1989 (1 quad = 10^{15} Btu = 1.06×10^{15} kJ). Oil and gas reserves are from (55) and are for conventional reserves only. Total recoverable reserves are the sum of measured, indicated and inferred, and undiscovered reserves; economically recoverable reserves are a smaller quantity. Coal reserves are from (56).

Energy source	Annual consumption (quad)	Sector with greatest dependence	Amount imported (%)	Ratio of estimated total recoverable reserves to utilization rate (years)
Petroleum	34.0	Transportation (97%)	45	16
Coal	19.0	Utilities (55%)	-14	>1000
Natural gas	19.5	Residential-commercial (33%)	6.7	35
Nuclear	5.7	Utilities (19%)		*
Other	2.9			
Total	81.3			

*U.S. uranium reserves are the largest in the world (56).

24), indicates that approximately 1.25 gallons of ethanol are needed to travel the same distance as that obtained from 1 gallon of gasoline in optimized engines. At the 1989 average wholesale gasoline price of \$0.655 per gallon (2), the selling price required for neat ethanol to compete with gasoline on an unsubsidized basis is \$0.52 per gallon. In the year 2000, with crude oil at the \$28 (1989) per barrel midrange price predicted by the Department of Energy (DOE) (4), gasoline can be expected to have a wholesale price of about \$0.88 per gallon (25), and a price of \$0.70 per gallon would be required for ethanol to be competitive as a neat fuel.

Air-quality impact. The Environmental Protection Agency (EPA) (22) has stated that significant long-term environmental benefits are available from the use of ethanol, methanol, or compressed natural gas as pure fuels in engines designed to take full advantage of their combustion properties. The prospect of emission reductions has motivated California to consider widespread substitution of methanol for gasoline and diesel fuel (26) and is also the driving force behind amendments to the Clean Air Act. Most air-quality calculations, including Ford's (27), have shown some improvement in urban ozone levels and a decrease in air toxics accompanying methanol use. Similar improvements are expected for ethanol because the differences between ethanol and methanol with respect to air pollution impact are likely to be small relative to the differences between either alcohol and gasoline (24, 28). Although the magnitude of anticipated improvements is small (probably 0 to 15%, depending on meteorologic conditions, the source of pollutants, and the model used), they are still significant because ozone reduction is so difficult to achieve.

Biomass Feedstocks

Feedstock options. Representative feedstocks for ethanol production include hardwood, a cellulosic raw material that can be grown as an energy crop; municipal solid waste (MSW), a prominent waste material; and corn, the primary raw material for the current U.S. fuel ethanol industry. Table 2 presents ethanol yields and the cost and energy inputs associated with production of these feedstocks. The cost of wood without coproduct credits (\$0.29 to \$0.40 per gallon) does not preclude selling ethanol at prices expected to be competitive with gasoline in the year 2000. The cost of separated MSW is potentially negative and often small relative to the required price for ethanol.

The cost of feedstock less coproduct credits can be quite low for corn (29), but only at low production levels. At levels higher than about 0.3 quad, the prices of both corn and grain would experience strong upward pressure (30). At the ethanol production potential of the current U.S. corn crop (~1.5 quad), by-product markets are expected to be saturated (31). At higher production levels, and thus without coproduct credits, corn is unlikely to be a feasible fuel ethanol feedstock in the absence of subsidies. Thus, although coproduction of ethanol and animal feed from corn may be desirable at low production levels and paves the way for cellulose-based technologies, economic considerations indicate that ethanol produced from corn cannot displace current transportation fuels to any significant extent.

The energy required for production of wood (~15% of the potential ethanol combustion energy) is acceptably small for a process devoted to production of a useful form of energy and is at least two times smaller than that required for corn production (Table 2). Source-separated MSW has no energy requirements related to its use as a feedstock for ethanol production. Potential ethanol yields per unit mass are nearly equal for corn and hardwood and are somewhat less for MSW.

Supply of cellulosic feedstocks. Sources of cellulosic materials can be divided into wastes from processes undertaken for purposes other than fuel production and crops grown specifically for fuel production. The primary waste categories are agricultural residues, forestry residues, and MSW. Table 3 presents ethanol production potentials for these wastes, which total about 4 quad.

Nonwaste cellulosic feedstocks may be woody or herbaceous high-productivity energy crops (HPECs) or may be trees produced by conventional forestry. Categories of land that might supply feedstocks include forest land that is not potential cropland and cannot support HPECs, existing cropland (cropland potentially available for energy crop production as a result of excess agricultural capacity), and potential cropland (land now in noncrop uses that could grow crops). For land categories capable of supporting HPECs, a range of ethanol production potentials is presented in Table 3, with the low value being based on the average productivity believed to be achievable with today's technology and the high value being based on productivities projected for future technology.

The considerable ethanol production potential of cropland idled in 1988 (3.0 to 5.9 quad) is likely to be a conservative estimate of future production potentials from existing cropland. A recent report to the Secretary of Agriculture (32) recommended that the development of new, nonfood products use the productive capacity of at

Table 2. Properties of potential ethanol feedstocks. All values are for potential ethanol calculated as reported in (57), with the fraction of total sugars fermented being 0.95 for corn and 0.9 for wood and MSW and a fermentation yield (mass ethanol per mass carbohydrate fermented) of 0.46.

Feedstock	Cost (\$/gallon of ethanol)		Energy for feedstock production‡ (fraction of ethanol combustion energy)	Yield§
	Feedstock*	Feedstock less coproducts†		
Wood	0.29-0.40	0.21-0.32	0.13-0.18	0.33
MSW	≤0.2		0	0.25
Corn	0.56-1.26	0.12-0.79	0.33-0.97	0.35

*Wood: HPEC produced for \$30 to \$45 (1990) per dry ton (58). MSW: a representative price paid for separated recyclable fiber, \$15 per ton, seen as a reasonable upper limit for the feedstock cost. Corn: at \$1.41 to \$3.16 per bushel, the range for the period 1981 to 1989 (59). †Wood: reflects value as a boiler fuel; calculated with a lignin content of 21% by weight valued at \$0.02 per pound (60). Corn: reflects value of animal feed coproducts (59). ‡Wood: HPEC (61) calculated from the methodology presented in (57); lower productivity methods have about half the indicated energy requirement. MSW: see text. Corn: see (46, 62). §Yield in terms of mass of potential ethanol per mass of dry feedstock.

Table 3. Land availability and production potential for cellulose ethanol.

Cellulose source	Land available (million acres)	Production potential* (quad)
Wastes†		
Agricultural		1.7
Forestry		1.4
MSW		0.7
Cropland‡		
Idled (1988)/excess (2012)	78/150	(3–5.9)/(5.7–11.4)
Potential	150	3.4–9.1
Forest land§	96	2.2
Total	324–396	12.4–26.5

*Yield assumptions are consistent with those described in Table 2. †Data are averages from sources compiled in (57); most sources consider the need to maintain soil fertility in estimating collectible agricultural and forest wastes. ‡Existing idled cropland for 1988 is from (63); anticipated excess cropland for 2012 is from (32), potential cropland is from (64). Ethanol production levels given correspond to the DOE Biofuels Feedstock Development Program's best estimates for current and anticipated HPEC productivity. Values (dry tons per acre per year, current/anticipated) are 5/10 for idled and excess cropland and 3/8 for potential cropland. §From (31), with calculation as described (57). ||Low value is for current HPEC productivity and 1988 existing cropland; high value is for anticipated HPEC productivity and projected available cropland.

least 150 million acres in the next 25 years. This large quantity of cropland is an indication that the historic problem of excess agricultural capacity in the United States is expected to continue and worsen. At projected land availability and energy crop productivities, excess cropland has an ethanol production potential of 11.4 quad. A large-scale fuel ethanol industry might be further supported by land in the potential cropland category. Because of the relatively low productivity of forest land and the consequent large land areas and loss of wildlife habitat accompanying the use of forest land for significant fuel production, this category may be less desirable for production of feedstocks.

Given the gap between current production of cellulosic materials for fuel and the production necessary to support a large-scale fuel ethanol industry, estimates for total ethanol production capacity are uncertain. The data presented above, however, suggest that cellulosic materials potentially available from energy crops, wastes, and conventional forestry could provide an amount of ethanol commensurate with current consumption of liquid transportation fuels in the United States. Previous lower estimates of the cellulose resource base (33) differ from the estimate presented herein in that they

primarily considered wastes. Because HPECs have a time to harvest of less than 1 year to 10 years, depending on the crop selected, production of cellulosic feedstocks could be accelerated rapidly.

Environmental impacts. Perennial cellulosic energy crops can be grown on marginal cropland with much less erosion risk than annual row crops, such as corn. Potential erosion risk should be limited to 1 to 2 years during stand establishment. Stand life for HPECs and perennial grasses is uncertain but is thought to be in the range of 10 to 25 years (34). Longer lived production systems could be used on erosive sites. Annual cellulosic energy crops could be grown on higher quality, less erosive cropland, perhaps in a crop rotation with conventional food crops. On the basis of the field research of the DOE Biofuels Feedstock Development Program, perennial HPECs such as short-rotation hardwoods and grasses require substantially less fertilizer and pesticides than corn (35, 36). Perennial species can translocate and reuse nutrients, and herbicide use is limited to 1 or 2 years at stand establishment.

Available information suggests that perennial cellulosic energy crops are more environmentally benign than conventional annual row crops. More experience with large-scale production is needed to confirm the expectation of investigators in the field that environmental problems accompanying well-managed production of cellulosic energy crops will be relatively minor for most sites.

Ethanol Production from Cellulosic Materials

Processing options. Several approaches have evolved for the conversion of cellulosic materials to ethanol; these differ primarily in the method of hydrolysis and the fermentation system used. Hydrolysis of cellulosic materials can be accomplished with acids or cellulase enzymes. Projected selling prices for ethanol produced from cellulose by acid hydrolysis are currently comparable to those for enzyme-based processes (37). Enzymatic processes are at a much earlier state of technological maturity; however, in the absence of unforeseen breakthroughs for acid-based processes, research is likely to result in enzyme-based processes that are significantly cheaper than acid-based processes. Steps in conversion of cellulosic biomass into ethanol by enzymatic processes are depicted in Fig. 1.

Energy balance. The ratio of energy output to energy input, R , may be defined for cellulose-based processes with reference to Fig. 1 as

$$R = \frac{1 + (3 * E)}{A + T + C + D + P} \quad (1)$$

where E is exported electricity, A is agricultural inputs, T is raw material transport, C is chemical inputs, D is distribution, P is plant amortization, and all energy flows are expressed as fractions of the lower heating value of ethanol. The 1 in the numerator represents ethanol and the multiplier of E reflects the displacement of thermal energy for conventional power generation. Estimated parameter values are as follows: $E = 0.08$ (38), $A = 0.15$ (Table 2), $T = 0.04$ (39, 40), $C = 0.01$ (41, 42), $D = 0.01$ (43), and $P = 0.04$ (44, 45). Thus, current understanding of ethanol production from cellulose is consistent with a value of 5 for R . In contrast, R is generally less than 1 for corn-based processes without coproduct credits and is approximately 1 if coproducts are considered (45, 46).

A key factor in considering the energetics of ethanol production from cellulose is the energy available from residues remaining after fermentation. It is thought that unfermentable raw material components, in particular lignin, can be mechanically dewatered and burned to provide 30,000 to 40,000 Btu per gallon of ethanol, an amount in excess of processing energy requirements for current designs with a wood feedstock (38). This excess energy can be used

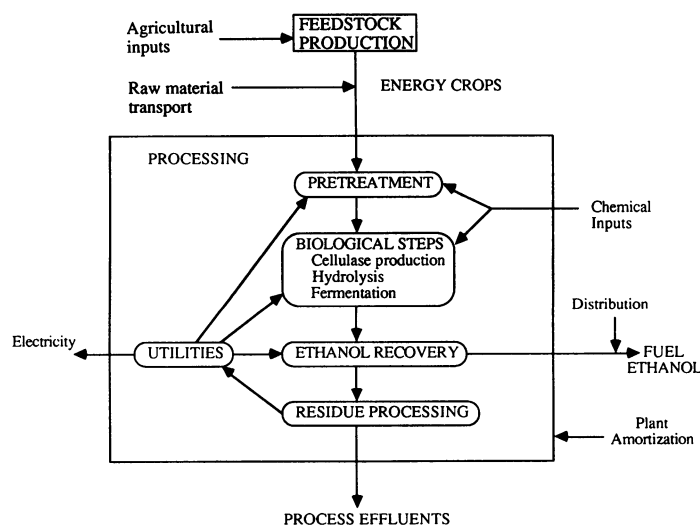


Fig. 1. Production of ethanol from cellulosic materials by means of enzymatic hydrolysis.

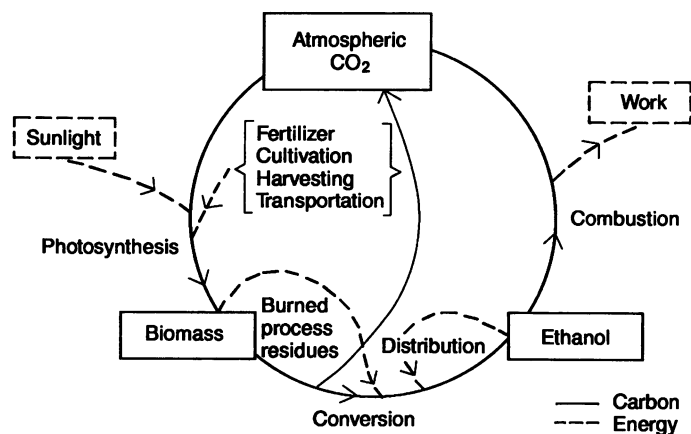


Fig. 2. Carbon and energy flows for production and utilization of fuel alcohol from biomass. [Adapted from (53) with permission of Humana Press, copyright 1989]

to produce electricity in a cogenerative fashion. The thermal efficiency (heat of combustion of ethanol plus three times the electricity production relative to the heat of combustion of the raw material) of ethanol production from cellulosic materials for a process with high yields is in the range of 45 to 70%, depending on the feedstock composition and process configuration.

Global climate change implications. Carbon dioxide production accompanies fermentation of the carbohydrate fraction of biomass to ethanol, combustion of unfermentable biomass fractions to provide process energy, and combustion of fuel ethanol to provide useful work. The quantity of CO₂ released, however, is precisely that which was previously removed from the atmospheric pool by photosynthesis in the course of feedstock production. The cellulose ethanol fuel cycle thus involves cyclic carbon flow (Fig. 2).

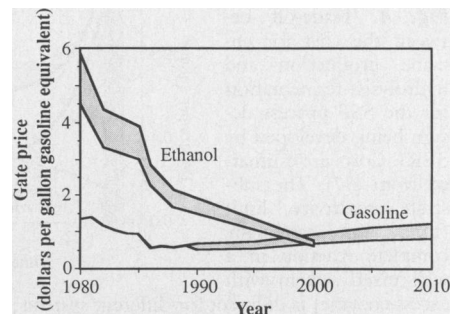
Energy inputs are required at several points to drive the cycle depicted in Fig. 2. Agricultural inputs can be satisfied by either fossil fuels or fuels that do not contribute to CO₂ accumulation in the atmosphere, such as ethanol in mobile applications and wood or lignin for stationary boilers. The same is true for smaller energy and material inputs associated with equipment depreciation, fertilizer production, and fuel distribution. An indication of the contribution of fuel options to CO₂ accumulation is the net carbon produced per unit energy N . For cellulose ethanol, this parameter may be estimated from

$$N = \left(\frac{f}{R} \right) C_f \quad (2)$$

where f is the fraction of energy inputs met by fossil fuels and C_f represents CO₂ produced per unit energy for fossil energy inputs. Although C_f will vary for different scenarios, a reasonable value is 80 mg of CO₂ per kilojoule (47), which is representative for gasoline. With $R = 5.0$ (see above), Eq. 2 indicates that N is 16 mg of CO₂ per kilojoule if only fossil fuels are used for energy inputs, corresponding to $f = 1$. N is 0 for the case in which energy inputs are provided by sources that do not contribute to CO₂ accumulation, however, corresponding to $f = 0$. Thus, current understanding of cellulose ethanol technology is consistent with a best case scenario involving no contribution to CO₂ accumulation and a worst case scenario resulting in a CO₂ contribution about one-fifth that of gasoline.

Environmental impacts. Airborne emissions, liquid effluents, and solid wastes from ethanol production processes appear to pose no problems that cannot be addressed by conventional waste-treatment technology (31, 48). Ethanol is substantially less toxic than methanol and gasoline at the same dosage levels (49). The predominant

Fig. 3. Past and projected costs (1988 basis) for ethanol and gasoline. Past gasoline prices are from (2); the range of future gasoline prices is based on DOE oil gasoline price projections (4). For ethanol, prices are estimated from past research and an aggressive program for future research. The range shown arises from assumed capital recovery, with the higher values being for a capital recovery factor typical of private financing and the lower values being for a capital recovery factor more likely for municipal or utility-like finance structures.



toxicity issue associated with ethanol use is intentional consumption as an intoxicant. Additives such as 3% gasoline, used in Brazil, probably will be added to discourage such consumption.

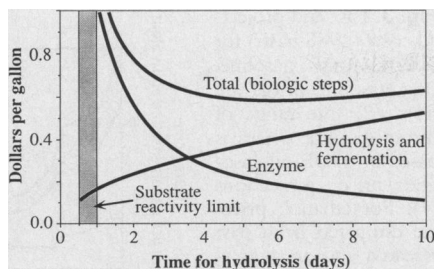
Conversion economics. As shown in Fig. 3, progress in cost reductions has been substantial over the last 10 years, resulting in an approximately threefold reduction in the projected selling price (37) to \$1.35 per gallon in 1988 for technology proven on a laboratory scale (42). Cost reductions to date stem from minimizing end-product inhibition of cellulase, improved cellulase enzymes and fermentative microorganisms, and improved systems for xylose fermentation. The current cost of producing ethanol from cellulose is the major impediment to utilization of this technology.

Given the cost of representative cellulosic feedstocks (Table 2) and the wholesale selling price required for ethanol to be competitive (see above), operating costs, capital recovery, and secondary raw materials will have to cost in the range of \$0.30 to \$0.40 per gallon to be competitive with gasoline prices anticipated in the year 2000. A cost ratio of selling price to primary raw material cost of a factor of 2 is unusually large for a commodity chemical (50), which supports our conviction that an economic process is realistic. This conviction is further supported by considerations addressed below.

Of the ethanol production steps (Fig. 1), only utilities and residue processing are well developed in the context of cellulose-based processes. Thus, the current technology for conversion of cellulosic biomass to ethanol has potential for significant improvements in the areas of pretreatment, biologically mediated process steps, and product recovery. Biologic process steps are the most costly by a factor of more than 2 in process designs to date, are the least well developed, and have the greatest potential for improvement (37, 51). Currently, the cost of enzyme constrains the reaction time to values far above the limit imposed by substrate reactivity (Fig. 4). Various improvements are being investigated that would lower the effective enzyme cost, including increasing the reactivity of the substrate after pretreatment, improving enzyme production systems, improving enzyme activity, and recycling enzyme. Both naturally occurring (52, 53) and genetically engineered (54) systems, wherein the fermenting organism produces its own cellulase, have been described. Such systems have the potential to produce enzyme at little or no incremental cost, in which case the cost of the biologic process steps becomes that of hydrolysis and fermentation only, and radical cost reductions can be anticipated. Reactor design for high-productivity solids conversion is another area with great potential for lowering the cost of biologic steps.

Reducing enzyme cost from that shown in Fig. 4 changes the minimum on the total cost curve to a reaction time at which the cost of hydrolysis and fermentation is also lower. Such coupled benefits are the rule rather than the exception when improvements in cellulose ethanol processes are considered. In general, improvements

Fig. 4. Trade-off between the cost for enzyme production and hydrolysis - fermentation for the SSF process design being developed by SERI. Costs are estimated from (37). The substrate reactivity limit (time for essentially complete reaction in a well-mixed system with excess enzyme) is different for different systems; the range indicated is from (53, 65).



in a given process step or parameter have pervasive impacts on several other process steps that may appear to be unrelated (37, 51). For example, an improved fermentation system that achieves a higher product yield will decrease the cost of every process step shown in Fig. 1 with the exception of product recovery. Further, improved ethanol tolerance can lower the costs of fermentation and also of product recovery and utilities. Coupled benefits such as these make process economics sensitive to improvements.

The goal of the DOE Ethanol from Biomass Program is to reduce the wholesale selling price of ethanol to \$0.60 (mid-1980s, basis) per gallon. On the basis of the significant opportunities for improvement associated with approaches such as those described above, the Solar Energy Research Institute (SERI) estimates that technology meeting this goal could be available by the year 2000, given aggressive R&D.

Concluding Remarks

The impacts of alternative fuel use on CO₂ accumulation, energy security, balance of payments, sustainable supply, and conversion-related environmental effects are determined primarily by the energy source rather than the fuel per se. The significant potential benefit of fuel derived from cellulosic biomass with respect to these issues results from the use of renewable nonfood feedstocks. Ethanol appears to score well in terms of fuel-determined impacts as well, which include engine performance, infrastructure compatibility, and utilization-related environmental effects.

Production of ethanol from cellulosic biomass is believed to be an emerging energy technology with particularly great potential for the U.S. transportation sector. Research to improve conversion processes and to develop cellulosic energy crops is necessary to reduce costs and to increase production potential. Success can reasonably be expected in both these areas in light of the immature state of current technology and the powerful approaches available.

REFERENCES AND NOTES

1. "Greater reliance on foreign oil feared as U.S. output tumbles," *New York Times*, 18 January 1990, p. A1.
2. *Mon. Energy Rev.*, DOE/ELA-0035(89/12) (DOE, Washington, DC, 1990).
3. *Econ. Indic. (Wash.)* (December 1989). Based on data for the first three quarters of 1989 and conservatively valuing imported petroleum products (about 10% of total petroleum consumption) at the cost of crude oil.
4. *Annual Energy Outlook* (Energy Information Administration, DOE, Washington, DC, 1990).
5. "Assessment of costs and benefits of flexible and alternative fuel use in the U.S. transportation sector, Progress Report One: Context and Analytical Framework," Rep. DOE/PE 0080 DE88 006893 (1989).
6. *EPA Lists Places Failing to Meet Ozone or Carbon Monoxide Standards* (EPA, Washington, DC, 1989).
7. A. G. Russell, D. St. Pierre, J. B. Milford, *Science* **247**, 201 (1990).
8. *Policy Options for Stabilizing Global Climate Change* (EPA, Washington, DC, 1989) [reported by E. Marshall [*Science* **243**, 1544 (1989)] and P. Zurer [*Chem. Eng. News* **67** (no. 13), 23 (1989)]; *Policy Makers Summary of the Scientific Assessment of Global Climate Change* (third draft report to the Intergovernmental Panel on

- Climate Change (IPPC), IPCC Group 1, Meteorological Office, Bracknell, U.K., May 1990).
9. J. A. Edmonds, W. B. Ashton, H. C. Cheng, M. Steinberg, Rep. DOE/NBB-0085 (1989).
10. *Energy Balances of OECD and Other Countries 1971-1987* (International Energy Agency, Paris, 1989).
11. H. Ahmad, N. Rask, E. D. Baldwin, *Biomass* **19**, 215 (1989).
12. *New Fuels Rep.* **11** (no. 13), 13 (1990) (available from J. E. Sinor Consultants, Inc., Niwot, CO); *Oxy-Fuel News* **1** (no. 50), 9 (1990).
13. "Fuel ethanol and agriculture: An economic assessment" [Rep. 562, U.S. Department of Agriculture (USDA), Washington, DC, 1986]; J. E. Murtagh, *Process Biochem.* **21** (no. 2), 61 (1986).
14. *Clean Fuels Rep.* **1** (no. 2), 82 (1990).
15. E. Anderson, *Chem. Eng. News* **65** (no. 43), 11 (1988).
16. H. Rothman, R. Greenshields, F. R. Calle, *The Alcohol Economy* (Pinter, London, 1983); H. Bernton, W. Kovarik, S. Sklar, *The Forbidden Fuel* (Boyd Griffin, New York, 1982); D. Houghton-Ailco, *Alcohol Fuels—Policies, Production and Potential* (Westview, Boulder, CO, 1982).
17. J. D. Ferchak and E. K. Pye, *Sol. Energy* **26**, 17 (1981).
18. *Air Quality Benefits of Alternative Fuels* (EPA, Washington, DC, 1987).
19. L. H. Browning, R. K. Pefley, T. P. Suga, *Proceedings of the 16th Intersociety Energy Conversion Engineering Conference* (American Society of Mechanical Engineers, New York, 1981).
20. C. Risch, paper presented to the California Air Resources Board Public Meeting on Clean Fuels, Sacramento, CA, 9 September 1988 (available from Ford Motor Company, Dearborn, MI).
21. "Comparative automotive engine operation when fueled with ethanol and methanol" (Rep. HCP/W1737-01 UC-96, DOE, Washington, DC, 1978).
22. R. D. Wilson, Statement before the Consumer Subcommittee on Commerce, Science, and Transportation, U.S. Senate, November 1987.
23. W. Bernhardt, *Proceedings of the International Symposium on Alcohol Fuel Technology—Methanol and Ethanol* (National Technical Information Service, Springfield, VA, 1978); W. H. Kampen, *Hydrocarb. Process.* **59** (no. 2), 72 (1980).
24. *Analysis of the Economic and Environmental Effects of Ethanol as an Automotive Fuel* (EPA, Washington, DC, 1990).
25. Supported by both historical precedent (in 1983, oil was \$28.99 per barrel and gas sold for \$0.882 per gallon) and by the approximately \$9 per barrel increment reflecting the added value of gasoline relative to crude oil during the 1980s; see (2).
26. *Air Quality Management Plan* (South Coast Air Quality Management District, El Monte, CA, 1988).
27. T. Y. Chang, S. J. Rudy, G. Kuntasal, R. A. Gorse, *Atmos. Environ.* **23**, 1629 (1989).
28. G. Z. Whitten, "Comparative ranking of the environmental impacts of alternative fuels" (Systems Applications, Inc., San Rafael, CA, 1989).
29. The difference between feedstock cost and by-product credits is the lower limit for the net feedstock cost in that capital and operating costs associated with coproduct production are not considered.
30. *Ethanol's Role in Clean Air* (Backgrounder Ser 1102-89, USDA, Washington, DC, 1989).
31. *Energy from Biological Processes*, vol. 2, *Technical and Environmental Analyses* (Office of Technology Assessment, Washington, DC, 1980).
32. *Report of the New Farm and Forest Products Task Force to the Secretary* (USDA, Washington, DC, 1987).
33. A. E. Humphrey, A. Moreira, W. Armiger, D. Zabriskie, *Biotechnol. Bioeng. Symp.* **7**, 45 (1977); T. W. Jeffries, *Adv. Biochem. Eng.-Biotechnol.* **27**, 1 (1983); T. K. Ng, R. M. Busche, C. C. McDonald, R. W. F. Hardy, *Science* **219**, 733 (1983); J. Young, E. Griffin, J. Russell, *Biomass* **10**, 9 (1986).
34. "Short rotation woody crops program annual progress report," *Oak Ridge Natl. Lab. Environ. Sci. Div. Publ.* **3030** (1988).
35. D. H. Strauss and L. L. Wright, in *Energy from Biomass and Wastes XIV*, D. L. Klass, Ed. (Institute of Gas Technology, Chicago, in press).
36. D. J. Parish, D. D. Wolf, W. L. Daniels, D. H. Vaughan, J. S. Cundiff, "Perennial species for optimum production of herbaceous biomass in the Piedmont, final report 1985-89," *Oak Ridge Natl. Lab. Publ.* **85-27413/5** (1990); J. H. Cherney, K. D. Johnson, J. J. Volenc, E. J. Kladvik, D. K. Green, "Evaluation of potential herbaceous biomass crops on marginal crop lands, final report 1985-1989," *Oak Ridge Natl. Lab. Publ.* **85-27412** (1990).
37. J. D. Wright, *Energy Prog.* **8** (no. 2), 71 (1988); *Chem. Eng. Prog.* **84** (no. 8), 62 (1988).
38. "Current SERI wood feedstock-based simultaneous saccharification and fermentation (SSF) process design."
39. Based on a 35-mile average travel distance and transport of biomass with 50% moisture by diesel truck requiring 2000 Btu per ton per mile; see (40).
40. M. DeLuchi, thesis, University of California, Davis (1990).
41. Chemical requirements are design specific, but corresponding energy flows are small in all cases that we have examined. For the SSF design considered here (42), the significant chemical flows are for H₂SO₄ and Ca(OH)₂ used in pretreatment. H₂SO₄ manufacture is an energy-yielding process [R. N. Shreve and J. A. Brink, *Chemical Process Industries* (McGraw-Hill, New York, 1977), p. 301]. The value given is essentially all for Ca(OH)₂ manufacture [F. Schwarzkopf, *Lime Burning Technology, A Manual for Plant Operators* (Kennedy Van Saun Corp., Danville, PA, 1974)]. The energy required for manufacture of ammonia and other chemicals used as nutrients for yeast growth is an insignificant contribution.
42. N. D. Hinman, J. D. Wright, W. Hoagland, C. E. Wyman, *Appl. Biochem. Biotechnol.* **20/21**, 391 (1989).
43. From (40), consistent with a large plant able to use pipeline transport to a significant extent.

44. Value used in (45) for a corn-based ethanol plant; believed to be conservative for an economical cellulose-to-ethanol process.
45. R. S. Chambers, R. A. Herendeen, J. J. Joyce, P. S. Penner, *Science* **206**, 789 (1979).
46. M. A. Johnson, *Energy* **8**, 225 (1983); J. M. Krochta, in *Proceedings of the Second International Conference on Energy Use Management* (Pergamon, Elmsford, NY, 1979), pp. 1956–1963; F. Parisi, *Adv. Biochem. Eng.-Biotechnol.* **28**, 41 (1983); T. Yorifugi, *Energy Dev. J.* **3**, 195 (1981).
47. Based on heat of combustion for petroleum liquids [*Basic Pet. Data Book* [(American Petroleum Institute, Washington, DC, 1989), vol. 9, no. 3], adding 19% for oil recovery, refining, and distribution (40)].
48. R. C. Loehr and M. Sengupta, *Environ. Sanit. Rev.* **16** (1985); E. D. Waits and J. L. Elmore, *Environ. Int.* **9**, 325 (1983).
49. Threshold Limit Values for Chemical Substances and Physical Agents in the Workman Environment with Intended Changes for 1980s (American Conference of Government Industrial Hygienists, Cincinnati, OH, 1980).
50. *Hydrocarb. Process.* **68** (no. 11), 85 (1989); *ibid.* **67** (no. 9), 61 (1988).
51. L. R. Lynd, *Appl. Biochem. Biotechnol.* **24/25**, 695 (1990).
52. M. K. Veldhuis, L. M. Christensen, E. I. Fulmer, *Ind. Eng. Chem.* **28**, 430 (1936); T. K. Ng, P. J. Weimer, J. G. Zeikus, *Arch. Microbiol.* **114**, 1 (1977).
53. L. R. Lynd, H. E. Grethlein, R. H. Wolkin, *Appl. Environ. Microbiol.* **55**, 3131 (1989).
54. J. N. Van Arsdell *et al.*, *Bio/Technology* **5**, 60 (1987); B. Surbrigen, M. J. Bailey, M. E. Penttila, K. Poutanen, M. Linko, *J. Biotechnol.* **13**, 267 (1990); M. E. Penttila, P. Lehtovaara, M. Bailey, T. T. Teeri, J. K. C. Knowles, *Gene* **63**, 103 (1988).
55. *National Assessment of Undiscovered Conventional Oil and Gas Resources, Working-Paper* (Working pap., U.S. Geological Survey and Minerals Management Service, March 1989); R. A. Kerr, *Science* **245**, 1330 (1989).
56. M. Grathwohl, *World Energy Supply* (de Gruyter, Berlin, 1982).
57. L. R. Lynd, *Adv. Biochem. Eng.-Biotechnol.* **38**, 1 (1989).
58. The indicated range is consistent with the evaluation of the DOE Biofuels Feedstock Development Program [R. D. Perlack and J. W. Ranney, *Energy* **12** (no. 12), 1217 (1987); (35)].
59. S. Kane, J. Reilly, M. LeBlanc, J. Hrubovcak, *Agribusiness* **5**, 505 (1989); *Feed Situation and Outlook Report* (USDA, FDS-314, Washington, DC, 1990).
60. C. E. Wyman and N. D. Himman, *Appl. Biochem. Biotechnol.* **24/25**, 735 (1990).
61. J. D. Ferchak and E. K. Pye, *Sol. Energy* **26**, 9 (1981); J. W. Ranney, L. L. Wright, P. A. Layton, *J. For.* **85** (no. 8), 17 (1987); N. Smith and T. J. Corcoran, *Am. Chem. Soc. Symp. Ser.* **144**, 433 (1981).
62. G. Marland and A. Turhollow, *Oak Ridge Natl. Lab. Environ. Sci. Div. Publ.* **3301** (1990).
63. *Agricultural Resources—Cropland, Water, and Conservation, Situational Outlook and Report* (USDA, Washington, DC, 1988).
64. “Basic Statistics, 1982 National Resources Inventory,” *USDA Soil Conserv. Serv. Stat. Bull.* **756** (1987).
65. H. E. Grethlein, D. C. Allen, A. O. Converse, *Biotechnol. Bioeng.* **26**, 1498 (1984).
66. We thank M. DeLuchi, P. Lorang, R. Moorer, and A. Turhollow for useful discussions and information. Publication 3644, Environmental Sciences Division, Oak Ridge National Laboratory.

Why Gases Dissolve in Liquids

GERALD L. POLLACK

The thermodynamics and statistical mechanics of solubility are fairly well understood. It is still very difficult, however, to make quantitative predictions of solubility for real systems from first principles. The purposes of this article are to present the results of solubility experiments in some prototype solute-solvent systems, to show how far they may be understood from molecular first principles, and to discuss some of the things that are still missing. The main systems used as examples have the inert gas xenon as solute and some simple organic liquids as solvents.

ALL GASES DISSOLVE IN ALL LIQUIDS, BUT THE ACTUAL solubilities range over many orders of magnitude. For inert gases at room temperature, for example, the solubility of Xe in *n*-octane, a common hydrocarbon liquid, is 470 times that of He in water. Gas solubility can vary much more for complex solutes and solvents. As an example, the solubility of the anesthetic gas halothane in olive oil is more than 10^6 times the solubility of common gases in liquid mercury.

Can the solubilities of gases in liquids be quantitatively understood from molecular first principles? The question can be generalized with the help of the Gibbs phase rule, according to which systems such as these with two components and two phases have two degrees of freedom, such as temperature and pressure. Therefore, the question may be enlarged to include: Can the temperature and pressure dependence of these solubilities be understood from molecular first principles?

One purpose of this article is to discuss how far we can go, using current experiments and modern theory, in answering these questions. Also discussed with the same ideas are some applications of solubility. Finally, there are some suggestions of what natural next steps would advance our understanding of the subject.

Solubility is an old subject, although most of the early interest was in solubility of solids in water, which is still an important area of research and applications. Aristotle knew that evaporation of seawater would recover dissolved salts, and there are records of a systematic study by Pliny the Elder of the relative solubilities of many solids in water.

Early quantitative measurements of the solubility of gases, a more difficult measurement, were made by William Henry (1), as well as by Cavendish, Priestley, and others. Henry studied the pressure and temperature dependence of air, H₂, N₂, O₂, and other gases in water. He discovered, among other things, that O₂ is more soluble than N₂ in water. This is an early example of the principle that is the basis of preferential extraction of one gas from a mixture of gases by use of a solvent. Since that time, the subject has been actively studied because of its fundamental interest and applications. More recently, extensive contributions to understanding gas solubility have been made by Hildebrand and his co-workers and by many others (2, 3). Review articles give comprehensive discussions of the subject as well as results for many solute-gas, solvent-liquid systems (4, 5).

Ostwald solubility (*L*) is an especially useful and also intuitive measure of gas solubility (6). It is defined as the ratio of the concentration of gas molecules dissolved at equilibrium in the liquid solvent to their concentration in the gas phase. In other words, *L* is the ratio: (moles of solute per liter of solution)/(moles of solute per liter of gas). We then can write

$$L = \rho_2^l / \rho_2^g \quad (1)$$

where ρ is the number density and subscripts 1 and 2 stand for, respectively, solvent and solute.

The author is in the Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824.