

AN OVERVIEW OF BIOMASS THERMOCHEMICAL LIQUEFACTION RESEARCH SPONSORED BY
THE U.S. DEPARTMENT OF ENERGY

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BACKGROUND

Biomass represents an important energy resource in the United States both at present and as a potential energy contributor for the future. In 1981, for example, it is estimated¹ that biomass contributed about 3.5% of the nations' energy supply, approximately equivalent with nuclear energy which contributed 3.8% in that year. With proper resource management and the development of efficient conversion processes, the Office of Technology Assessment has estimated² the potential contribution of biomass to the United States energy supply could range as high as 17 quadrillion Btu per year--almost 20% of current United States energy consumption. Similarly, the Energy Research Advisory Board (ERAB) has estimated³ that biomass could potentially supply the nation with about 10 quadrillion Btu by the year 2000.

A wide variety of biomass resources such as wood and forest product residues, grasses, agricultural crops and their residues, and animal wastes can be used as energy feedstocks. As an abundant, renewable, domestic energy resource, biomass can help the United States reduce its dependence on imported oil and natural gas. Liquid fuels derived from biomass are expected to contribute significantly to the energy potential from this resource.

Liquid fuels from biomass offer several advantages over the biomass resource itself. Perhaps most important, liquid fuels have a higher energy density. The energy content of wood, for instance, is about 8500 Btu/lb, roughly half that of liquid hydrocarbon fuels. The effective bulk energy density of biomass solids on a volumetric basis is even lower if the void space between the solids is considered. A cubic foot of dry wood chips for instance, has an energy content of about 90,000 Btu. This is less than one-tenth the energy density of gasoline which contains about 928,000 Btu/ft³. The higher energy density of liquid fuels from biomass allows the products to be transported more economically and to be more easily stored. Liquid fuels also match existing end-use patterns, particularly in the transportation sector. Biomass is the only renewable energy technology capable of addressing this need for transportation fuels.⁴

Thermochemical conversion processes offer promising methods for converting biomass to gasoline-compatible liquid fuels. Thermochemical conversion processes employ elevated temperatures to convert the biomass feedstock. Thermal conversion processes are well suited to conversion of wood and crop residues which account for about 96% of the biomass resources in the United States.² These processes can convert 85 to 95% of the organic material in such feedstocks with little sensitivity to variations in the feed material.

Biomass direct liquefaction processes are those which produce liquids as primary initial products, usually at moderate temperatures (250 to 600°C). Pyrolytic and catalytic liquefaction processes which produce biocrude oils are examples. The biocrude oils would be suitable for some uses as produced or for upgrading into gasoline-compatible fuels. As will be described in greater detail later, the biocrude oils are quite different chemically than petroleum crude oils, and different refining and upgrading procedures are necessary. Indirect liquefaction processes,

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by comparison, first convert the biomass to simple gaseous components including H₂ and CO and then synthesize these into liquid products. Methanol production is an example. Mechanical extraction of natural products from various biomass species followed by limited thermal or physical treatment can also supply liquid fuels. Various seed oils, for instance, have been used as extenders for diesel fuels.

In this paper we present an overview of biomass direct liquefaction research being sponsored by the U.S. Department of Energy's Biomass Thermochemical Conversion Program. Pacific Northwest Laboratory provides field management for this program as shown in Figure 1.

BIOMASS DIRECT LIQUEFACTION RESEARCH

Liquid fuels research sponsored by the Thermochemical Conversion Program focuses on biomass direct liquefaction processes capable of producing true hydrocarbon fuels. This is achieved by first converting the biomass feedstock to a biocrude product using various liquefaction processes. The crude oils produced in these processes are subsequently upgraded into true hydrocarbon products. The ability to generate true hydrocarbon fuels is very important to ensure compatibility with existing gasoline based fuels and fuel distribution systems. Thermochemical conversion processes are necessary for producing true hydrocarbons from biomass.

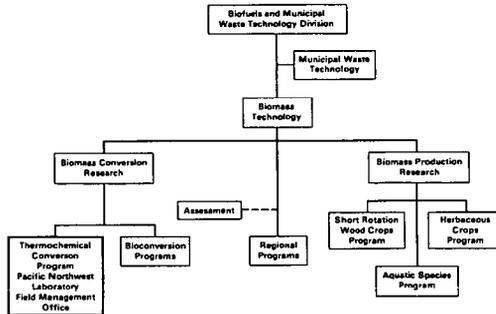


Fig. 1 - Organization of the Biomass Thermochemical Conversion Program

Projects being funded by the Biomass Thermochemical Conversion Program are shown in Figure 3. The research is directed at exploring of methods for generating biocrude liquids and at upgrading them into high value hydrocarbon fuels.

PRODUCTION OF BIOCRUDE LIQUIDS

The initial step in the conversion of biomass to hydrocarbon fuels is the production of an intermediate biocrude liquid. This step can be accomplished using several different approaches. These are discussed below.

PYROLYTIC LIQUEFACTION - Pyrolysis refers to the heating of biomass in the absence of air. Traditionally, pyrolysis has been used to produce charcoal. Conventional pyrolysis typically produces about one-third each gases, pyrolysis oils, and char. The process is inefficient because large quantities of low-value liquids and gases are formed in addition to desired solid products. Batchwise, often primitive, conversion units have also added to the inefficiency of conventional pyrolysis processes.

In recent years, the concept of rapid pyrolysis has emerged as a promising alternative for producing liquid fuels. By carefully controlling both the heating rate and the temperature, the yields of liquid biocrude products can be increased to over 65% by weight on a moisture, ash-free basis.⁵ Under some conditions, up to about 20% high value olefinic products can be produced.⁶

Georgia Tech Research Corporation, Atlanta, Georgia, is conducting research on rapid pyrolysis of biomass with the goal of producing low cost liquid products. The research makes use of an entrained flow pyrolyzer where biomass is converted primarily to liquid products under conditions of moderate heating rates and temperatures. The system, as shown schematically in Figure 3, consists of an entrained, upflow reactor and an oil recovery system that allows partial on-stream fractionation of the product. Georgia Tech Research Corporation has established the interdependence of the reaction temperature and residence time on pyrolysis oil yield. Testing over temperatures from 400 to 550°C gave mass yields of moisture-free oil ranging from 31 to 53%. Additional testing should complete parameter optimization studies.

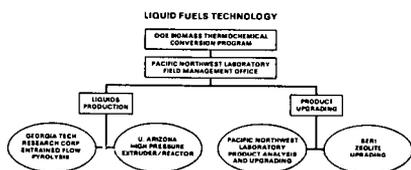


Fig. 2 - Liquid Fuels Projects Sponsored by the Thermochemical Conversion Program

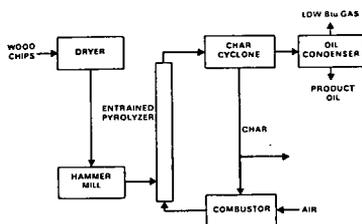


Fig. 3 - Schematic Diagram of Entrained-Flow Pyrolysis Reactor at Georgia Tech Research Corporation

CATALYTIC LIQUEFACTION - Catalytic direct liquefaction research, at this time, is based on a concept first proposed by the Pittsburgh Energy Research Center. In this concept, biomass is mixed with recycled wood oil and sodium carbonate catalyst along with a H₂/CO reducing gas. The mixture is injected into a high-pressure vessel (3000 psi) and heated to about 350°C. The product stream is cooled and flashed into a pressure let-down vessel. The oil phase product is withdrawn and part of it is recycled for use as slurry medium.

In 1980 and 1981, this process and an aqueous slurry version, proposed by Lawrence Berkeley Laboratory, were tested in a DOE research facility located at Albany, Oregon. This research showed the technical feasibility of producing biomass derived liquids by both the oil slurry and aqueous slurry process variations. In one test run during 1981, over 11,000 lbs of direct liquefaction oils were produced during operation in the oil slurry mode. The tests, however, also showed the need to reduce the large oil recycle requirement in order to improve process economics. The Thermochemical Conversion Program is attempting to improve the competitiveness of direct liquefaction through the use of increased feedstock slurry concentrations.

The University of Arizona, Tucson, Arizona, is conducting research on an advanced concept for direct liquefaction that would use very concentrated biomass slurries. The goal of this work has been to use a polymer extruder as a slurry feeding/pumping device. The modified extruder/feeder system is capable of handling slurries as concentrated as 60% wood solids in biomass oil. Conventional systems, by comparison, typically cannot handle slurries containing over about 20% wood. The University of Arizona had designed and constructed and integrated extruder/static mixer liquefaction system as shown in Figure 4. The static mixer is expected to allow adequate mixing and agitation of the viscous slurries.

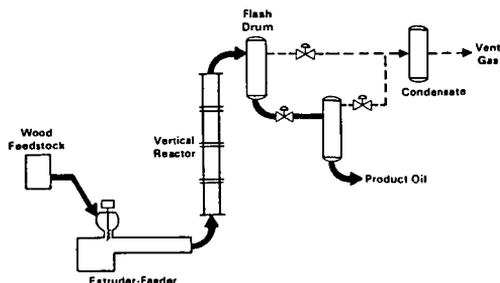


Fig. 4 - Schematic Diagram of Catalytic Liquefaction Unit at the University of Arizona

The University of Arizona has completed construction of the research unit and has begun experimental operation. Results to date show that the unit can be operated consistently and reliably over a variety of experimental conditions. The biocrude product produced is low in oxygen content and has a high heating value. Properties of the oil are summarized in Table 1.

Table 1 - Properties of Crude Oil from the Wood Produced by the University of Arizona (Dry Basis)

Elemental Analysis:

C	83.4%
H	7.9%
O	8.5%
Heating Value (HHV)	16,000 Btu/lb

During 1987, the University of Arizona will operate the experimental unit to determine the effect of lowering or eliminating both the carbonate catalyst and the reducing gas. Preliminary results show that the reactor can operate when those two additives are eliminated, but the effect on product quality has not yet been determined.

PRODUCT CHARACTERIZATION AND UPGRADING

In addition to research on liquefaction concepts, the Thermochemical Conversion Program is also sponsoring research on the characterization of the biocrude products and their subsequent upgrading into gasoline compatible hydrocarbon fuels. This research is described below.

Pacific Northwest Laboratory, Richland, Washington, is conducting research on the characterization and upgrading of both pyrolytic and catalytic liquefaction oils. Characterization studies indicate that there are significant differences between the pyrolytic and the catalytic liquefaction oils. As shown in Table 2, pyrolysis oils contain more oxygen and are less viscous than the catalytic liquefaction products. The catalytic liquefaction products contain large quantities of phenolic compounds while the pyrolysis oils have large concentrations of organic acids. These differences directly impact the methods for upgrading these products.

Table 2 - Biomass Liquefaction Products Comparative Analytical Data

<u>Elemental Analysis (MAF)</u>	<u>Catalytic Liquefaction Oil (PERC-Albany TR12)</u>	<u>Pyrolysis Oil (Georgia Tech #11)</u>
Carbon	81.0%	59.2%
Hydrogen	10.2%	7.0%
Oxygen	8.8%	33.8%
Nitrogen	0.1%	0.1%
Sulfur	1.5%	1.4%
<u>Moisture and Heating Value</u>		
% H ₂ O	7.3	19.7
raw ² HHV	14,200 Btu/lb	7,950 Btu/lb
MAF HHV	15,300 Btu/lb	9,800 Btu/lb
<u>Other Properties</u>		
viscosity cps @ 40°C	400,000	62
density g/ml @ 23°C	1.14	1.24
pourpoint	27°C	-15°C

Research at PNL has concentrated on upgrading the biocrude liquids to gasoline-like motor fuels. This research uses nickel/molybdenum and cobalt/molybdenum catalysts in a continuously fed, bench-scale reactor to hydrotreat the liquefaction crude oils. Initial research has focused on the catalytic liquefaction oils due to their lower initial oxygen content and higher stability. Hydrotreating under conditions of 350 to 400°C at pressures of 2000 psi selectively eliminates oxygen and yields primarily hydrocarbon materials. Comparisons of key constituents and of relative properties of the crude and upgraded products are shown in Tables 3 and 4. Research indicates that the octane number for the hydrocarbon product is about the same as straight run gasoline from petroleum sources.

Table 3 - Comparison of Typical Constituents of Biomass Catalytic Liquefaction Biocrude Oil and Hydrotreated Product (Albany TR-7 Oil)

<u>Biomass Crude Product</u>	<u>Refined Biomass Oil</u>
Cyclic Keytones	Cyclohexane
Unsaturated Cyclic Keytones	Alkyl-Cyclohexanes (to C-10)
Alkyl-Phenols	Benzene
Methoxy-Phenols	Toluene
Di-Phenols	Xylene
Napthols	Other Alkyl-Benzenes

Table 4 - Comparison of Properties of Biocrude Oils and Hydrotreated Product (Albany TR-7 Oil)

	<u>Biocrude Oil</u>	<u>Refined Biomass Oil</u>
Hydrogen to Carbon Ratio	1.21	1.61
Oxygen Content (% MAF Basis)	11	0.3
Density (g/cm ³)	1.19	0.83
Viscosity (cPs @35°C)	100,000	1.1
Heating Value (HHV, MAF Basis)	15,800	18,900

Pacific Northwest Laboratory also initiated research on the upgrading of the pyrolytic liquefaction oils. The pyrolytic oils are expected to be less expensive to produce but more difficult to upgrade due to their higher oxygen content and lower stability. The lower stability of the oil results in extensive char formation and reactor plugging when the pyrolysis oils are hydrotreated under conditions similar to the catalytic liquefaction products. Preliminary research has indicated that a two-step process may be feasible for upgrading the pyrolysis oils. The initial step would use a mild treatment with a nickel catalyst at relatively low temperature (260 to 280°C) followed by a second hydrotreating step similar to that use with the catalytic liquefaction products. Additional research on this concept will be conducted in FY86.

Solar Energy Research Institute (SERI), Golden, Colorado, is also conducting research on the upgrading of biomass pyrolytic liquefaction oils. The concept being explored uses zeolite catalysts to convert the pyrolysis oils to hydrocarbon fuels. The pyrolysis oil vapors would be reacted on the catalyst directly downstream from the pyrolysis reactor, eliminating the need for intermediate condensation of the pyrolytic products. The zeolite catalysts could also eliminate the need for hydrogen in the upgrading process. The zeolite catalysts are known to produce gasoline-like hydrocarbons from a variety of oxygenated feedstocks such as methanol.

Preliminary studies at SERI using mass spectroscopic techniques showed that zeolite catalysts are reactive with respect to the biomass tars and will produce hydrocarbon products. During 1986, SERI completed modification of their ablative pyrolysis reactor to include a slipstream reactor so the pyrolytic vapors could be directly upgraded. Using a zeolite catalyst donated by Mobil Corporation, SERI has now shown that the catalyst can effectively deoxygenate biomass vapors to produce hydrocarbons. In 1987, research is continuing to determine catalyst lifetimes, the extend of carbon deposition, and related factors in order to optimize reaction conditions.

ADDITIONAL INFORMATION

Detailed descriptions of all the research and development projects funded by the Biomass Thermochemical Conversion Program are given in the Proceedings of the 1985 Biomass Thermochemical Conversion Contractors' Meeting, October 1985. This document, PNL-SA-13571/CONF-8510167, is available from the National Technical Information Service, United States Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

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