Conversion of biomass to fuel and chemical raw material

After calculating the potential of biomass production for fuel mainly from agriculture, B.A. Stout reviews the different techniques for converting the rather bulky biomass into a usable form of energy, starting from direct combustion to anaerobic digestion to production of ethanol through alcohol fermentation.
J. Wiegel discusses in detail the direct conversion of cellulose, the most abundant plant product, to ethanol by the single bacterium, *Clostridium thermocellum,* and also by a defined mixed culture.
The problem of degrading cellulose by microorganisms is reviewed by K.E. Eriksson whose main emphasis is on cellulose degrading fungi.
The different ways in which lignins are degraded are summarized by T. Higuchi (aerobic sytems) and J.-P. Kaiser and K. Hanselmann (anaerobic ones). Some possible uses for this second most abundant biomass component are proposed; however, the full and imaginative exploitation of lignin as a raw material remains a challenge for chemists in the future.

Agricultural biomass for fuel

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Introduction

The U.S. energy problem. The united States imported about 8 million barrels of oil each day in 1979. At a cost approaching $30 per barrel, the annual cost amounted to about 80 billion dollars! Needless to say, excessive dependence on foreign oil imports has resulted in serious trade deficits. Inflation, fueled in part by energy problems, has been unacceptably high. Thus, the soundness of the U.S. dollar, our economic wellbeing and even our national security are all inextricably bound to the energy problem.
There is no overall energy shortage: for all practical purposes the sun radiates an infinite energy supply, nuclear reactions release huge amounts of energy and coal supplies are extensive. But can we manage these vast energy resources in an economically and environmentally acceptable manner?

Biomass – what is it and how can it be used for fuel?

What is biomass? It's everything that grows – all organic matter except fossil fuels. Examples of biomass available for substitute fuels include traditional agricultural crops and residues, animal manure, forests, aquatic plants, algae and other microorganisms. Biomass contains energy stored from the photosynthetic process – starches, sugars, cellulose, lignin, etc. Dry biomass contains perhaps 16 MJ/kg – more than one-half as much as a pound of coal! Biomass has many uses – as food, fiber, soil organic matter, bedding, structural material, and it may be used for fuels. The latter is not a new concept. Homes and industry in the U.S. were once heated and powered by wood before fossil fuels (coal, oil and natural gas) displaced wood as the major fuel. In the meantime, however, our national policy of cheap oil and strict environmental regulations has gradually led to the present situation where domestic oil no longer satisfies our vast oil appetite. Now we must turn to, and develope, other energy options.
Dry biomass can be burned to produce heat, steam and/or electricity, and it can be converted to liquid or gaseous form for use in mobile vehicles by anaerobic fermentation, alcoholic fermentation, or gasification.
The use of biomass for fuels raises complex and widely diversified issues and its impact must be assessed variously according to specific feedstocks, geographic areas, conversion technology and end-use application. Although some generalizations are possible, few similarities exist among the use of corn to produce alcohol to operate an internal-combustion engine in Indiana, a wood-fired electric generating plant in Vermont or a kelp farm off the California coast.

How large is the potential for biomass production?

Food for humans is the most important use of biomass. Feed for livestock, organic matter for soil conservation and nutrients, bedding, and structural materials are other important biomass uses. The question is – can U.S. agriculture meet all these biomass needs and still produce a surplus for use as a fuel? And can our forests be managed in such a way as to meet the needs for lumber, paper and other forest products and still provide fuels?

Biomass from agricultural residue. According to Stanley Barber, Professor of Agronomy at Purdue University, an estimated 360 million metric tons of residues are produced each year from 10 major crops in the U.S.[1]. Not all residue is collectible with present machinery and some must remain on the land to maintain it within acceptable erosion limits. The above estimate excludes at least 2 t/ha corn and soybean residues and 0.5 t/ha of small grain residues that were likely left in the field. 71 metric tons of collectible 'surplus' residue (usable) might be considered for fuel – with 87% from corn and small grains (table 1).

Growing crops for fuel. Agricultural crops grown under modern management methods are effective multipliers of fossil energy by capturing and converting solar radiation. Table 2 shows yields in tons and net energy as well as the net energy ratio for various crops. Yields averaged over 15 t/ha per year for Napier grass, kenaf and corn. Napier grass provided the greatest net energy return followed by whole corn plants, kenaf, slash pine, alfalfa, and corn kernels. The net energy ratio indicates slash pine returns 26.8 times as much energy as is required to produce the crop; this is followed by alfalfa (15.1), kenaf (13.6) and Napier grass (13.4)[2,3].

Calvin has written extensively about the direct photosynthetic production of hydrocarbons from Euphorbias, Aselepias and other hydrocarbon-containing plants[4].

Lipinsky at the Battelle Memorial Institute has focused on the use of sweet sorghum and sugar crops for fuel or industrial feedstock[5]. The ethanol concept has the potential for a positive net energy return if the byproducts are utilized effectively.

Opinions differ on the availability of land for biomass production. Zeimetz estimates that over 90% of the 190 million ha of U.S. cropland is of sufficient quality to support biomass production. However, conservation measures must be applied to about one half of this land to prevent soil and environmental degradation[6]. An additional 89 million ha of pasture and rangeland have the potential for sustaining biomass crops. Another 65 million ha of forest land might be suitable for growing biomass for energy. Whether or not this land would actually be used for biomass crops depends on price/cost relationships. Much of the land would require investment to bring it to its full production potential. Also, withdrawal of cropland, pasture, range and forest lands for biomass farms or any other use might conflict with the growing demand for food, feed and fiber products.

Larsen et al.[7] emphasize that crop residues on the land are not necessarily surplus. It is difficult to say how much residue can be removed because the answer depends on so many site specific factors – soil type and fertility level, topography, and climate. Posselius and Stout[8] have developed a computer program that determines how much crop residue can be removed from each field considering wind and water erosion, nutrient removal and other factors.

Forages. The present production on pasture and haylands in the U.S. provides feed for the nation's livestock with little surplus. By developing a new market for biomass fuels, millions of tons of additional biomass could be produced from the current pasture and hayland acreage (tables 3 and 4). The 'surplus' in table 4 is 93 million metric tons if 2.5 t/ha is produced above and beyond livestock feed requirements and 186 million metric tons if 5 t/ha are produced. Additional fertilizer would be needed, but Barber[1] estimates a favorable energy output/input ratio of 8:1 for producing biomass on hayland.

The combined output of residues and forages could produce 2–4 · 10^{18} J of energy or 15–30 million m^3 of

Table 1. Collectible 'surplus' residues

Crop	Amount (mega tons metric)
Corn	34
Small grains	31
Rice	5
Sorghum	1
Sugarcane	½
Total:	71

Source: Barber[1].

Table 2. Energy potential for various crops

Crop	Yield (t/ha-year)*	Net energy produced (GJ/ha)**	Net energy ratio***
Alfalfa	12.1	202	15.1
Corn, whole	19.3	324	13.0
Corn, kernels	7.7	161	8.6
Kenaf	19.5	309	13.6
Napier grass	50.2	803	13.4
Slash pine	14.5	238	26.8
Wheat, whole	7.4	114	8.0
Wheat, grain	2.9	43	3.4

* t/ha-yr means metric tons/hectare/year;
** GJ = gigajoule = 10^9 joules;
*** $\frac{\text{gross energy produced} - \text{energy input}}{\text{energy input}}$.

Source: Keener and Roller[2].

Table 3. Present pasture and hayland in Eastern U.S.

Region	Hay	Cropland pasture	Non-cropland pasture
	(million hectares)		
Northeast	2	2	1
North Central	7	8	8
South	3	9	10
Total:	12	19	19

Source: Barber[1].

Table 4. 'Surplus' biomass potential from pasture and hayland in Eastern U.S. (yield in addition to livestock needs).

Region	+ 2.5 t/ha (million metric tons)	+ 5 t/ha
Northeast	11	22
North Central	43	86
South	39	77
Total:	93	186

Source: Barber[1].

alcohol per year, enough to substitute for 5–9% of the nation's gasoline supply.

DOE estimates of available biomass raw material. The U.S. Department of Energy alcohol fuels policy review commissioned 5 individual studies to assess biomass raw material availability and economics[9]. While the focus was on alcohol fuels, the data assembled give a good overview of biomass availability for any fuel use.

To clarify the meaning of 'available' feedstocks, consider that usually, 'available' refers to what is non-competitive with the clearly higher values of a particular feedstock. Assuming no new or marginal cropland is brought into production, available grain crops are generally those which can be grown on existing cropland in the absence of any USDA policy of production restriction and which are not needed for projected demands of food, feed or export markets. Food processing wastes or by-products include such things as citrus rind, pulp, and corn starch strains from a corn sweetener plant.

Available crop residues exclude an average of 35% of all residues estimated as the minimum the farmer must leave on the land. The amount of residue that must be returned to the land is highly site specific and depends on the soil type, topography, climatic factors and crops[10].

The maximum available U.S. biomass resources total 700 million dry metric tons annually (table 5). Wood accounts for 61% of this total, agricultural residues 23%, municipal solid waste 10%, grains 5% and food processing wastes 1%. A more conservative estimate of 72.8 million dry metric tons of biomass potentially available from wastes supplemented by grains grown on set-aside lands is given by DOE[1].

Significance of biomass fuels. Clearly, millions of tons of biomass could be available for fuel. Researchers at Purdue University[11] estimated the technical energy potential for direct combustion of biomass (excluding grains) to be $1.7\text{–}3.4 \cdot 10^{18}$ J. The technical potential for alcohol production (using residues, forage and grains) would be 42–68 million m^3 per year or 9–15% of the U.S. gasoline consumption. These numbers represent the technical potential only. The Office of Technology Assessment[12] concluded that $11\text{–}16 \cdot 10^{18}$ J could be produced from biomass by the year 2000 if biomass fuels were vigorously promoted. Where biomass is available and the technology for using it for fuel in a cost-effective manner exists or can be developed, it seems prudent to do so. For a nation that uses $79 \cdot 10^{18}$ J of energy each year, biomass fuels are likely to provide only a small percentage of our national energy needs. But if biomass fuels meet 1% of our nation's energy needs, this is significant!

Biomass conversion technologies

Many processes or technologies exist for converting biomass to a more useful form for fuel or industrial feedstocks. Most are classified as wet or dry processes (fig. 1). Dry processes include direct combustion and gasification; wet processes include anaerobic and alcohol fermentation. (Methanol production is not discussed because it is not normally made from agricultural feedstocks.) The 2 primary uses of this energy are heat and fuel for mobile vehicles.

Table 5. Projected maximum U.S. biomass resources available

	Quantities in million dry metric tons per year							
	1980		1985		1990		2000	
	Quantity	%	Quantity	%	Quantity	%	Quantity	%
Wood*	453	61	421	56	389	49	498	48
Agricultural residues	175	23	200	26	218	28	252	24
Grains**								
Corn	20	–	18	–	7	–	–	–
Wheat	11	–	14	–	15	–	18	–
Grain sorghum	4	–	3	–	3	–	3	–
Total grains	34	5	35	5	25	3	21	2
Sugars**								
Cane	–	–	3	–	12	–	12	–
Sweet sorghum	–	–	5	–	51	–	144	–
Total sugars	–	–	7	1	63	8	156	15
MSW	78	10	83	11	90	11	105	10
Food processing wastes	6	1	7	1	8	1	10	1
Total	746	100	753	100	793	100	1042	100

* Assumes wood from silvicultural energy farms starting in 1995.
** Estimates for grains and sugars assume an aggressive development program to establish sweet sorghum as a cash crop. This program would divert land from corn in 1990 and 2000 - 1.9 and 2.8 million hectares (4.7 and 7 million acres) respectively.
Source: Department of Energy[9]. The report of the alcohol fuels policy review, p.48.

If heat is needed and the biomass is relatively dry, direct combustion may be the most efficient and effective process. Heat may be used to produce steam and electricity if desired. Various gasification processes will produce a low or medium Btu gas (gas of low or medium caloric value, about ¼ and ½ of natural gas respectively) if that energy form is desired for stationary engines or heat.
If the biomass is wet, e.g., animal manure, anaerobic fermentation will yield a low Btu gas, primarily methane. For mobile vehicles requiring a high energy density fuel (most commonly a liquid), synthetic liquid fuels may be produced from many feedstocks. Alcohol fuels may be produced by direct fermentation of sugar crops or by hydrolysis of starches or cellulosic materials followed by fermentation (fig. 2).

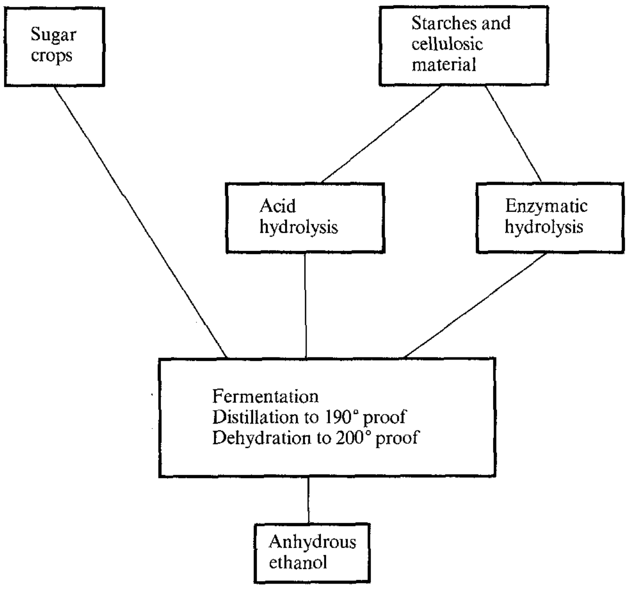

Figure 1. Process alternatives for converting biomass to gaseous, liquid or solid fuels.

Direct combustion. Technology for direct combustion is old and highly developed. It is in wide use commercially, accounting for most of the $1.9 \cdot 10^{18}$ J of energy presently generated from wood. Much research is under way to develop suitable combustion systems for wet biomass and to study optimum particle size, feeding systems, particulate control, biomass mixtures with oil or coal, suspended burning systems, etc.
Buchele[13] and others have conducted research on converting the energy value of cornstalks to useful forms by burning cornstalks as a companion fuel with high sulfur coal in boilers at electric generating plants. Shredded cornstalks were fed to the traveling-grate boiler of the Ames, Iowa, power plant at a rate of 4.5 t/h. The stalks burned well with no special problems.

Burning in an excess of air. One purpose of burning is to eliminate unwanted waste; burning in a open pile and incineration are examples. Some type of furnace is required to collect and distribute the heat generated, and combustion may occur inside or outside tubes. Provisions must be made to: a) introduce the organic particles or shredded material; b) provide an adequate air flow to maintain an excess oxygen supply; c) remove the residue or ash; and d) control particulate emissions. Air flow may be by natural or forced draft.
There are two types of air-suspended combustion systems: a) those which suspend the burning fuel in the gas stream in the combustion enclosure; and b) those which suspend the fuel in the gas stream and in another medium, the fluidized bed. Advantages of flue-gas stream suspension include a more rapid response to automatic control, an initial cost saving due to lack of grate surface and mechanical stoking devices, and the ability to complete combustion with a much smaller percentage of excess air in the furnace.
Fluidized-bed suspension burning systems have all

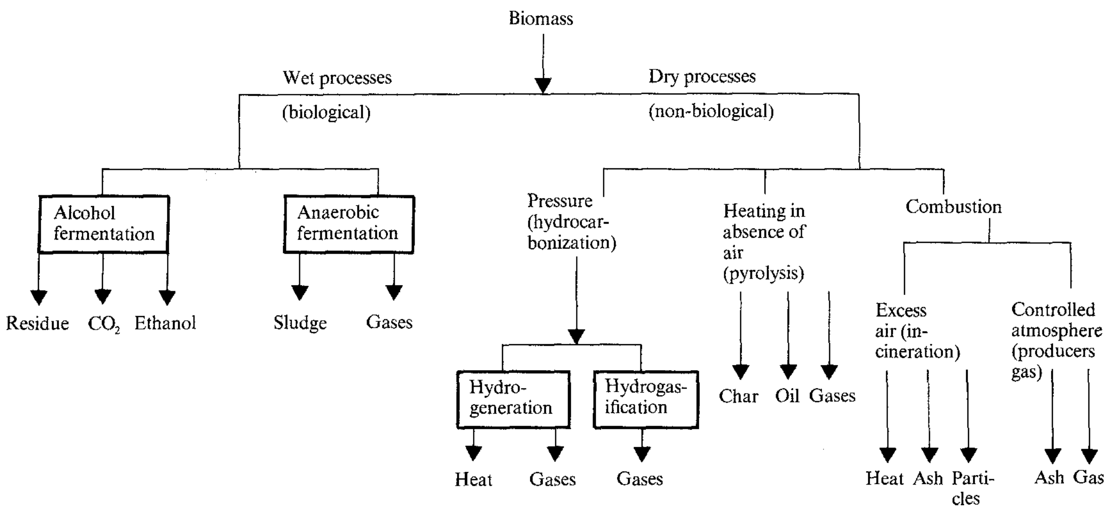

Figure 2. Production of 200° proof anhydrous ethyl alcohol from starch, sugar or cellulosic materials.

the advantages of the fluegas stream suspension, plus one that is important when a system must operate intermittently. Fluidized beds, usually sand, comprise a 'termal flywheel' or large capacity. Once operating temperature is reached, they retain heat over a long period, losing only about 110 °C during an overnight shutdown. The savings of auxiliary fuel for preheat on the next start-up are appreciable.

Burning in a controlled atmosphere. Gasification is the conversion of a solid or liquid to a gas. If the oxygen supply is restricted, incomplete combustion occurs releasing combustible gases such as carbon monoxide, hydrogen and methane. A solid residue or char remains. Gasification is discussed in detail later.

Heating in the absence of air. Pyrolysis is the transformation of an organic material into another form by heating in the absence of air. If heat is applied slowly, the initial products are water vapor and volatile organic compounds. Increased heat leads to recombination of the organic materials into complex hydrocarbons and water. The principal products of pyrolysis are gases, oils and char.

Producer gas generation. A producer gas generator produces a combustible gas from crop residues, wood chips or charcoal. (During World War II, in Europe and Japan, producer gas generators or gasifiers were often used to operate tractors, automobiles and buses, because petroleum was scarce.) The feedstock is heated to 1000 °C and reacts with air, oxygen, steam or various mixtures of these to produce a gas containing about 30% carbon monoxide (CO), 15% hydrogen (H_2) and up to 3% methane (CH_4) (table 6).

Table 6. Gas analysis from an updraft producer gas generator using charcoal

	Percentage by volume
CO	25–30
H_2	10–14
CO_2	5–8
O_2	0.5–1.5
CH_4	0–2.5
N_2 and others	50–53

Source: Posselius et al.[14]. An updraft producer gas generator, p. 3.

There are 2 basic generator designs: the updraft and the downdraft. In an updraft generator, hot gases flow counter to the feedstock. Part of the fuel stock is pyrolyzed and the resulting gas has a high tar content. In the downdraft system, pyrolysis products are broken down as they pass through the reaction zone before combining with the exiting gases. Since downdraft generators have the potential to eliminate tar from gas, they are probably better suited for burning crop residues as a fuel source[15].

Anaerobic digestion

Anaerobic digestion is a conversion process for wet biomass such as animal manure, municipal sewage and certain industrial wastes. Through this process complex organics are converted into methane and other gases. An effluent is also produced which can be used as fertilizer or animal feed. An extensive bibliography[16] on anaerobic digestion was prepared for EPA in 1978.

Anaerobic digestion is a biological process carried out by living microorganisms:

Organic matter + bacteria + water → methane + carbon dioxide + hydrogen sulfide + stabilized effluent.

This process occurs only in the absence of free oxygen. Methane-forming bacteria are sensitive to environmental conditions such as pH (6.6–7.6 optimum), temperature (35 °C and 54 °C are 2 preferred levels), and carbon/nitrogen ratio (30^{-1} optimum).

Man-made digesters, or containers that keep the feedstock isolated from air can be of either the batch or continuous flow type. Advantages of the batch type include:

- feedstock availability is often sporadic and comes in batches;
- daily management is minimal; and
- relatively inexpensive.

Disadvantages of the batch type are:

- much labor is needed to load and unload digester;
- gas production is sporadic; and
- not as efficient as continuous digester.

Table 7. Approximate daily production and heat values for biogas

Livestock (454 kg b.wt)	Approximate biogas production (m^3/day)	Approximate heat value (MJ)*	Approximate equivalents Gasoline (l)**	Diesel fuel (l)**	Natural gas (m^3)**	Propane (kg)**
Beef	0.85	19	0.57	0.53	0.51	0.4
Dairy	1.3	29	0.87	0.76	0.76	0.6
Poultry broilers	2.6	58.3	1.7	1.6	1.6	1.2
Poultry layers	2.0	45.6	1.4	1.2	1.2	1.0
Swine	0.82	18.4	0.57	0.49	0.48	0.4

* Assumes biogas containing 60% methane or heating value 22 MJ/m^3.
** Heating values: gasoline, 5.6 MJ/l; diesel fuel, 37.1 MJ/l; natural gas, 37 MJ/m^3; propane, 49 MJ/kg.

While early digesters were usually of the batch type, the continuous flow type is considered an improvement.

Although many factors affect output, table 7 illustrates the gas production rate and energy output for various feedstocks. To translate energy output into common language, the daily manure from a single 630-kg dairy cow could produce 1.8 m^3 of biogas[17].

Biogas consists of 60–70% methane, 30–40% carbon dioxide and a trace of hydrogen sulfide, ammonia gas and water vapor. Biogas has an energy content around 22 MJ/m^3. Methane or biogas are 'permanent' gases and cannot be liquified at any pressure at commonly occurring temperatures, seriously limiting their use in mobile vehicles.

These gases are better suited for use in high compression (13–14:1) stationary engines designed or modified to operate on methane. In biogas-powered stationary engines, waste heat can be recirculated in the digester coil and gas can be used as it is produced without a compressor storage unit. Full engine power is realized only if carbon dioxide is removed from the biogas mixture to increase the energy content of the gas. Longer engine life is attained if hydrogen sulfide is also eliminated from the gas before use.

Biogas may be used to heat livestock buildings by scrubbing H_2S only, but the 30–40% CO_2 will necessitate additional venting and this requires more heating energy. The CO_2 would not present a problem in greenhouse heating, however.

Digester waste or sludge is an excellent fertilizer containing all the potassium and phosphorus and up to 99% of the nitrogen originally in the manure. In addition, trace elements such as boron, calcium, iron, Mg, S and Zn remain unchanged. Sludge could also be used in livestock rations if mixed with molasses, grains and roughage. Water must be removed by centrifuge to concentrate the protein, but some of the protein will be dissolved in the water and lost.

The relative economy of an anaerobic digester is probably the most important factor in determining its feasibility. However, an accurate economic picture for the anaerobic digester is difficult to project if specific aspects of its implementation remain unknown: a) the cost of energy; b) what will sludge be used for; c) what type of system will be used; d) how much salvaged material will be used; and e) what is the nature of the farm operation. Nevertheless, rough guidelines can be provided. One method of analysis gives the estimated digester construction costs per animal. These estimated costs range from \$200 to \$300/cow and from \$40 to \$120/pig. A second method considers both construction costs and potential economic returns to provide the minimum digester size (in animal units) necessary for economic feasibility. Estimates for the minimum digester size for economic viability range from a 200- to 400-cow digester.

Alcohol fuels

Ethyl alcohol (ethanol) is made by fermentation of sugars. Where grains or other starchy materials are used this step is preceded by enzymatic conversion of starches[18]. Much research is underway to hydrolyze cellulosic materials and then convert them to alcohol.

Ethanol is a premium fuel and can be blended with unleaded gasoline and burned with no modification of today's engines. A 10% blend of ethyl alcohol with 90% unleaded gasoline is presently being marketed as 'Gasohol'.

Ethanol costs more than gasoline today but the technology for producing it is very dynamic. Much controversy surrounds the energy balance, but the latest technology yields a positive net energy return[19]. Furthermore, there is no reason to use petroleum in the production of alcohol.

Alcohol plant sizes range from less than 4 kL/day (classified as a small scale by the Department of Energy)[9] to more than 75 ML per year. Large plants offer economies of scale, but farm level plants may be competitive when collection, storage and transportation costs are minimal[20,21].

The technology and thus the economics of producing alcohol are quite dynamic. Many have taken firm stands against alcohol fuels based on obsolete data. There is every reason to expect that with improved technology – heat recycling, improved distillation methods, membrane separation and integrated systems which permit wet feeding of by-products – the energy balance and economics of alcohol production can be improved. Certainly, it is in our national interest to attempt to make alcohol an attractive extender of scarce gasoline.

Ethanol is an excellent fuel for spark-ignition engines and may be considered for diesel engines, gas turbines, fuel cells and petrochemical feedstocks[18,19]. Many reports on alcohol fuel applications are available. For example, the American Petroleum Institute Task Force EF-18 reviewed the properties of ethanol and methanol and their suitability as automotive fuels[22]. It concluded that since alcohol fuels are more expensive than gasoline, their best use would be in premium fuel applications where their clean burning and low nitrogen oxide formation characteristics could be used advantageously. Straight alcohol fuels, if used in engines specifically designed for optimum use of their properties, offer potential advantages that could outweigh the disadvantages in certain situations[23].

Major issues

Biomass for fuels is a complex subject involving the growth, collection, densification, transport, conversion and utilization of organic material. Often, biomass for fuels must compete with important alternative uses. The impact of biomass for fuels on food, feed and fiber prices is not fully known. And the need to return organic material to the soil for erosion control and organic matter maintenance continues to be of concern. Also competition between food crops and fuel production from biomass is an unresolved issue and will need a great deal more attention[24]. Certainly, a net energy gain from biomass fuels relative to the petroleum input is essential for a successful biomass fuels program. However, an overall net energy gain may not be necessary in the short run if a low quality bulky fuel is upgraded to a high quality clean burning fuel, especially a high energy density fuel to power existing mobile vehicles.

Finally, a word on the autonomy of a fuels program. Of course, economics drives our free enterprise system. Although our economic system is already highly distorted by regulations, subsidies and tax incentives, a biomass fuels program should eventually stand on its own. Temporary subsidies and incentives may be justifiable to promote development of such a program due to the high risks and uncertainties involved.

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Ethanol from cellulose

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Summary. An excess of organic waste, containing up to 60% cellulose and hemicellulose is produced worldwide. The conversion of this cellulosic material to ethanol is discussed: The two-step process consisting of a hydrolysis step to glucose and the subsequent fermentation by yeasts; and the one-step process, a fermentation of the cellulose by the anaerobic thermophile *Clostridium thermocellum,* or by a thermophilic, anaerobic, defined mixed culture. The use of the latter seems to be very feasible. To achieve an economic process, it is suggested to combine this approach with a thermophilic fermentation of the effluent and/or stillage obtained to produce methane.