Fuel production from biomass: generation of liquid biofuels

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Abstracts: *Anaerobic fermentation processes may also be used to produce liquid fuels from biological raw materials. An example is the ethanol production from glucose, known as standard yeast fermentation in the beer, wine and liquor industries. It has to take place in steps, such that the ethanol is removed (by distillation or dehydrator application) whenever its concentration approaches a value (around 12%) which would impede reproduction of the yeast culture.*

Keywords: *biomass, liquid biofuels, methanol.*

INTRODUCTION

In order to reduce the primary biological material (e.g molasses, cellulose pulp or citrus fruit wastes) to glucose, the hydrolysis process may be used. Some decomposition takes place in any acid solution, but in order to obtain complete hydrolysis, specific enzymes must usually be provided, either directly or by adding microorganisms capable of forming such enzymes. The yeast fungi themselves contain enzymes caable of decomposing polysaccharides into glucose.

The theoretical maximum efficiency of glucose-to-ethanol conversion is 97%, and, according to Calvin (1977), the Brazilian alcohol industry in 1974 obtained 14% of the energy in the raw sugar input, in the form of ethanol produced by fermentation of just the molasses residue from sugar refining, i.e. in addition to the crystallised sugar produced. A current figure is 25% (see Fig. 1) for an optimised plant design.

Mechanical energy input, e.g. for stirring, could be covered by the fermentation wastes if they were burned in a stea power plant. In the European example, these inputs amount to about a third of the energy inputs throught the sugar itself.

Alternative fermentation processes based on molasses or other sugar-containing materials produce acetone-butanol, acetone-ethanol or butanol-isopropanol mixtures, when the proper bacteria are added. In addition, carbon dioxide and small amounts of hydrogen are formed.

DIRECT PHOTOSYNTHETIC PRODUCTION OF HYDROCARBONS

Oil from the seeds of many plants, such as rape, olive, groundnut, corn, palm, soy bean, and sunflower, is used as food or in the preparation of food. Many of these oil will burn readily in disel engines and can be used directly or mixed with diesel oil of fossil origin, as they are indeed in several pilot projects around the world. However, in most of these cases the oil does not constitute a major fraction of the total harvest yield, and any expansion of these crops to provide an excess of oil for fuel use would interfere with food production. A possible exception is palm oil, because inter-cropping of palm trees with other food crops ma provide advantages such as retaining moisture and reducing wind erosion. Much interesr is therefore concentrated on plants that yield hydrocarbons and that, at the same time, are capable of growing on land unsuited for food crops.

The gopher plant has about 50% sterols (on a dry weight basis) in its latex, 3% polisoprene (rubber), and a number of terpenes. The sterols are suited as feedstocks for replacing petroleum in chemical applications. Yields of first-generation plantation experiments in California are 15-25 barrels of crude oil equivalent or some 144 GJ ha^{-1} (i.e., per $10^4 \, m^2$).

ALCOHOL FERMENTATION

The ability of yeast and bacteria such as Zymomonas mobilis to ferment sugar-containing material to form alcohol is well known from beer, wine, and liquor manufacture. If the initial material is cane sugar, th fermentation reaction may be summarised as

$$C_6H_{12}O_6 \rightarrow 2C_2H_2OH + 2CO_2 \qquad (1)$$

The energy content of ethanol is 30 MJ kg^{-1}, and its octane rating is 90-100. With alternative fermentation bacteria, the sugar may be converted into butanol, $C_2H_5(CH_2)_2OH$. In Brayil, the cost of ethanol is finally coming down to that of gasoline.

In most sugar-containin plant material, the glucose molecules exist in polymerised form such as starch or cellulose, of the general structure $(C_6H_{10}O_5)_n$. Starch or hemicellulose is degraded to glucose by hydrolysis, while lignocellulose resists degradation owin to its lignin content. Lignin glues the cellulosic material together to keep its structure rigid, whether it be crystalline or amorphous. Wood has a high lignin content (about 25%), and straw also has considerable amounts of lignin (13%), while potato or beet starch contain very little lignin.

Some of the lignin seals may be broken by pre-treatment, ranging from mechanical crushing to the introduction of swelling agents causing rupture.

The hydrolysis process is given by

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow 2C_2H_2OH \qquad (2)$$
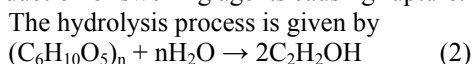
In earlier times, hydolysis was always achieved by adding an acid to the cellulosic material. During both world wars, Germany produced ethanol from cellulosic material by acid hydrolysis, but at very high cost. Acid recycling is incomplete; with low acid concentration the sugar already formed from hemicellulose is destroyed.

Consequently, alternative methods of hydrolysis have been developed, based on enzymatic intervention. Bacterial (e.g., of the genus Trichoderma) or fungal (such as Sporotrichum pulverulentum) enzymes have proved capable of converting cellulosic material, at near ambient temperatures, to some 80% glucose and a remainder of cellulosic material, at near ambient temperatures, to some 80% glucose and a remainder of cellodextrins (which could eventually be fermented, but in a separate step with fermentation microorganisms other than those responsible for the glucose fermentation).

The residue left behind after the fermentation process can be washed and dried to give a solid product suitable as fertilisr or as animal feed. The composition depends on the original material, in particular with respect to lignin content (small for residue of molasses, beets, etc., high for straws and woody material, but with fibre structure broken as a result of the process described above). If the lignin content is high, direct combustion of the residue is feasible, and it is often used to furnish process heat to the final distillation.

The outcome of the fermentation process is a water-ethanol mixture. When the alcool fraction exceeds about 10%, the fermentation process slows down and finally halts. Therefore, an essential step in obtaining fuel alcohol is to separate the ethanol a step that may make the overall energy inputs (fertiliser, vehicles, machinery) and all process inputs (cutting, crushing, pre-treatment, enzyme recycling, heating for different process steps from hydrolysis to distillation), as well as energy for transport, is, in existing operations such as those of the Brazilian alcohol programme, around 1.5 times the energy outputs (alcohol and fertiliser if it is utilised). However, if the inputs are domestic fuels, for example, combustion of residues from agriculture, and if the alcohol produced is used to displace imported oil products, the balance might still be aquite acceptable from a national economic point of view.

If, further, the lignin-containing materials of the process are recovered and used for process heat generation (e.g. distillation), then such energy should be counted not only as input but also as output, making the total input and output energy roughly balance. Furthermore, more sophisticated process design, with cascading heat usage and parallel distilation columns operating with a time displacement such that heat can be reused from column to column, could reduce the overall energy inputs to 55-65% of the outputs.

Radically improved energy balances would emerge if distillation could be replaced by a less energy intensive separation method. Several such methods for separating water and ethanol have been demonstrated on a laboratoryu scale, including: drying with desiccants such as calcium hydroxide, cellulose, or starch; gas chromatography using rayon to retard water, while organic vapours pass through; solvent extraction using dibutyl phthalate, a water-immiscible solvent of alcohols; and passage through semi-permeable membranes or selective zeolite absorbes and phase separation. The use of dry cellulose or starch apears pariculary attractive, because over 99% pure alcohol can be obtained with less than 10% energy input, relative to the combustion energy of the alcohol. Furthermore, the cellulosic material may be cost-free, if it can be taken from the input stream to (the fermentation reaction being wet anyway). The energy input of this scheme is for an initial distillation, bringing the ethanol fraction of the aqueous mixture from an initial 5-12% up to about 75%, at which point the desiccation process is started. As can be seen from Figure 1, the distillation energy is modest up to an alcohol content of 90% and then starts t rise rapidly. The drying process thus substitutes for the most energy-expensive part of the distillation process.
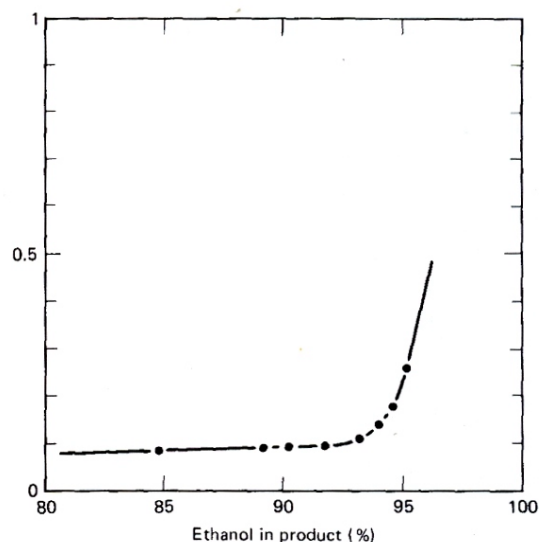

Figure1. Distilation energy for ethanol-water mixture, as a function of ethanol content

The ethanol fuel can be stored and used in the transportation sector much the same way as gasoline. It can be mixed with gasoline or can fully replace gasoline in spark ignition engines with high compression ratios. The knock resistance and high octane number of ethanol make this possible, and

with pre-heating of the alcohol (using combustion heat that is recycled), the conversion efficiency can be improved. Several countries presently use alcohol-gasoline blends with up to 10% ethanol.

This does not require any engine modification. Altering the gasoline Otto engines may be iconvenient in a transition period, but if alcohol distribution networks are implemented and existing gas stations modified, then the car engines could be optimised for alcohol fuel without regard to present requirements. A possible alternative to spark ignition engines is compression ignition engines, where autoignition of the fuel under high compression (a ratio of 25) replaces spark or glow plug ignition. With additives or chemical transformation into acetal, alcohol fuels could be used in this way. Ethanol does not blend with diesel oil, so mixtures do require the use of special emulsifiers. However, diesel oil can be mixed with.

A number of concerns with regard to the environmental impacts of yhe ethanol fermentation energy conversion chain must be considered. First of all, the biomass being used may have direct uses as food or many be grown in competition with production of food. The reason is, of course, that the easiest ethanol fermentation is obtained by starting with a raw material with as high a content of elementary sugar as possible, that si, starting with sugar cane or cereal grain. Since sugar cane is likely to occupy prime agricultural land, and cereal production must increase with increasing world population, neither of these biomass resources should be used as fermentation inputs. However, residues from cereal production and form necessary sugar production (present sugar consumption is in many regions of the world too high from a health and nutrition point of view) could be used for ethanol fermentation, toghether with urban refuse, extra crops on otherwise committed land, perhaps aquatic crops and forest renewable resources. Recycling nutrients, and covering topsoil to preven erosion are very appropiate in connection with the enhanced tillage utilisation that characterises combined food and ethanol production schemes.

The hydrolysis process involves several potential environmental impacts. If acids are used, corrosion and accidents may occur, and substantial amounts of water would be required to clean the residues for re-use. Most acid would be recovered, but some would follow the sewage stream. Enzymatic hydrolysis would seem less cumbersome. Most of the enzymes would be recycled, but some might escape with waste water or residues. Efforts should be made to ensure that they are made inactive before any release. This is particularly important when, as envisaged, the fermentation residues are to be brought back to the fields or used as animal feed. A positive impact ts the reduction of pathogenic organisms in residues after fermentation. Transport of biomass could

involve dust emissions, and transport of ethanol might lead to spills (is insignificant amounts, as far as energy is concerned, but with possible local environmental effects), but overall the impacts from transport would be very small.

Finally, the combustion of ethanol in engines or elsewhere leads to pollutant emissions. Compared with gasoline combustion, emissions of carbon monoxide and hydrocarbons diminish, while those of nitrous oxides, aromatics, and aldehydes increase, assuming that modified ignition engines are used. With special ethanol engines and exhaust controls, critical emissions may be controlled. In any case, the lead pollution still associated with gasoline engines in some countries would be eliminated.

The energy balance of current ethanol production from biomass is not very favourable. A European study has estimated the energy flows for a number of feedstocks. The highest yield of about 100 GJ ha^{-1} is found for sugar beets, shown in Figure 1, but the process energy inputs ad alloted life-cycle inputs into technical equipment are as large as the energy of the ethanol produced. A part of this may be supplied from biogas coproduced with the ethanol, but the overall enrgy efficiency remains low.
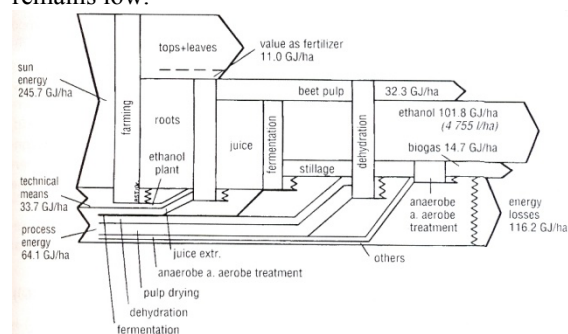

Figure 2. Energy flows in the production of ethanol from sugar beets. Energy inputs to biomass growth,harvesting and transport are not indicated

In a life-cycle analysis of ethanol production, the fact that such production is currently based upon energy crops rather than on residues (sugar cane or beets rather than straw and husk) means that all energy inputs and environmental impacts from the entire agricultural feed-stock production should be included along with the impacts pertaining to the ethanol plants and downstream impacts. Clearly, it is very difficult in this mode to balance energy outputs and inputs and to reach acceptable impact levels. The interest should therefore be limited to bio-energy processes involving only residues from an otherwise sensible production (food or wood).

METHANOL FROM BIOMASS

There are various ways of producing methanol from biomass sources, as indicated in

Figure 3. Starting from wood or isolated lignin, the most direct routes are by liquefaction or by gasification. The pyrolysis alternative gives only a fraction of the energy in the form of a producer gas.
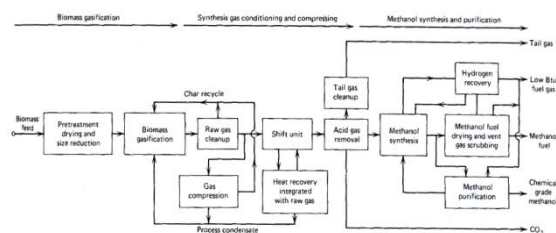

Figure 3. Non-food energy uses of biomass

By high-pressure hydrogenation, biomass may be transformed into a mixture of liquid hydrocarbons suitable for further refining or synthesis of methanol, but all methanol production schemes so far have used a synthesis gas, which may be derived from wood gasification or coal gasification. The low-quality producer gas resulting directly from the wood gasification is a mixture of carbon monoxide, hydrogen gas, carbon dioxide, and nitrogen gas. If air is used for gasification, the energy conversion efficiency is possible, and the gas produced has less nitrogen conformed with heat from solar collectors, for example, in a fluidised bed gasifier maintained at 500^0C.

The producer gas is cleaned, CO_2 and N_2 as well as impurities are removed (the nitrogen by cryogenic separation), and methanol is generated at elevated pressure by the reaction

$$2H_2 + CO \rightarrow CH_3OH. \qquad (3)$$
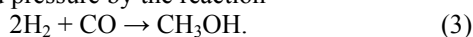
The carbon monoxide and hydrogen gas (possibly with additional CO_2) is called the synthesis gas, and it is usually necesary to use a catalyst in order to maintain the proper stoichiometric ratio between the reactants of (3). A schematic process diagram is shown in Figure 4.

Figure 4. Schematic flow diagram for biomass to methanol conversion process

An alternative is biogas production from the biomass folowed by the methane to methanol reaction,

$$2CH_4 + O_2 \rightarrow 2CH_3OH \qquad (4)$$

Also used in current methanol production from natural gas. Change of the H_2/CO stoichiometric ratio for (4) is obtained by the shift reaction (5)

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (5)$$
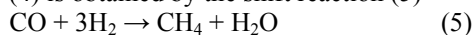
Steam is added or removed in the presence of catalyst (iron oxide, chromium oxide).

The conversion efficiency of the synthesis gas to methanol step is about 85%, implying an overall wood to methanol energy efficiency of 40-50%. Improved catalytic gasification techniques raise the overall conversion efficiency to some 55%. The currently achieved efficiency is about %0%, but all life-cycle estimates of energy inputs

have not been included or performed. The octane number of methanol is similar to that of ethanol, but the heat of combustion is less, amounting to 18 MJ kg^{-1}. However, the engine efficiency of methanol is higher than that of gasoline by at least 20% for current motor car engines, so an effective energy content of 22.5 MJ kg^{-1} is sometimes quoted. Methanol can be mixed with gasoline in standad engines, or used in specially designed Otto or disel engines, such as a spark ignition engine run on vaporised methanol, with the vaporisation energy being recovered from the coolant flow. Uses are similar to those of ethanol, but several differences exist in the ssessment of environmental impacts, from production to use (e.g. toxixity of fumes at filling stations).

The gasification can be made in closed environments, where all emissions are collected, as well as ash and slurry. Cleaning processses in the methanol formation steps will recover most catalysts in re-usable form, but other impurities would have to be disposed of along with the gasification products. Precise schemes for waste disposal have not been formulated, but it seems unlikely that all nutrients could be recycled to agri- or silviculture as in the case of ethanol fermentation. However, the production of ammonia by a process similar to the one yielding methanol is an alternative use of the synthesis gas. Production of methanol from eucalyptus rather than from woody biomass has been studied in Brayil. More fundamental studies aiming to better understand the way in which methanol production relies on degradation of lignin are ongoing.

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