Turning crop waste into chemicals and fuel

We read much about how ethanol, methane (or methanol), hydrogen, and seed oils could be important fuels of the future. Some studies have suggested that agricultural materials could produce more than half the liquid fuel presently used for transport in Australia. These materials could also supply many chemicals used in industry.

A drawback with a number of these schemes is that they employ raw materials that could be used as human food. Dr Martin Playne and Dr Russell Smith, of the CSIRO Division of Chemical and Wood Technology, have been working on a system that may be able to produce comparable quantities of fuel from crop and wood residues — bagasse, cereal straw, bran, sawdust, and the like. In addition, the fermentation technique they are developing produces compounds that could be used as chemical feedstocks or solvents, and the economics of its use for this purpose appear favourable.

To date the most favoured biomass–fuel processes have been the use of yeast to produce ethanol from sugars and the heating of dry plant materials to produce gases that a catalyst can convert to methanol. Other possibilities that have been entertained include simple burning of crop wastes to recover heat energy, and using bacteria to produce methane gas in anaerobic digesters.

While some anaerobic bacteria are adept at producing methane, many others produce compounds called volatile fatty acids as a product of their digestion processes.

A 1926 Ballot, one of the few remaining examples. In its hey-day, cars of this sort travelled France testing a ketone fuel derived from sawdust.

Anaerobic bacteria can turn this bagasse (sugar cane waste) into liquid fuel.

Volatile fatty acids — such as acetic (in vinegar), propionic, and butyric acids — have high energy contents and could be used as chemical feedstock. Alternatively, these acids can be simply converted to their corresponding ketones. The best-known example is acetone, which forms from acetic acid when the acid is heated at about 250°C in the presence of catalysts and in the absence of oxygen. Conversion from acid to ketone is a familiar chemical process, and has relatively low energy requirements. Ketones can be used as fuels, or as fuel extenders and fuel octane improvers. In this latter role they would be more environmentally acceptable than the lead compounds used at present.

Dr Playne envisages a scheme with four stages:

- ▷ pre-treatment of the fibrous crop residue to increase the fermentability of the lignocellulose
- ▷ fermentation of the lignocellulose by mixed cultures of anaerobic bacteria to volatile fatty acids
- ▷ separation of the acids from the fermentation broth through a novel membrane
- ▷ conversion of the concentrated acids to ketone mixtures by heat

An artificial rumen

Formation of volatile fatty acids by fermentation is very common. It occurs in your compost heap, in your lower gut, between your teeth in dental plaque, in septic tanks and sewage-treatment works, in the mud floor of lakes, and in the main stomach (or rumen) of cattle and sheep.

Indeed, in ruminants, the process is the very basis of their existence. Nearly all the energy they require is derived directly from volatile fatty acids produced by bacteria in their rumens. Without cellulose-degrading bacteria, the animals could not digest the pastures they eat.

Anaerobic bacteria form different products in varying proportions depending upon the micro-organisms present, type of feedstock, pH, nutrients, and the level of enzyme inhibitors. Major products are always acids, carbon dioxide, and some hydrogen; sometimes alcohol is produced.

The idea is to try to reproduce the conditions found in the rumen in an efficient industrial-scale digester. The research is guided by the extensive knowledge that animal nutritionists have built up on the subject of rumen fermentation. Indeed, Dr Playne's previous work was in the field of rumen biochemistry.

And so he starts with a mixed bacterial culture derived from compost and sheep's rumen. Different bacteria multiply or decline in number according to the feedstock and conditions in the fermenter, and typically three or four microbial species come to dominate in a population that may approach 10^{13} micro-organisms per litre. Some of the bacteria in the mixed cultures feed on the products of others, a synergistic effect that leads to a concentration of acids stronger than any could achieve individually.

But what's wrong with alcohol fermentation by yeasts? The main consideration is that yeasts need sugary or starchy materials — just those substances that are used for human food. On the other hand, lignocellulose is a huge resource that is poorly utilized at present, and not for food. It can be converted to sugar before fermentation to alcohol, but this is expensive and not all the sugars formed can be used by yeasts. Furthermore, distillation of ethanol uses a lot of energy.

Of course, anaerobic bacteria can work very well on sugar and starch if these are available (in cannery waste, for example). Preliminary estimates indicate that ketones could be produced from crop and wood residues for much the same cost as fuel ethanol produced from sugar cane or oil derived from coal. However, producing methanol from straw would probably be cheaper. So ketones are not competitive as fuels at present, but may become so at much the same time as other alternatives to petroleum.

Some figures on cost are given in the accompanying box.

More significantly, though, fatty acids and ketones are much in demand as chemical feedstocks and solvents, and it appears that the cost of producing them by fermentation is about the same as their current market cost from petrochemical sources. This suggests that the first products of this fermentation process would be used in industry, rather than as a fuel.

Back in 1926, several cars were road-tested in France using ketone fuels made from sawdust by a combined fermentation and pyrolysis process. Abundant petroleum fuel came along soon after and stopped further development of this idea.

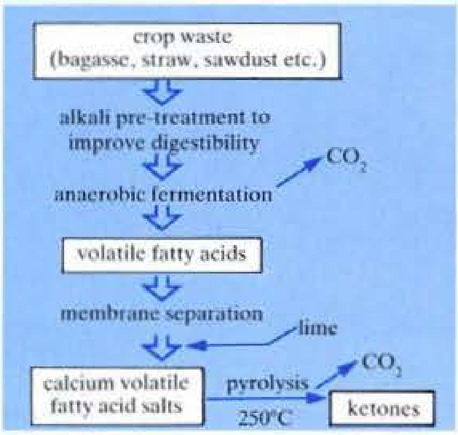
Dr Playne thinks the concept is worth reviving. It was suggested in 1976 by Dr Don Weiss, then Chief of the CSIRO Division of Chemical Technology. Dr Playne and Dr Smith have been working on the project since 1977, helped by a 3-year grant from NERDDP. Some aspects of the research have involved collaboration with Melbourne University's Department of Microbiology. Current research indicates that it is possible, on a laboratory scale at least, to convert 60% of the energy contained in bagasse to a ketone form, a promising result.

Different mixed cultures of anaerobic bacteria will produce these volatile fatty acids in different proportions. When the acids are heated, they break down to ketones (for example, acetic acid forms acetone).

Acids produced by anaerobic fermentation

$H.COOH$	formic
$CH_3.COOH$	acetic
$CH_3.CH_2.COOH$	propionic
$CH_3.CH_2.CH_2.COOH$	butyric
$CH_3.(CH_2)_3.COOH$	valeric
$CH_3.(CH_2)_4.COOH$	hexanoic
$CH_3.CHOH.COOH$	lactic
$COOH.CH_2.CH_2.COOH$	succinic

Ketones from crop wastes



Using this scheme, more than 60% of the energy in the feedstock can be transformed into ketones. Ketones can be used as fuel or as chemical feedstock.

Pre-treatment

In order to achieve such good results, it is necessary to increase the digestibility of the plant material with a simple pre-treatment with an alkali. Treatment with sodium hydroxide (caustic soda) or ammonia can increase the digestibility of bagasse from 25% (without treatment) to 60%. It opens up the lignocellulose fibres, making them more accessible to attack by the bacteria.

Dr Playne and co-workers in the Division have been closely examining this aspect of the process, and have found that more brutal pre-treatments can further improve digestibility. For example, they have found a combination of alkali, steam, and explosive depressurization that's particularly effective. Bagasse digestibility can be increased to more than 75% by cooking it for 5 minutes at 200°C in a 6% ammonia solution and then quickly releasing the pressure. (The process, known as 'explosion pulping', was developed by Dr Heikki Mamers of the Division, and was described in *Ecos* 21.)

For most of his investigations, Dr Playne has elected to work with bagasse. It is more digestible than wood waste, and large quantities accumulate at sugar mills. As well, the group has carried out some experiments on wheat straw and wood chips (both hard and soft woods).

Of course, any extra treatment costs money, and the cost of explosion pulping has been estimated at between $30 and $50 per tonne of bagasse treated. Whether the additional digestible matter produced is worth this is a difficult economic question. A similar question arises when the cost of alkali is considered. These costs have to be balanced against others — of raw materials, storage, and plant.

Dr Playne believes that ultimately a choice will have to be made between steam processing and alkali treatment and he suspects that the alkali route will give better value for money. It has the advantage that the alkali acts as a neutralizing agent to the volatile fatty acids. This means that more fermentation can take place before the bacteria become inhibited by the acidity of their own by-products.

In the choice of alkali, ammonia has the advantage that it does not lead to salt-disposal problems; also it acts as a fertilizer for the micro-organisms. If sodium hydroxide were used, some 30 kg or more of sodium ions would need to be disposed of for each tonne (dry weight) of bagasse processed.

Unfortunately, ammonia is quite expensive, and Dr Playne has been studying the effectiveness of other alkalis such as sodium carbonate and lime (calcium hydroxide). Lime is the cheapest alkali going, and it works well in a fermenter, even when added at concentrations as high as 300 g per kg of bagasse. Its only disadvantage is that calcium salts tend to form a hard scale, and any production scheme would need to take care of this aspect.

Laboratory experiments

Dr Playne has obtained yields of volatile fatty acids as high as 74% by weight of digestible organic matter in bagasse, or 54% of total dry weight. These figures, and the speed of production, are much greater than those previously achieved. While the conversion performance is not up to that achieved in sugar fermentation, bagasse is a much cheaper starting material than sugar.

Dr Playne believes it should be possible to raise the productivity figures still further. Creating conditions conducive to the growth of the bacteria calls for the right mixture of nutrients and the optimum temperature (35-9°C) and pH (6–7). Oxygen must be totally excluded.

Production of methane gas can occur, but this can be prevented quite easily, resulting in the production of acids and carbon dioxide gas only. However, halting carbon dioxide production is theoretically impossible, even though it represents some carbon loss. It has the advantage that oxygen is removed, leaving behind more energy-rich (and oxygen-depleted) fatty acids. The best approach is to minimize production of carbon dioxide by aiming for cultures that produce long-chain acids.

The question of costs

A preliminary costing of the process was completed in 1979. This indicated that production costs for mixed ketones would be between 22 and 56 cents per litre. The wide range resulted from the many unknown factors involved so early in the research and development stage of the project. For example, nothing much was known of the life of the membranes to be used in the product-recovery step. How often would they need replacing?

Since 1979, flow rates of acids across the membranes have been increased five-fold and the scientists are much surer of the yields of acids and ketones that they can obtain reliably. Acid yields of 640 kg, or ketone yields of 472 litres, are obtainable from 1 tonne of dry bagasse.

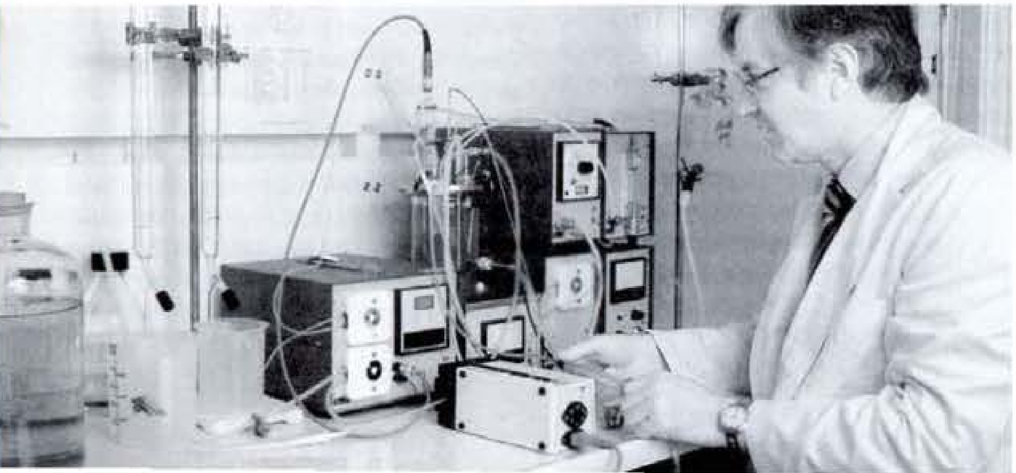
The result is that, even after allowing for the devaluation of money that has occurred since 1979, current costs lie between 22 and 30 cents per litre of ketones. Mixed ketones, while having an obvious niche in the market traditionally filled by methyl ethyl ketone as a solvent, would have to compete with other octane improvers and bridging agents used in the fuel industry.

If the pyrolysis stage is dropped off the process, mixed acids can be obtained. Cost of production of these is estimated to be much less — between 15 and 24 cents per kilogram. While there is no established market for a feedstock of short-chain-length mixed acids, current bulk-selling prices in Australia are about 80 cents per kg for acetic acid and about $1.00 per kg for propionic acid.

One problem is that the microbes' growth is hindered by the products — the very acids we want — of their own growth. In the mixed cultures used at present it is difficult to exceed 20 g of acids per litre without causing the fermentation to become inhibited.

However, Dr Playne believes it may be possible to select groups of organisms able to grow in much higher acid concentrations (60–90 g per L). After all, the age-old aerobic process of producing vinegar from alcohol takes place at high concentrations.

Dr Playne adjusts an automatic fermenter that is producing propionic acid from sugars.



At low pH, the acids change to an un-ionized state, and inhibitory effects become stronger. Alkalis can be added to raise the pH, but unfortunately this makes the acid separation process more difficult, as un-ionized acids are easier to separate out, no matter what the method used.

So overcoming the inhibition problem is an important aim of the research. It can be tackled in a number of other ways — one is a two-stage fermenter system; another is continuous removal of the acid products.

Separation crucial

Up till now we haven't mentioned how the acids would be separated from the fermentation broth; actually it is a crucial step with a major influence on the economics of the whole scheme.

The liquid stream from the fermenter contains a wide range of materials, including undigested lignocellulose, microbes, colloids, inorganic salts, dissolved ammonia and carbon dioxide, and organic chemicals.

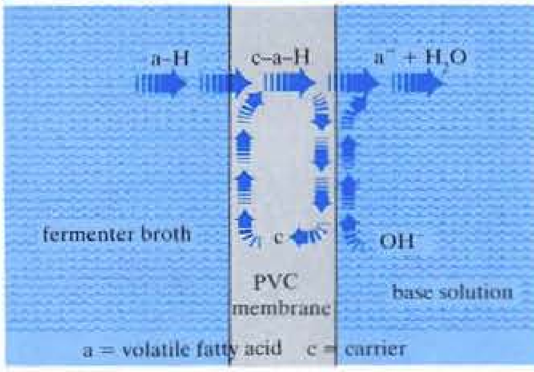
Only 1–2% (by weight) of this brew will comprise the volatile fatty acids we are after. Acetic acid forms 60–80% of all the acids produced.

After extraction of the acid product, the microbial cells could be either recycled back to the fermenter or harvested and sold as a protein-rich feed.

Methane digestion has the advantage that the methane spontaneously separates. Ethanol is sufficiently volatile that distillation from a yeasty beer is reasonably low in energy cost. However, the volatile fatty acids are close to water in their volatility. So if distillation is used to separate them out, extended processes, high in energy consumption, are needed.

Dr Smith has assessed a variety of alternatives, and has decided that separation by selective membranes offers the best prospect of success. He is working on the development of polyvinylchloride-based membranes that incorporate special acid-carrying entities.

How membrane separation works



The scientists are developing membranes, based on polyvinylchloride, that incorporate a special carrier. The carrier very much speeds up the separation of the volatile fatty acids from the fermenter broth.

These carriers — tri-n-octyl phosphine oxide is a good one — selectively pick up the volatile fatty acids from the fermenter and transport them across the membrane; then they are taken up as calcium salts by the solution on the other side. Since no phase change is involved, the energy consumption is small.

At present the flow of acids through the membranes is about half what the scientists believe is needed for an economic process. As well as improving the flow, they need to learn more about the life-time of the membranes and how prone the system is to fouling.

Separation is the step with the greatest number of unknowns, particularly with regard to cost. Further research under way seeks to maximize the permeability and durability of the membranes, to minimize their cost, and to reduce the amount of water that under some conditions gets transported with the acids.

As well as being the key to the viability of a process that makes excellent use of crop wastes, the membranes could find many uses in other industrial and food processes.

Andrew Bell

More about the topic

Acidogenic fermentation of wastes to produce chemicals and liquid fuels. M.J. Playne and B.R. Smith. *Proceedings, First ASEAN Workshop on Fermentation Technology, Kuala Lumpur, February 1982.*

Recovery of volatile fatty acids from fermenter effluents and their conversion to liquid fuels. B.R. Smith and M.J. Playne. *Proceedings, First ASEAN Workshop on Fermentation Technology, Kuala Lumpur, February 1982.*

Increased digestibility of bagasse by pretreatment with alkalis and steam explosion. M.J. Playne. *Biotechnology and Bioengineering*, 1984, **26** (in press).