The decomposition of ammonia on calcined dolomite cannot be explained by its larger surface area as compared to other materials.

The presence of simulated dry fuel gas nearly inhibited the ammonia decomposition, probably due to the formation of carbonaceous material on the surface of dolomite. The dolomite could be regenerated if the carbon was burned off.

Steam inactivated the dolomite.

Hydrocarbons from the Catalytic Pyrolysis of Biomass

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In earlier publications it was shown that it is possible to directly convert wood in a gas–solid catalytic fluid bed to methane with a 75–80% carbon conversion, in a hydrogen atmosphere at 1 atm pressure. Use of alternative catalysts and processing conditions yields a variety of other products. In particular, it is possible to obtain from wood or cellulose much improved yields of olefinic compounds in the C_2 to C_6 range as compared to those reported for uncatalyzed high-temperature fast pyrolysis. Product analyses and yields for several catalysts are reported, and the yields from wood and from cellulose are compared. Some speculations are offered on the possible mechanism of the new thermocatalytic conversion process.

Introduction

The development and utilization of an atmospheric-pressure fluidized bed biomass fast pyrolysis process (the Waterloo Fast Pyrolysis Process or WFPP) has been described by Scott and Piskorz,[1-3] Piskorz et al.,[4] and Scott et al.[5] Results have been obtained by using a bench-scale unit (20–100 g/h) and also using a larger scale system (1–5 kg/h). The purpose of the studies has been to determine the conditions for maximum yield of liquids from a biomass feedstock. Because of the high liquid yields obtained, among the highest reported for any thermal pyrolysis process (70–80% of the dry wood fed), this pyrolysis oil may have the potential to compete as a fuel oil or as a source of chemicals.

The pyrolysis oil may contain up to 40 wt % oxygen, which decreases the energy density of the fuel. Indeed, it might be considered a "liquid wood" in energy terms. Furthermore, the nature of the functional groups containing oxygen causes the oil to be thermally unstable, resulting in limiting its uses without further refining either to an alternative fuel oil or to serve as a source of oxychemicals. Conversion processes to obtain hydrocarbon

products of greater utility especially as transportation fuels are, therefore, of interest.

Although the oxygen is present in the pyrolysis liquids as oxychemicals which may have themselves a high value, because of the demand for hydrocarbon transportation fuels or octane enhancers, many attempts have been made to "upgrade" the crude pyrolysis liquids to gasoline or diesel oil fractions.

Two general approaches have been used to the present, first to hydrogenate the crude pyrolysis liquid, or, second, to directly catalytically hydrogenate or reform the pyrolysis vapors (usually by a dehydration catalyst) in a second stage reactor. The first of these, direct hydrogenation, has been developed by Elliott et al.[6] and by Elliott and Baker[7] for pyrolysis oils from peat using high hydrogen pressure and hydrotreating catalysts in a two-stage process. About a 30–35% yield of hydrocarbon liquids could be obtained. In our laboratory, Piskorz et al.[8] have shown that by use of a nonisothermal plug flow packed bed hydrotreater the pyrolytic lignin fraction can be converted to liquid hydrocarbons in the gasoline and diesel oil range in a 64% yield (equivalent to 10–15% of the wood fed). Therefore, the technology for production of a hydrocarbon transportation fuel from biomass has been achieved, although not yet optimized, nor integrated with possible other

(1) Scott, D. S.; Piskorz, J. *Can. J. Chem. Eng.* **1982**, *60*, 666-674.
(2) Scott, D. S.; Piskorz, J. *Can. J. Chem. Eng.* **1984**, *62*, 404-412.
(3) Scott, D. S.; Piskorz, J. In *Bioenergy 84*; Egneus, H., Ellegard, A., Eds.; Elsevier Applied Science: London, 1985; Vol. III, pp 15-22.
(4) Piskorz, J.; Scott, D. S.; Radlein, D. In *Production, Analysis and Upgrading of Pyrolysis Oils from Biomass*; ACS Symposium Series 376; Soltes, E. J., Milne, T. A., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 16, pp 167-178.
(5) Scott, D. S.; Piskorz, J.; Radlein, D. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 581-588.

(6) Elliott, D. C.; Baker, E. G.; Piskorz, J.; Scott, D. S.; Solantausta, Y. *Energy Fuels* **1988**, *2*, 234-235.
(7) Elliott, D. C.; Baker, E. G. In *Energy from Biomass and Wastes X*; Klass, D. L., Ed.; Institute of Gas Technology: Chicago, 1987; pp 765-784.
(8) Piskorz, J.; Majerski, P.; Radlein, D.; Scott, D. S. *Energy Fuels* **1989**, *3*, 723-726.
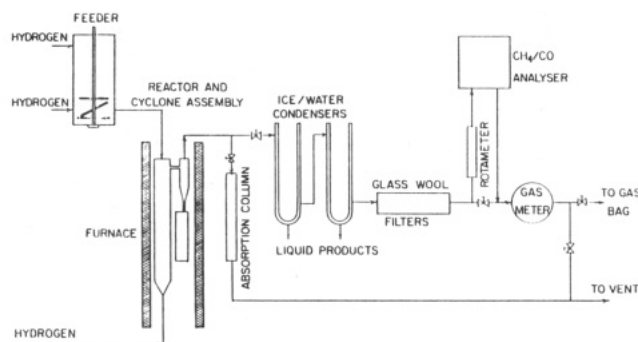
Figure 1. Process flow diagram for catalytic hydrogasification of wood.

schemes for coproducing additional valuable chemicals. While some encouraging results have been achieved, the process is not yet judged to be economic, although it has the potential to be so.[11]

The second approach, to process pyrolytic vapors in a second reactor, has been described by Marshall[9] and by Diebold and Scahill[10] using nickel catalysts and/or zeolite catalysts at atmospheric pressure. This approach is under active development, especially at SERI,[10] and initial results have been encouraging.

The present work is a preliminary exploration of the possibility of obtaining significant yields of hydrocarbon fuels and chemicals from wood in a one-step atmospheric-pressure catalytic flash pyrolysis process in a hydrogen atmosphere. This concept is a direct outgrowth of the success of the WFPP in obtaining high liquid yields by fast pyrolysis of biomass in a bed of fluidized sand particles. Replacement of the sand by an appropriate nickel catalyst and by the use of an hydrogen atmosphere at WFPP optimal conditions was shown by Garg et al.[12] to give wood carbon conversions to methane of 75% (equivalent to about 38 wt % of the feed). Use of different catalysts suggests that other products might be obtainable in useful amounts; in particular, improved yields of C_2+ hydrocarbons were sought.

Experimental Section

A process flow diagram of the experimental system is shown in Figure 1. Hydrogen at 1.5 L/min was used to transport the feedstock particles (cellulose or wood) continuously into the fluidized bed reactor at feed rates of 10–100 g/h. Hydrogen also entered the base of the reactor at 4–5 L/min to fluidize the bed of catalyst particles (250–590 μm). The process operated under atmospheric pressure, so that hydrogen partial pressures in the reactor were always a little less than 1 atm. All solid, liquid, and gaseous products were collected, and a material balance was carried out. The experimental results are raw data and have not been normalized, nor are any values determined by difference. The concentrations of methane and carbon monoxide were also continuously monitored as the experiment progressed.

Char particles, as well as fines produced by catalyst abrasion, were collected in the cyclone and char pot assembly. The remaining pyrolysis products leaving the reactor passed through two ice-water condensers and a cotton-wool filter in series. The liquid products (about 95% water) drained into a sample vial attached at the bottom of each condenser. Any entrained con-

(9) Marshall, A. J. Catalytic Conversion of Pyrolysis Oil in the Vapor Phase: M.A.Sc. Thesis, Dept. of Chemical Engineering, University of Waterloo, 1984.

(10) Diebold, J. P.; Scahill, J. W. *Energy Prog.* 1988, *8*, 59–65.

(11) Elliott, D. C.; Beckman, D.; Ostman, A.; Solantausta, Y.; Gevert, S. B.; Hornell, C.; Kjellstrom, B. A Technical and Economic Analysis of Direct Biomass Liquefaction. In *Energy from Biomass and Wastes XIII*; Institute of Gas Technology: Chicago, 1989; paper 45.

(12) Garg, M.; Piskorz, J.; Scott, D. S.; Radlein, D. *Ind. Eng. Chem. Res.* 1988, *27*, 256–264.

densed droplets and any remaining particles were trapped by the cotton-wool filter, while the gaseous products were collected in a 180-L polyethylene bag.

The product recovery system was designed to permit a complete material balance to be obtained since each unit, as well as the connecting lines, could be disassembled and weighed before and after the experiment. The condensers and all the lines were washed with methanol at the conclusion of a run to obtain the "methanol solubles" composed of tar and water.

Analysis of product gases (except for H_2 which could not be determined as a reaction product) was carried out by gas chromatography, and identification of unknown materials was confirmed by GC/MS. Liquid product analysis was done by Karl Fischer titration for water and by GC/MS or HPLC for other components. Two different feed materials were studied: cellulose and poplar wood.

Avicel PH-102 microcrystalline cellulose was used in this study and is described by the manufacturer as a purified, depolymerized, α-cellulose derived from fibrous plants, relatively free from organic and inorganic contaminants (less than 10 ppm heavy metals), and containing +99% of cellulose (C 44.4%, H 6.2%, O 49.3%). The degree of polymerization reported by Piskorz et al.[13] was 227 (determined by the viscosity method using standard G-24P of the Canadian Pulp and Paper Association).

In the experiments with wood, International Energy Agency (IEA) Aspen Poplar standard sawdust was used (a plantation hybrid from Eastern Canada). The sample was composed of 49.1% cellulose, 20.5% hemicellulose, and 23.5% lignin, on a moisture- and ash-free basis, and contained 49.0% C and 6.1% H.

Results and Discussion

The effects of catalyst composition, operating conditions, and selected feedstocks on the yield of C_2+ components were studied by using a bench-scale pyrolysis unit.

Ten commercial catalysts were tested in this screening study, as well as three catalyst supports and four laboratory prepared catalysts (including a shape-selective catalyst) and a sulfided commercial catalyst. The conditions selected for the screening experiments were 500 °C, 0.50–0.60 s vapor residence time, and a weight hourly space velocity (WHSV) of about 1.00 g of wood/g of catalyst/h. Fe, Ni, Co, Zn, Zr, Cr, Mo, W, Si, Al, Ti, and Mg were used in either their oxide or reduced form and either singly or in combination with up to five elements on one catalyst. Cellulose was used for the screening experiments due to its importance as the major component of biomass feedstocks as well as its well-defined composition.

The operating variables investigated were the WHSV, temperature, and vapor residence time.

Experiments with Avicel PH-102 cellulose and IEA Aspen Poplar were conducted to determine the effect on product composition of a change in feedstock and enhance understanding of possible modes of action of the catalyst.

Product yields are reported as percent by weight of feed on a moisture-free and ash-free basis. Hydrogen atmosphere was used in all the catalytic experiments. Usually, the experiments were of 30 min duration, employed 40 g of catalyst in the fluidized bed, and consumed 20 g of feedstock (at a feed rate of about 40 g/h) fed continuously into the reactor.

Work previously reported from this laboratory[12] showed that direct methanation of wood was possible at 1 atm pressure using a catalyst as the fluidized bed solid in a hydrogen atmosphere. Carbon conversions of 75% to methane were achieved over nickel catalysts. The fact that catalytic hydrodeoxygenation is occurring is shown by the data given in Table I, comparing pyrolysis results for

(13) Piskorz, J.; Radlein, D.; Scott, D. S.; Czernik, S. *J. Anal. Appl. Pyrolysis* 1989, *16*, 127–142.

Table I. Hydrogasification with Different Bed Materials at 550 °C IEA Aspen Poplar (106-250 μm), Hydrogen Atmosphere

	run no.		
	G-42	G-36	G-28
fluidized bed material	sand	alumina support	Lab(3) Ni Cat., 8.8% Ni
bed particle size, μm	250-300	250-590	250-590
residence time, s	0.37	0.44	0.44
WHSV, 1/h[a]	1.82	1.17	1.69
total yield of components, wt % of feed, MF			
CO	10.66	12.95	6.21
CO_2	8.25	11.21	7.34
CH_4	1.63	2.57	42.27
C_2^+	2.97	4.55	0.18
total gas	23.5	31.3	56.0
char	9.34	21.86	10.70
tar	51.87	8.15	0.98
water	14.91	28.83	39.81
total yield	99.6	90.1	107.5
selectivity for CH_4,[b] %	12	13	87

[a] WHSV = feed rate to catalyst ratio, g/(h g of catalyst). [b] Based on gas phase carbon.

poplar wood with different bed solids, all in a hydrogen atmosphere. In the absence of hydrogen, the catalyst will act like sand primarily as a heat carrier for pyrolysis, although some minor gas-phase reactions may occur. Subsequent work in our laboratory with different catalysts has increased the carbon conversion to CH_4 to 83-85%. Table I shows clearly that it is not a simple methanation of pyrolytic carbon monoxide which is occurring, since the CH_4 yield greatly exceeds the CO normally formed in thermal pyrolysis. While the char yields are largely unaffected, the tar production is small. It would appear, therefore, that direct hydrodeoxygenation of pyrolytic tar vapors is occurring on the catalyst, in part possibly by cracking to form CO which is then methanated.

Further work was undertaken to screen the effects of different catalysts, especially to select those which gave improved yields of C_2^+ hydrocarbons. A comparison of uncatalyzed pyrolysis and catalyzed pyrolysis with a Co–Mo catalyst is shown in Table II. The interesting aspect of these results is the fact that over Co–Mo the production of methane is minimized, and there is a greatly increased yield of C_2^+ hydrocarbons, representing about a 31% carbon conversion to C_2^+ components (that is, all C_2, C_3, and C_4 hydrocarbon gases and the portion of the C_5 and higher hydrocarbons appearing in the product gases), and a 38% carbon conversion to hydrocarbons including methane. Tar yields are higher than over nickel reflecting the lesser cracking activity of the Co–Mo catalyst for these tar vapors.

Table III gives results for several catalysts illustrating the wide range of effectiveness of these materials in achieving substantial hydrodeoxygenation of cellulose to light hydrocarbons. The best result shown in Table III represents a 48% carbon conversion to C_2^+ hydrocarbons, or a 54% C conversion to hydrocarbons including methane. (Note that the tar fraction, which may be largely higher molecular weight hydrocarbons, is not included in the C-conversion figures.)

A comparison of results for a pure microcrystalline cellulose (Avicel) and for wood is shown in Table IV. Interestingly, the carbon conversions to C_2^+ components is about the same for both, but because of its lower oxygen content, the weight percent yield of C_2^+ hydrocarbons

Table II. Effect of Catalyst and Atmosphere: Overall Yields IEA Aspen Poplar (106-250 μm), 497 °C

|	run no.	
	22M	44M
atmosphere	nitrogen	hydrogen
catalyst	Ottawa sand	5.0% CoO, 19% MoO_3 on alumina
residence time, s	0.63	0.59
WHSV, g/(g h)	0.53	0.50
total yield of components, wt % of feed, MAF basis		
char	14.70	9.93
tar	61.11	8.38
water	12.17	33.26
total gas	13.99	42.95
carbon monoxide	5.03	13.43
carbon dioxide	6.96	7.09
methane	0.34	4.39
ethylene	0.15	2.51
ethane	0.04	3.10
propylene	0.07	2.73
propane		0.81
acetaldehyde	0.34	0.11
butenes	0.05	0.84
butanes		1.45
unidentified	0.27	0.13
unidentified		0.06
cyclopentenes		3.08
benzene	0.75	2.32
toluene		0.91
total recovery, %	102.0	94.5
total feed carbon in gas component, wt %		
methane	0.52	6.79
C_2^+	2.85	30.87
hydrocarbon	3.37	37.65
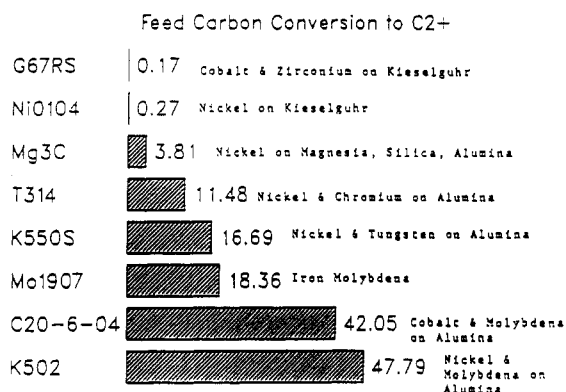
Figure 2. Catalyst screening: summary of C_2^+ results. Carbon conversion to C_2^+. Hydrogen atmosphere, Avicel PH-102 cellulose (74-149 μm), 500 °C, F/C = 0.61-1.10 g/h. Average 0.57 s vapor residence time.

from wood is somewhat higher than that from cellulose.

Finally, Figure 2 shows a comparison of carbon conversion results to C_2^+ hydrocarbons for many of the catalysts tested in this work. It is apparent that hydrocarbon yields, even at the nonoptimized conditions used, are sufficiently high to suggest that further study is warranted, given the very simple nature of the catalytic Waterloo Fast Pyrolysis Process. Comparison of our results in Table IV with those from fast high-temperature pyrolysis[14,15] for wood shows that total hydrocarbon yields in this work were

(14) Graham, R. G.; Freel, B. A.; Bergougnou, M. In *Research in Thermochemical Biomass Conversion*; Bridgewater, A. V., Kuester, J. L., Eds.; Elsevier: London, 1988; pp 585-596.

(15) Mok, L. K.; Graham, R. G.; Overend, R. R.; Freel, B. A.; Bergougnou, M. In *BioEnergy 84*; Egneur, H., Ellegard, A., Eds.; Elsevier: London, 1985; pp 23-30.

Table III. Catalyst Screening at WHSV = 1.0 g/(g h): Hydrogen Atmosphere, Avicel PH-102 Cellulose (74–149 μm), 500 °C

	run no.				
	37M	18M	36M	34M	25M
catalyst	5.0% CoO, 19% MoO_3, alumina	55% Mo, 11.5% Fe	4.5% NiO, 14% MoO_3, alumina	5.5% NiO, 20% WO_3, alumina	9% NiO, 66% MgO
WHSV, g/(g h)	0.86	0.61	0.93	0.94	1.01
res time, s	0.60	0.56	0.57	0.59	0.54
total yield of components, wt % of feed, MAF basis					
char	2.02	4.79	7.20	15.87	11.00
tar	3.69	24.69	7.01	3.93	39.35
water	41.30	39.98	40.53	39.19	21.46
total gas	45.9	58.5	49.6	34.2	20.3
CO	11.93	39.94[a]	12.08	16.16	5.64
CO_2	8.84	7.75	8.48	5.99	5.83
CH_4	2.70	1.00	3.47	3.07	6.81
C_2^+	22.45	9.83	25.56	8.94	2.04
total recovery	92.9	128.0	104.3	93.2	92.1
total feed carbon in gas component, wt %					
methane	4.56	1.68	5.85	5.19	11.50
C_2^+	42.05	18.36	47.79	16.79	3.81
hydrocarbon	46.61	20.04	53.64	21.98	15.31

[a] Probably high due to oxygen from catalyst because this catalyst was only 24% prereduced.

Table IV. Comparison of Results for Cellulose and Wood Alumina Support, 499 °C, 0.57 s Hydrogen

	run no.			
	27M	42M	50M	49M
feed type	cellulose	cellulose	wood	wood
catalyst	5.0% NiO, 19% MoO_3	5.0% CoO, 19% MoO_3	4.5% NiO, 14% MoO_3	4.5% CoO, 20% MoO_3
WHSV, g/(g h)	1.18	1.12	0.64	0.62
total yield of components, wt % of feed, MAF basis				
char	4.85	4.12	10.74	14.41
tar	5.00	7.74	8.72	7.80
water	40.71	38.59	31.71	32.04
total gas	47.4	42.0	46.9	46.3
CO	11.62	12.96	12.93	13.46
CO_2	6.56	9.25	7.09	7.84
CH_4	15.58	2.32	6.88	5.58
C_2^+	13.65	17.47	19.95	19.45
total recovery	98.0	92.4	98.0	100.6
total feed carbon in gas component, wt %				
methane	26.29	3.92	10.64	8.63
C_2^+	25.46	32.74	34.13	33.26
hydrocarbon	51.75	36.66	44.77	41.89

higher (26% vs 18.8%) and yields of C_2+ hydrocarbons in particular were much higher (20% vs 10.7%).

The range of light hydrocarbons produced is shown for one run in Table II (run 44M) and amounts to 22.4% of the wood weight fed, or 52% of the gas weight produced. Product gas from this run on a dry basis, H_2 free, is about 36% CO, 12% CO_2 and 52% hydrocarbons by volume. The hydrocarbon gases produced, excluding methane, are about 60 mol % olefinic. In general, for the Ni/Mo and Co/Mo catalysts studied, the majority of the C_2+ hydrocarbons were olefinic or aromatic.

Inasmuch as the light hydrocarbon fraction contains very little oxygen, yields on an oxygen free basis of light hydrocarbons could be up to 59% by weight of the CH content of the feed. The tar yield of 4–8% shown in Table II or Table III is also largely hydrocarbons, and inclusion of this fraction would increase the total hydrocarbon yield to over 30% of the dry wood fed.

In view of the fact that these preliminary results have not been optimized for most of the operating parameters, yields of hydrocarbons by this method are sufficiently high to appear to warrant further research.