NREL/TP-431-4831 • UC Category: 245 • DE92010569

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A Division of Midwest Research Institute
Operated for the U.S. Department of Energy
under Contract No. DE-AC02-83CH10093

May 1992

On September 16, 1991 the Solar Energy Institute was designated a national laboratory, and its name was changed to the National Renewable Energy Laboratory.

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Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A02

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CATALYST AND FEEDSTOCK EFFECTS IN THE THERMOCHEMICAL CONVERSION OF BIOMASS TO LIQUID TRANSPORTATION FUELS

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ABSTRACT

The thermochemical conversion of biomass feedstocks to liquid transportation fuels can be accomplished by three processes, namely gasification, high-pressure liquefaction, and pyrolysis. In this study, the pyrolysis option is selected which is followed by the catalytic upgrading of pyrolysis vapors to aromatic and olefinic hydrocarbons (PYROCAT process). The aromatics constitute a high-octane gasoline blend, while the olefins can be utilized as feedstocks for various chemicals.

The PYROCAT process has been studied in a laboratory-scale fixed-bed catalytic reactor. Consecutive biomass samples were pyrolyzed rapidly in steam at 550°C and atmospheric pressure, and then the pyrolysis vapors were passed over a zeolite catalyst. The catalytic upgrading products were monitored in real-time using molecular-beam mass-spectrometry (MBMS). The yields of major products were estimated from mass-spectral data. Several zeolite catalysts were screened in the upgrading process and promising catalysts with high yields were identified. Feedstocks studied included: the woody biomass species aspen (*Populus tremuloides*), basswood (*Tilia americana*), and willow (*Salix alba*); the three isolated components of wood lignin, xylan and cellulose; and the herbaceous species bagasse (*Saccharum spp.* hybrid), wheat straw (*Triticum aestivum*), and Sericea lespedeza (*Lespedeza cuneata*).

1. INTRODUCTION

The periodic occurence of oil crises in the world, along with the threat of environmental degradation caused by acid rain, smog, ozone, and carbon monoxide pollution have increased the need for and interest in renewable sources of energy. Biomass, as the most abundant renewable energy resource in the world and capable of facile conversion to liquid fuels, presents a more environmentally sound alternative than fossil fuels. In biomass, solar energy is stored as chemical energy through the photosynthetic activity of plants. Although the stored energy can be recovered by combustion, the lower energy density of biomass (10-20 MJ/Kg)[1] as a solid fuel makes it less favorable than fossil fuels for transportation. An inherent problem associated with the utilization of biomass as fuel results from its high oxygen content (35-45% wt). In biomass pyrolysis, where no reducing agent is present, oxygen must be removed as CO_2 or CO to increase the hydrogen content of the products[2]. Another difficulty stems from the highly dispersed nature of biomass, which adds considerable cost to the transportation and processing of this fuel. On the other hand, some advantages of biomass over fossil fuels include low sulfur content (typically 0.1%) and low ash (0.1-3%). Also, if biomass is produced at a sustainable rate, carbon dioxide production from the combustion of biomass fuels can be counterbalanced by that removed from atmosphere during photosynthesis. Thus, the overall bioenergy cycle will have no net contribution to the global warming. Furthermore, the emission of other major air pollutants (nitrogen oxides and hydrocarbons) are considerably lower for oxygenated biofuels than those from fossil fuels[3]. These advantageous features make biomass an environmentally sound alternative fuel for future energy needs.

Options for the production of high-density liquid fuels from biomass consist of biochemical and thermochemical conversion processes. These processes are currently under development at the National Renewable Energy Laboratory (NREL). The thermochemical processes include gasification, high-pressure liquefaction, and low-pressure pyrolysis to produce pyrolysis oil (biocrude). Although biocrude is a low-viscosity oxygenated liquid, perhaps suitable for combustion in furnaces and turbines, the deoxygenation of the vapors by shape-selective catalytic upgrading at atmospheric pressure[4-15] can result in a gasoline-like hydrocarbon blend, which presents a more attractive option. In this paper, we discuss the pyrolysis option and examine the catalytic deoxygenation of biocrude to aromatic and olefinic hydrocarbons (PYROCAT process). The screening results of various shape-selective catalysts are presented. Also some potential biomass feedstocks, which were analyzed by conventional methods, are evaluated for the thermochemical conversion process.

2. MATERIALS AND METHODS

2.1 Biomass Feedstock Preparation

Biomass feedstocks in this study consisted of both herbaceous and woody species. The wheat straw (*Triticum aestivum*) and sugar cane bagasse (*Saccharum spp.* hybrid) are standard reference biomass materials, obtained from the National Institute of Standards and Technology (NIST). The aspen (*Populus tremuloides*), willow (*Salix alba*), basswood (*Tilia americana*), and Sericea lespedeza (*Lespedeza cuneta*) were taken from the NREL's biomass collection. The NREL biomass samples were ground in a Wiley mill to pass through a 1-mm screen. No further preparation was carried out on these samples. The cellulose sample was Avicel PH-102 (FMC Corp., Philadelphia, Pennsylvania) with an average particle size of 90 µm. The hemicellulose was an acetylated, alkali free xylan prepared from aspen wood by H. Schroeder of the Colorado State University, Fort Collins, Colorado. The lignin was a ball mill/enzyme liberated sample prepared from cottonwood (*Populus deltoides*, clone #42-7) at NREL. Some of the biomass samples were analyzed for their elemental composition (C, H, O, N, and ash) by Huffman Labs (Golden, Colorado).

2.2 Catalyst Preparation

Catalyst samples were obtained from F. V. Hanson and D. C. Longstaff of the University of Utah. Samples included the pure crystalline form of ZSM-5 variations. The structural details of these catalysts cannot be disclosed at this time because of proprietary reasons. A sample of commercial ZSM-5 with binder (catalyst 6) was provided by Mobil Research and Development Corporation. Overall, 17 catalysts were tested for the thermochemical conversion of biomass. Approximately 1.0 g of the catalyst was sieved to a mesh size of 25-45 and was packed in the reactor between quartz wool on both sides (see Figure 1).

2.3 Catalytic Upgrading of Pyrolysis Vapors

Biomass samples were pyrolyzed in steam at 550°C, and the pyrolysis vapors were immediately passed through a fixed bed of zeolite catalyst. Samples were introduced in batches of approximately 30 mg and were repeated in triplicate. A two-stage quartz reactor with dual-bed configuration (as shown in Figure 1) was used in both catalyst and feedstock screening experiments. This symmetrical reactor configuration, interfaced with the molecular-beam mass-spectrometer (MBMS)[16] allows rapid comparisons of two catalysts and allows the study of longevity of catalysts under severe operating conditions. Steam and helium carrier gases were passed through the inner tubes at various flow rates. The outer flow of helium was used for the dilution of gaseous products for MBMS sampling[12] and for the introduction of standard calibration mixtures to the MBMS without disturbing the catalyst beds. The temperature control of the pyrolysis and catalytic cracking zones was achieved by a four-zone furnace surrounding the reactor.

3. RESULTS AND DISCUSSION

3.1 Catalyst Screening

Gaseous product yields (as weight percent of the oven-dry feedstock) for each catalyst in the conversion of biomass pyrolysis vapors were determined from the MBMS results. The quantitation method was based on the calibration of mass spectrometer intensities. The procedure has been previously described[15]. Yields of two major classes of hydrocarbons, namely aromatics and olefins, were determined. The aromatics measured consisted of benzene, toluene, xylenes, phenol, cresol, styrene, naphthalene, and methyl naphtalene. The olefins accounted for were in the C_2-C_6 range (ethylene, propylene, butenes, pentenes, and hexenes). Although the yields were determined under different conditions of weight-

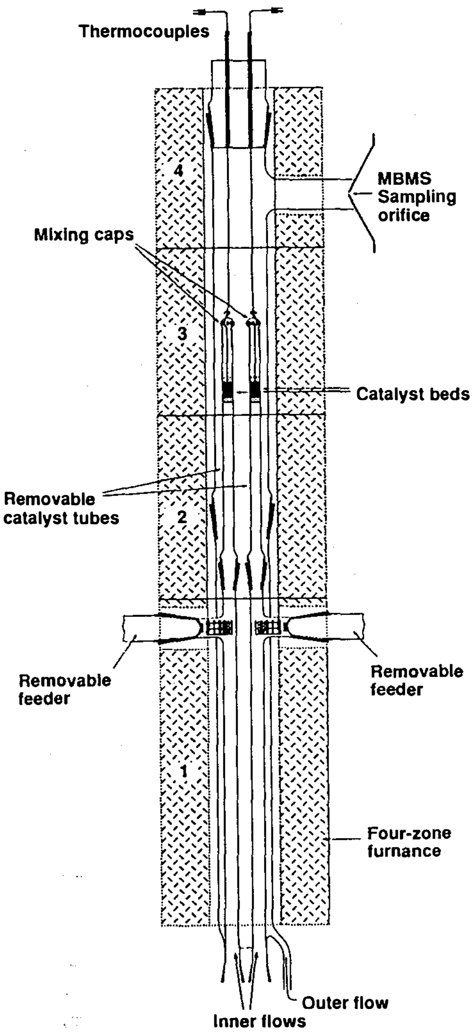

Fig. 1. The reactor configuration for catalyst and feedstock screening tests

hourly space velocity (WHSV) and steam-to-biomass ratio (S/B), only maximum yields for each catalyst under optimal conditions of WHSV and S/B are reported here. WHSV is inversely proportional to the residence time of the pyrolysis vapors in the catalyst bed. It should be noted that the calculated WHSV in this work represents an average value by approximating the biomass pulse with a square pulse of equal area. All measurements of yields were taken during the steady-state behavior of the catalyst and before any deactivation caused by coking occured. The maximum yields for 17 catalysts, when basswood is used as the feedstock, are shown in Figure 2. These values are averages from three replicate experiments with standard deviations shown on the graph.

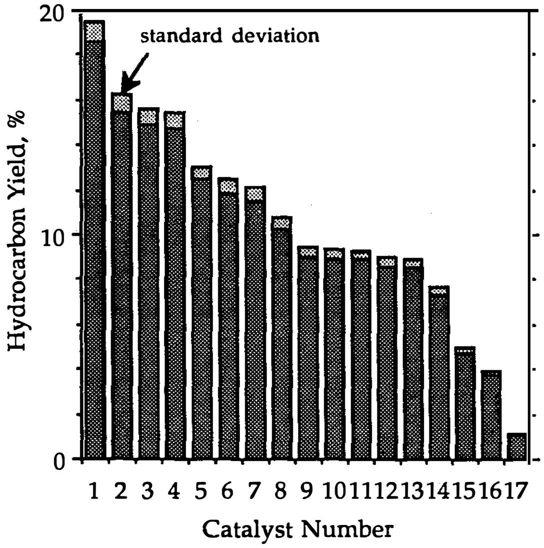

Fig. 2. Catalyst screening results at optimum conditions for the conversion of basswood

The ranking of catalyst activities was found to be similar to that reported for refuse-derived fuel (RDF)[15]. Four promising catalysts (1 through 4) produced high yields of hydrocarbons (15% or higher). From a simplistic point of view, one can calculate the maximum limit on the yield of olefins and aromatics from basswood (48.1% C, 6.3% H, and 45.2% O) based on purely stoichiometric considerations and arbitrary selection of products:

Wood to aromatics (yield = 25.5%),

$$CH_{1.57}O_{0.70} \longrightarrow 0.79CH_{1.25} + 0.21CO_2 + 0.29H_2O \quad (1)$$

Wood to olefins (yield = 23.6%),

$$CH_{1.57}O_{0.70} \longrightarrow 0.70CH_2 + 0.31CO_2 + 0.09H_2O \quad (2)$$

It was assumed in the above calculations that only 60% of wood was converted to pyrolysis oil with the same elemental composition as wood itself. Under actual experimental conditions, CO is also produced, which slightly reduces the theoretical upper limits on yields. The aromatics in the above calculations were assumed to have an average empirical formula of $CH_{1.25}$, similar to that of xylene (C_8H_{10}). Figure 2 indicates that for catalyst 1, about 75% of the limit on the combined yields of olefins and aromatics has been achieved.

3.2 Feedstock Screening

Three herbaceous species, three woody species, and isolated xylan, cellulose and lignin were evaluated for the thermochemical conversion by

PYROCAT. One catalyst with moderate activity (catalyst 6) and one set of industrially acceptable operating conditions (WHSV of 6 and S/B of 1) were selected for these experiments. The results are presented in Figures 3 and 4 for aromatics and olefins, respectively. Experiments were in triplicates, and the standard deviations are shown on the graph bar.

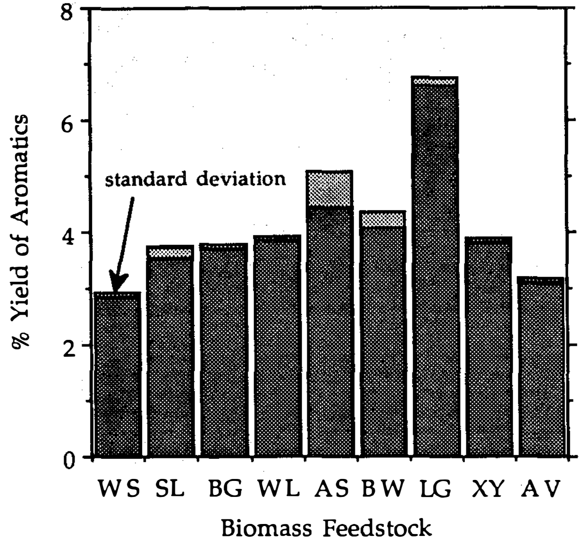

Fig. 3. The yields of aromatic hydrocarbons from various feedstocks; WS=wheat straw, SL=sericea lespedeza, BG=bagasse, WL= willow, AS=aspen, BW= basswood, LG=lignin, XY=xylan, AV=avicel.

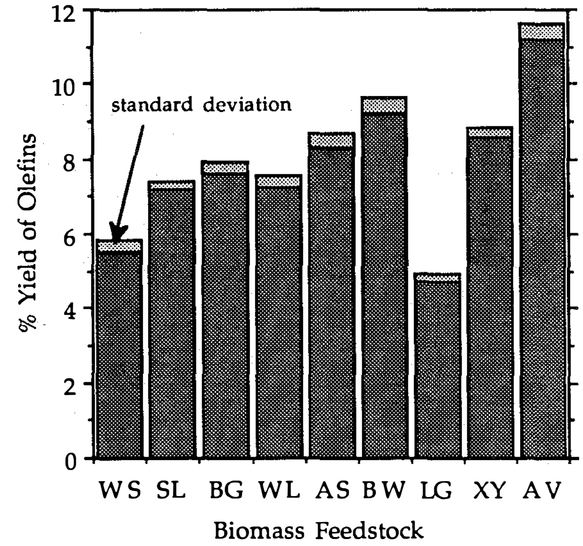

Fig. 4. The yields of olefinic hydrocarbons from various feedstocks

On the basis of the total yield of hydrocarbons, the biomass species can be classified into three groups: high hydrocarbon yielding species such as aspen and basswood; intermediate hydrocarbon yielding species such as willow, sericea lespedeza, and bagasse; and low hydrocarbon yielding species such as wheat straw. The yield of hydrocarbons from these biomass species is affected by several factors including ash and nitrogen contents. Biomass feedstocks with high ash content tend to produce light gases in high yields because of the catalytic activity of the alkali metal salts in the ash[17]. This results in low yields of hydrocarbons. The high ash content also promotes charring reactions, which reduce the amount of volatile pyrolysis vapors available for catalytic upgrading to hydrocarbons. The high nitrogen content of feedstocks also tends to promote reactions between the amino compounds and the carbohydrates at high temperatures of pyrolysis. These reactions result in char formation. However, if a suitable pretreatment process is devised to reduce the ash and nitrogen contents of these feedstocks, they could find application in thermochemical conversion processes. The total yield of hydrocarbons from basswood lies between that of lignin, cellulose, and hemicellulose, as expected. Also the high yield of aromatics from lignin can be attributed to the high polyphenolic structure of lignin.

4. CONCLUSIONS

The following conclusions can be drawn from the present study:
- The MBMS system provides a rapid screening tool for catalysts, feedstocks, and operating conditions.
- Promising catalysts have been identified that result in high yields of hydrocarbons, approaching 75% of the theoretical upper limits.
- The upgrading products can be used as a high-octane aromatic gasoline blend.
- The yields of hydrocarbons from various biomass species appear to be influenced by their nitrogen or ash content, which results in char formation.

5. ACKNOWLEDGMENTS

The catalyst synthesis work was performed by Francis Hanson and Daniel Longstaff of the University of Utah. Also, one catalyst sample was provided by the Mobil Research and Development

Corporation. The authors wish to thank Helena Chum, Thomas Milne, Joseph Bozell and James Diebold of the National Renewable Energy Laboratory (NREL) for their helpful suggestions and comments. The funding support of the DOE Office of Transportation Technologies, Biofuels Program is greatly appreciated.

6. REFERENCES

(1) Laughton, M. A. (ed), Renewable Energy Sources: Watt Commision Report Number 22, Elsevier Appl. Sc., New York, 1990, pp. 99-116.

(2) Diebold, J. P., and Scahill, J. W., "Biomass-to-Gasoline (BTG): Upgrading Pyrolysis Vapors to Aromatic Gasoline with Zeolite Catalysts at Atmospheric Pressure," Pyrolysis Oils from Biomass, ACS Symposium Series 376, ed. E. J. Soltes and T. A. Milne. Washington: ACS, 1988, pp. 264-276.

(3) Cannon, J. S., Drive for Clean Air, Inform Inc., New York, 1989, pp. 45-76.

(4) Kaliaguine, S., "Upgrading Pyrolytic Oils from Wood," Wood Liquefaction Specialists Meeting . University of Sasketchewan, 1982, pp. 75-125.

(5) Chantal, P. D., Kaliaguine, S., Grandmaison, J. L., and Mahay, S., "Production of Hydrocarbons from Aspen Poplar Pyrolytic Oils over HZSM-5," Applied Catalysis, vol. 10, 1984 pp. 317-332.

(6) Prasad, Y. S. and Bakhshi, N. M., Applied Catalysis, vol. 8, 1985, p. 71.

(7) Prasad, Y. S., Bakhshi, N. M., Matthews, J. F., and Eager, R. L., Can. J. Chem. Eng., vol. 64, 1986, p. 278.

(8) Mathews, J. F., Tepylo, M. G., Eager, R. L., and Pepper, J. M., "Upgrading of Aspen Poplar Wood Oil over HZSM-5 Zeolite Catalyst," Can. J. Chem. Eng., vol. 63, 1986, pp. 686-689.

(9) Hanniff, M. I. and Dao, L. H., "Conversion of Biomass Carbohydrates into Hydrocarbon Products," Energy from Biomass and Wastes X., ed. D. L. Klass. London: Elsevier Applied Sciences Publishers, 1987.

(10) Diebold, J. P.; Chum, H. L.; Evans, R. J., Milne, T. A., Reed, T. B., and Scahill, J. W., "Low Pressure Upgrading of Primary Pyrolysis Oils from Biomass and Organic Wastes," Energy from Biomass and Wastes X., ed. D. L. Klass. London: Elsevier Applied Sciences Publishers, 1987, pp. 801-830.

(11) Evans, R. J. and Milne, T. A., "Molecular-Beam Mass-Spectrometric Studies of Wood Vapor and Model Compounds over HZSM-5 Catalyst," in Pyrolysis Oils from Biomass, ACS Symposium Series 376, ed. E. J. Soltes and T. A. Milne. Washington: ACS, 1988, pp. 311-327.

(12) Milne, T. A., Evans, R. J., and Filley, J., "MBMS Studies of HZSM-5 Activity During Wood Pyrolysis Product Conversion," Research in Thermochemical Biomass Conversion, ed. A. V. Bridgewater and J. L. Kuester. New York: Elsevier Applied Science Publishers, 1988, pp. 910-926.

(13) Chen, N. Y., Walsh, D. E., and Koenig, L. R., "Fluidized Bed Upgrading of Wood Pyrolysis Liquids and Related Compounds," Pyrolysis Oils from Biomass, ACS Symposium Series 376, ed. E. J. Soltes and T. A. Milne. Washington: ACS, 1988, pp. 277-289.

(14) Renaud, J., Grandmaison, J. L., Roy, C., and Kalliaguine, S., "Low-Pressure Upgrading of Vacuum-Pyrolysis Oils from Wood," Pyrolysis Oils from Biomass, ACS Symposium Series 376, ed. E. J. Soltes and T. A. Milne. Washington: ACS, 1988, pp. 290-310.

(15) Rejai, B., Evans, R. J., Milne, T. A., Diebold, J. P., and Scahill, J. W. "The Conversion of Biobased Feedstocks to Liquid Fuels Through Pyrolysis," Proc. Conference on Energy from Biomass & Wastes XV, Washington D.C., March 1991.

(16) Soltys, M. N. and Milne, T. A., The SERI High Pressure Molecular-Beam Mass Spectrometric Sampling System, SERI/TR-622-1172, National Renewable Energy Laboratory, Golden, 1982.

(17) Pan, W., and Richards, G. N., "Influence of Metal Ions on Volatile Products of Pyrolysis of Wood," J. Anal. Appl. Pyrolysis, vol. 16, 1989, pp. 117-126.