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Ethanol from Cellulose Biomass *Not* Sustainable nor Environmentally Benign

Major technical and economic hurdles remain in getting ethanol from plant wastes, while burning ethanol produces carcinogens and increases ozone levels in the atmosphere.
Dr. Mae-Wan Ho

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Cellulosic ethanol the 'green gold'

One main limit to getting ethanol out of plant material is that most of the sugar substrate, apart from the starch in corn kernels and other grain, is unavailable for fermentation by bacteria and other microbes. It is locked away in cellulose, the fibrous materials that make up 75 to 85 percent of the plant, the rest being lignin, the woody material.

However, a cocktail of enzymes called cellulases are able to break down cellulose into sugar units, which can then be fermented by microbes into ethanol (see Box). That means grass, straw, and other crop residues can also be turned into ethanol. That has been hailed as the 'green gold' that could replace imported 'black gold' crude oil [1], and is widely seen to have the potential of substantially reducing our consumption of fossil fuel.

"It is at least as likely as hydrogen to be an energy carrier of choice for a sustainable transportation sector," the National Resources Defense Council (NRDC) and the Union of Concerned Scientists said in a joint statement. Shell Oil predicted the global market for biofuels such as 'cellulosic ethanol' would grow to exceed $10 billion by 2012.

A study funded by the Energy Foundation and the National Commission on Energy Policy concluded that "biofuels

coupled with vehicle efficiency and smart growth could reduce the oil dependency of our transportation sector by two-thirds by 2050 in a sustainable way." 'Smart growth' is a planning term which means growth that maximise sustainable development of cities in transport and other energy savings.

Cellulosic ethanol can be produced from a wide variety of feedstocks including agricultural plant wastes (corn stover, cereal straws, sugarcane bargasse), plant wastes from industrial processes (sawdust, paper pulp) as well as energy crops such as switchgrass.

Lee Lynd, engineering professor at Dartmouth, has been working with the Gorham Paper Mill to convert paper sludge to ethanol. Lynd said, "This is genuinely a negative cost feedstock. And it is already pretreated, eliminating a step in the conversion process."

The company Masada Oxynol is planning a facility in Middletown, New York, to process municipal solid waste into ethanol. After recovering recyclables, acid hydrolysis will be used to convert cellulosic materials into sugars. "The facility will provide both economic and environmental value," said David Webster, Executive Vice President of Masada. The process reduces or eliminates landfills. By-products of the process include gypsum, lignin and fly ash. The lignin will be recovered for burning to make the plant self-sufficient in energy, the fly ash can be put back into the soil as fertiliser.

How cellulases make cellulose a feedstock for ethanol

The cellulose crystal unit consists of thousands of strands, each strand made up of hundreds of glucose units linked up together. The cellulose is wrapped in a sheath of hemicellulose and lignin, which protects the cellulose from being broken down. Hemicellulose is easier to break down than cellulose [2]. A combination of mild heat, pressure and acidic (or basic) conditions will break the hemicellulose into its component mixture of sugars, mainly xylose.

Scientists in the National Renewable Energy Laboratory (NREL) of the Department of Energy (DOE) used dilute sulphuric acid to hydrolyse (break down by reacting with water) the hemicellulose/lignin sheath, exposing the cellulose. To hydrolyse cellulose chemically requires higher temperature and pressure and stronger acid conditions, involving rather expensive processing equipment; which is why they have looked to enzymes, *cellulases* , to do the trick.

Although humans cannot digest cellulose, cattle, termites, beaver, and mushrooms can. Some bacteria, fungi and insects produce cellulases themselves, other animals play host to bacteria that produce cellulases in their digestive tracts.

Most cellulases are complexes of three enzymes working together to hydrolyse cellulose. First, an *endoglucanase* breaks one of the chains within the cellulose crystal structure, then, an *exoglucanase* attaches to one of the loose ends, pulls the cellulose chain out of the crystal structure, and works its way down the chain, breaking off units of cellobiose (two glucose units joined together). Finally, a beta-glucosidase splits the cellobiose into two glucose molecules, which can then be fermented into ethanol.

Bringing production costs down

The cellulases needed for breaking down cellulose so far

have come from fungi, in particular from *Trichoderma reesei* . NREL scientists have investigated other sources, such as the bacterium *Acdiothermus cellulolyticus* , which they found in the hot springs of Yellowstone National Park. But bacterial exoglucanases are not usually as good as the fungal ones, though they tolerate high temperatures. A next step is to combine high temperature tolerance with the efficiency of the fungal enzyme. NREL and DOE have contracted the world's largest enzyme companies, Genecor International and Novozymes to reduce the cost of producing cellulases down to a range of $.10-$.20 per gallon of ethanol, and they have succeeded [1].

A further improvement involves the simultaneous action of enzyme and fermenting microbes, so that as the sugars are produced by the cellulases, the microbes ferment the glucose to ethanol [3].

Iogen Corporation based in Ottawa, Canada [4] was the first to develop the enzyme process for getting ethanol from cellulose. It has built the world's first and only demonstration scale facility to convert cellulose biomass to ethanol. The facility processes 40 tons of wheat straw per day, and Iogen became the first company to commercialise cellulosic ethanol in April 2004. The primary consumer so far has been the Canadian government, which along with the US government (particularly the DOE's NREL) has invested millions of dollars into helping commercialise cellulosic ethanol

Cellulosic ethanol sustainable?

A preliminary life-cycle analysis of cellulosic ethanol showed it reduces greenhouse gas emission by 89 percent over reformulated gasoline. By contrast sugar-fermented ethanol reduced GHG emissions by an average of 13 percent [5]. The energy yield appeared better than anything else, with a ratio of output over input of 1.98, which means that for every unit of energy input almost 2 units energy of cellulosic ethanol is produced; although this is very likely to be inflated due to flawed accounting procedures ("Biofuels for oil addicts", this series).

Can the US agricultural systems support large-scale cellulosic ethanol production? Is there sufficient land? Can biomass be supplied without impacting the cost of agricultural land, competing with food production and harming the environment? The answer to these questions ranges from no to a qualified yes, contingent upon R&D efforts, technological innovation and government policy [1].

One estimate says that for producing 50 billion gallons

ethanol per year from cellulosic biomass, the waste stream would supply only 40 to 50 percent of the feedstock, the rest has to come from energy crops such as corn and switch grass, without large impacts on the agricultural system. But beyond that level, there would be implications for the cost of cropland and competition with food crops.

The US is set to consume 290 billion gallons of gasoline a year in cars and trucks by 2050. Increasing vehicle efficiencies to 50 mpg or better and instituting smart growth policies could reduce consumption to 108 billion gallons by 2050.

According to the NRDC report, *Growing Energy* [6], the number of gallons of ethanol currently produced per dry US ton of biomass is 50 US gallons, or 208.93 litre/metric tonne (which compares poorly with 371.75 l/tonne from corn grain [7]). That needs to improve to 117 gallons per dry ton (488.89 l/tonne), the equivalent of 77 gallons of gasoline. If yield improvements of switch grass predicted at 12.4 dry tons per acre (27.77tonne/ha) could be realised – which is more than twice the current average of 5 dry tons per acre - then an estimated 114 million acres dedicated to switchgrass could provide sufficient biomass to produce 165 billion gallons ethanol by 2050 (equivalent to 108 billion gallons of gasoline). This would take up 26.4 percent of US total harvested cropland, or 12.2 percent of total farmland, and would almost certainly impact on food production.

A big idea for making biofuels economical and efficient is to develop biorefineries, analogous to petrol refineries, where crude oil is converted into fuels and co-products such as fertilizers and plastics. In the case of a biorefinery, the plant biomass feedstock will produce diverse products such as animal feed, fuels, chemicals, polymers, lubricants, adhesives, fertilizers and power.

John Sheehan of NREL has been using process simulation software to look at biorefinery design. "Scale is a huge issue," said Sheehan. He has discovered that biorefineries need to process 5 000 to 10 000 tons of biomass per day to be economically viable. "Below 2 000 tons per day, capital costs skyrocket."

A study from the US DOE and USDA published April 2005 [8] concluded that forestland and cropland have the potential to provide a 7-fold increase in the amount of biomass currently consumed by bioenergy and biobased products - in excess of 1.3 billion dry tons – which is sufficient to satisfy more than one-third of the current demand for transport fuels. More than 25 percent would come from extensively managed forestlands and about 75 percent

from intensively managed croplands. The majority primary resources would be logging residues and fuel treatments (to reduce fire hazards) from forestland, and crop residues and perennial crops from agricultural land.

This estimate is based, among other things, on (optimistic) projections of substantial crops yield increases, especially a 50 percent yield boost in the major bioenergy corn crop, and 60 m acres of perennial bioenergy crop (such as switchgrass) planted on 'idle' cropland including 8 m acres previously planted with soybean crop.

It is clear that unless fuel consumption is substantially reduced from current levels, biofuels from energy crops cannot replace fossil fuel without impacting on food production.

Further developments

A further constraint in getting ethanol from plant biomass is that many of the non-glucose sugars contained in hemicellulose, such as xylose, are not fermented into alcohol by the usual microbes. Cellulose makes up 40-50 percent dry weight of biomass, and hemicellulose 20-35 percent.

Lonnie Ingram, Professor of microbiology at University of Florida Institute of Food and Agricultural sciences made headline news [9] because his research team has genetically engineered a strain of *E. coli* bacterium to produce ethanol from xylose [10]. It has been commercialised with help from the US DOE. The company, BC International Corp., based in Dedham, Mass., holds exclusive rights to use and license the engineered bacterium.

The *E. coli* was engineered by transferring into it the genes needed to ferment sugars – pyruvate decarboxylase and alcohol dehydrogenase – from the bacterium *Zymomonas mobilis* , and fermented xylose with a yield of ethanol at 95 percent of the theoretical [11].

Greg Luli, vice-president of research for BC International said the firm plans to build a 30 million gallon biomass to ethanol plant in Jennings Louisiana, expected to be operational by the end of 2006 [9]. Waste from the sugarcane industry in Louisiana will be the plant's main feedstock.

Parallel developments are taking place in Europe. A pilot plant was announced by the Swedish company Etek Etholtekhnik AB to produce 400-500 litres of ethanol a day from a feedstock input of 2 tonnes of dry biomass [12]. The plant is designed for a two-step dilute acid hydrolysis

process and a combination with enzyme hydrolysis. The feedstock is softwood, but other biomass like hardwood and annual corps such as straw and reed canary grass will also be tested. The pilot plant is to be located in Ornskildsvik in northern Sweden, close to an existing sulphite pulp ethanol plant. Three Universities in the region - Umeå University, Mid Sweden University and The Technical University of Lulea – own the plant.

Still uneconomical and unsustainable

One problem with the technology of fermenting xylose with bacteria, summed up by a group of professors at Massachusetts Institute of Technology (MIT) in a White Paper submitted to the MIT Council on Energy [13] is that a rather dilute ethanol solution is produced, at most 5-6 percent, compared with the 12 percent for cornstarch fermented with yeast. Lonnie Ingram's xylose-fermenting *E. coli* yields a 4.5 percent solution of ethanol [14]. The reason is that certain compounds accumulate during the fermentation of sugar-mixtures from biomass that inhibit microbial growth. In other words, the bacteria produce beer, not wine; and the extra water required in the fermentation process plus the extra energy needed to distil the ethanol will make it uneconomical and unsustainable .

The MIT professors also questioned whether the idea of a biorefinery to make use of byproducts from fermentation is economically feasible. They propose to use biotechnology to create microbes that can overcome the growth inhibition to improve the yield and productivity of ethanol from biomass. If they do, they had better make sure the genetically engineered bacterium does not escape into the environment, and this applies to all other genetically engineered bacteria that make ethanol from cellulose biomass.

Some years ago, soil scientist Elaine Ingham and her graduate student Michael Holmes tested a genetically engineered bacterium *Klebsiella planticola* that produced ethanol from wood debris and found it killed *all* the wheat plants in every microcosm tested [15, 16].

Environmental impacts of ethanol

Is ethanol really cleaner and greener than gasoline? In a Senate Hearing on The National Sustainable Fuels and Chemicals Act 1999, the NRDC gave evidence [17] that combustion products of ethanol include formaldehyde and acetaldehyde, both known carcinogens ; and that increased use of ethanol may also increase atmospheric levels of peroxyacetylnitrate (PAN).

They referred to a University of California report on health effects of oxygenates including ethanol [18] (chemicals containing oxygen added to fuels to make them burn more efficiently), which stated that using ethanol would result in increased atmospheric concentrations of acetaldehyde and PAN. Acetaldehyde has been listed as a Toxic Air Contaminant in California based on evidence of carcinogenicity and while PAN is "genotoxic [causes genetic damage] and produces respiratory and eye irritation and may produce lung damage."

The NRDC pointed out that increased use of ethanol in fuel might lead to an increase in ethanol exposure via inhalation, which could result in the range of known toxicities associated with ingested ethanol. They also warned of emissions of nitric oxides and volatile organic compounds that are ozone precursors.

Recently, Cal Hodge of A Second Opinion Inc. reported that ozone levels in the atmosphere increased in California in 2003 associated with the switch to 10 percent ethanol from methyl tertiary butyl ether in gasoline a year ago [19]. The ozone exceedances in California's South Coast Air Basin were twice those of the previous three years, while the maximum ozone concentration was up by 22 percent. This increase in ozone was indeed correlated with increase in emissions of nitric oxides and volatile organic compounds, which escaped the notice of the US Environmental Protection Agency (EPA). The EPA gave ethanol in gasoline a clean bill of health using a flawed model for the tests that did not take into account the fact that ethanol tends to produce more nitric oxides, that it tends to permeate through the seals in automotive fuel systems and to degrade driveability thereby increasing exhaust emissions. He called for "banning, not expanding" the use of ethanol in US gasoline.

The Institute of Science in Society, PO Box 51885, London NW2 9DH
telephone: **[44 20 8452 2729] [44 20 7272 5636]**

General Enquiries sam@i-sis.org.uk - Website/Mailing List press-release@i-sis.org.uk - ISIS Director m.w.ho@i-sis.org.uk