PLANT BIOMASS: THE SUSTAINABLE SOURCE OF ENERGY AND OF INDUSTRIAL ORGANIC CHEMICALS Miller, Joseph

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ABSTRACT: We have developed efficient economic continuous processes for the dilute acid hydrolysis of the cellulose of plant biomass (ligno-cellulose) to glucose, for fermentation to ethanol; of the hemicellulose to pentoses and associated processes for the conversion of pentoses via furfural to tetrahydrofurfuryl nitrate (THFN) – a safe cheap additive which allows azeotrope ethanol to substitute Diesel fuel. The lignin is converted via lignin coke by reaction with steam to Synthesis Gas for C-1 chemistry, including methanol, whose conversion to aromatics to C-10 is well-known as is the Fischer-Tropsch process to produce liquid fuels which can be cracked, reformed etc.: "Fischer-Tropsch petrochemistry". The aromatics include benzene, toluene and the xylenes while the conversion of ethanol to ethylene, propylene and the butylenes is also well-known. Thus globally the seven prime raw materials of industrial organic chemistry, currently produced from petroleum and natural gas, can be substituted. As a bonus we have shown that the autohydrolysis of plant biomass produces an excellent feed for ruminants. Keywords: acid hydrolysis; biomass conversion; chemicals from biomass.

We demonstrate in this paper how plant biomass (ligno-cellulose) can provide for a sustainable future without petroleum, natural gas and petrochemistry providing energy and industrial organic chenicals. It is not only a *renewable resource* but its very growth *consumes* carbon dioxide – the villain among greenhouse gases – as well as producing oxygen. It has been estimated that the world's land masses produce *annually* some one hundred billion tons dry weight of plant biomass.

It is convenient now to present in chart form the principal products and prime raw materials currently obtained from petroleum, natural gas and petrochemistry.

Principal Products and Prime raw materials from Petroleum and Natural Gas

Methane Ethane Propane* Butane* Gasoline Diesel Oil Heavy fuel oils Lubricating Oils/Greases Asphalt (residue)

* The main components of liquefied petroleum gas (LPG).

The seven prime raw materials of industrial organic chemistry: 1.Methane (and **C-1** chemistry via CO/H₂) 2.Ethylene (said to be the prime source of ca. 40% of all industrialized organic chemicals) **3.Propylene 4.Butylenes** 5.Benzene 6.Toluene **7.Xylenes**

It is convenient to present next some basic data on Plant Biomass [ligno-cellulose] as a % age of dry weight, and structures:

Some basic data on Plant Biomass (as a % age of dry weight)

Type Principal Components	Wood	Agricultural residues
Cellulose	40 – 45	up to 40
Hemicellulose	15 – 30	15 – 26
Lignin	20 – 35	22 – 30
Ash	up to 1	1 - 8

The following generic structure serves for cellulose and hemicellulose.



Cellulose R=CH₂OH; Hemicellulose R=H

A part-structure of lignin



The use of lignin is discussed below.

A summary of the principal processes for plant biomass utilization follows-shown for sugar-cane bagasse (an agricultural residue).



Some additional comments are appropriate:

1. Ethanol as its azeotrope with water is a good substitute for gasoline and is so used in Brazil for 1-2 million cars and light vehicles. Ethanol with added THFN (tetrahydrofurfuryl nitrate) serves well as a substitute for ordinary Diesel fuel, proven by extensive road tests. As little as 3-4% THFN seems to be effective.

Ordinary Diesel fuel is improved (higher cetane number) by adding THFN. Methanol with added THFN also serves as a substitute for ordinary Diesel fuel.

2. As already emphasized, ethanolic fermentation is a key component in substituting fossil fuels by plant biomass. This is already carried out on an enormous scale in Brazil using sucrose (from sugarcane) even though batch processes are used: it can just as easily be carried out using glucose. In the long-term *continuous* ethanolic fermentation will be highly desirable. There is already know-how for this in Brazil and in other countries, so that it should not be too long before large-scale commercial continuous ethanolic fermentation processes are in place. 3. There is no need to restrict ethanolic fermentation to the sole use of *Saccharomyces cerevisiaea*: research is active in the employment of other micro-organisms. A bacterium of the *Zymomonas* genus is especially promising with the advantage of being able to ferment to 18% ethanol. The possibility of *continuous* fermentation is also being studied.

4. The principal challenge with the ethanol scenario remains the development of energy-sparing processes for separating ethanol from ethanol-water mixtures. The most promising possibilities at present are (a) the use of membrane technology; (b) the use of a low-pressure system with heat exchangers, in which ethanol is continuously pumped off. The development of thermophilic bacteria for ethanolic fermentation may also make a positive contribution to the solution of this problem.

5. What about Lignin? Its key planned use is to convert it to Synthesis gas (CO/H₂). Thus

Lignin coke + H₂O (g) \rightarrow CO + H₂

This can be coupled with the Synthesis gas shift reaction to produce more hydrogen: $CO + H_2O(g) \rightarrow CO_2 + H_2$

These are essential for the overall substitution of C-1 chemistry of petrochemistry by plant biomass. It needs to added that the corresponding reactions with Coal/Coke/Lignite + $H_2O(g) \rightarrow CO + H_2$, would form a key part of a scenario for the interim substitution of Petroleum and Natural gas by Coal and Lignite *etc*.

6. Our presentation has already illustrated how plant biomass can subtitute petroleum, natural gas and petrochemistry.

To round off the picture it is worth re-emphasizing some recent developments and selecting new developments/perspectives.

1. Large-scale *continuous* processes of ethanolic fermentation should become commercially available in the not-too-distant future.

2. (a) Use of micro-organisms other than *Saccharomyces cerevisiaea* for ethanolic fermentation – Zymomonas bacteria are very promising candidates
 (b) possible use of thermophilic bacteria.

3. Development of energy-sparing processes for separating ethanol from ethanol-water mixtures remains something of a challenge, although there are promising developments.

4. Bacterial conversion of glucose to hydrogen (and water). The inventors are studying the possibility of converting cellulose to hydrogen – sometimes referred to as "the Clean fuel" since its combustion forms water.

5. Use of ethanol, methanol and hydrogen in fuel cells is a real possibility.

6. Use of hydrogen for catalytic reduction of carbon dioxide to methanol.
7. Use of methanol and ethanol to produce methyl- and ethyl-tertiary butyl ethers (MTBE and ETBE), especially ETBE, to improve conventional gasoline – higher octane number and less noxious exhaust gases in particular.

8. Aerobic fermentation of sugars to Single Cell Protein (SCP). As example a product with 45-50% protein has been obtained using *Torula utilis*.

9. Aerobic fermentation of methanol to SCP.

10. Aerobic fermentation of sugars to amino-acids.

11. Aerobic fermentation of glucose using *Alcaligenes entrophus* to give a stereoregular biodegradable copolymer of γ -hydroxybutyric acid and δ -hydroxyvaleric acid: HO(CH₂)₃CO₂H and HO(CH₂)₄CO₂H.

12. Anaerobic fermentation of organic residues, including "rubbish", to methane (so-called Biogas).

13. Well-known fermentation routes to acetic, butyric, citric and lactic acids, to acetone, butanol, butylenes, glycol *inter alia*.

14. Genetic modification of plants so as to increase the amount of biomass. As example a current study in Brazil is concerned with increasing the biomass produced in Eucalyptus plantations.

15. In those areas where "Biodiesel" is a valid additional option it will be necessary in the future to use methanol and ethanol from biomass.

16. There are many areas of the world unsuitable for commercial crops which could be utilized to produce plant biomass.

17. A key aspect of the utilization of Plant Biomass to substitute petroleum, natural gas and petrochemistry is that its very growth consumes carbon clioxide. This does not diminish the importance of chemical and enzymatic studies specifically directed to recycling carbon dioxide;

18. Auto-hydrolysis of plant biomass produces an excellent feed for ruminants.

References

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Thank you