

THE PRODUCTION AND EVALUATION OF OILS FROM THE STEAM PYROLYSIS OF POPLAR CHIPS

D.G.B. Boocock, A. Chowdhury, and S.G. Allen
Department of Chemical Engineering and Applied Chemistry, University of Toronto
200 College Street, Toronto, Ontario Canada M5S 1A4

and
R. Douglas Hayes
Energy, Mines and Resources, Ottawa, Canada

INTRODUCTION

In the early 1970's, as a response to the world oil crisis, two water-based technologies for the thermal liquefaction of woody biomass were studied extensively. The first of these, based on Bergstrom's earlier work (1), employed sodium carbonate as a soluble catalyst, and carbon monoxide as a reducing gas (2,3). The second technology, also based on earlier work, used nickel metal catalysts and hydrogen (4). In all cases the substrate was powdered wood slurried in water, and, in those studies using nickel metal as catalyst, it was not clear what role the catalyst played. In particular it was realised that the wood must yield gases or liquid before the catalyst could intervene. If liquids were formed, then the role of the catalyst/hydrogen system would be stabilisation, since under moderate heating rates, biomass alone in water does not yield significant quantities of oil. The stabilisation could also involve upgrading, if such things as oxygen content and viscosity were also decreased.

In subsequent experiments (5) we semi-continuously fed slurries of powdered wood along with nickel carbonate and hydrogen to a reactor. The feed, on entering the reactor, was heated sufficiently rapidly that the nickel carbonate decomposed to nickel oxide instead of reducing to nickel metal. In addition, when product was discharged from the reactor, both char and oil--the latter in 25 per cent yield--were present. We reasoned that the oil yield was initially higher, but that, because of the unavoidable, prolonged residence time up in the reactor, and the absence of the stabilising system (no nickel metal), some of the oil had charred.

As a test of this theory, powdered wood was heated rapidly, together with only water, in small reactors to 350°C, and then quenched (6). Oil yields (acetone-soluble) in up to 50 per cent by weight were obtained.

Until this time, all studies in both technologies had been confined to powdered wood or sawdust, the general opinion being that heat and mass transfer limitations in larger wood pieces would prevent liquefaction. However, we studied the liquefaction of single poplar chips (6.5 mm square cross section) in the same small reactors, and showed they were completely liquefied at 300°C and above (7). Steam entered the chips, swelling them and disrupting the matrix. The oil which was formed appeared to be stabilised by the presence of liquid water. The chemical conversions were obviously delayed relative to powdered wood, and some poplar clones yielded up to 6 per cent phenol from the chips, but not from the powdered form. Scanning electron microscopy showed liquefaction at the cellular level (8,9). On the surface the middle lamella merged with the cell walls and the matrix then flowed and engulfed the cells. Inside the chips, spherical structures appeared, particularly on the walls of vacuoles. These structures eventually filled irregular cavities which formed in the matrix. Gas or vapour bubbles could also be seen in the flowing matrix.

On the basis of these results it was decided that a laboratory unit should be constructed for the purpose of studying commercial-size (and larger) chips. The overall unit is shown schematically in Figure 1.

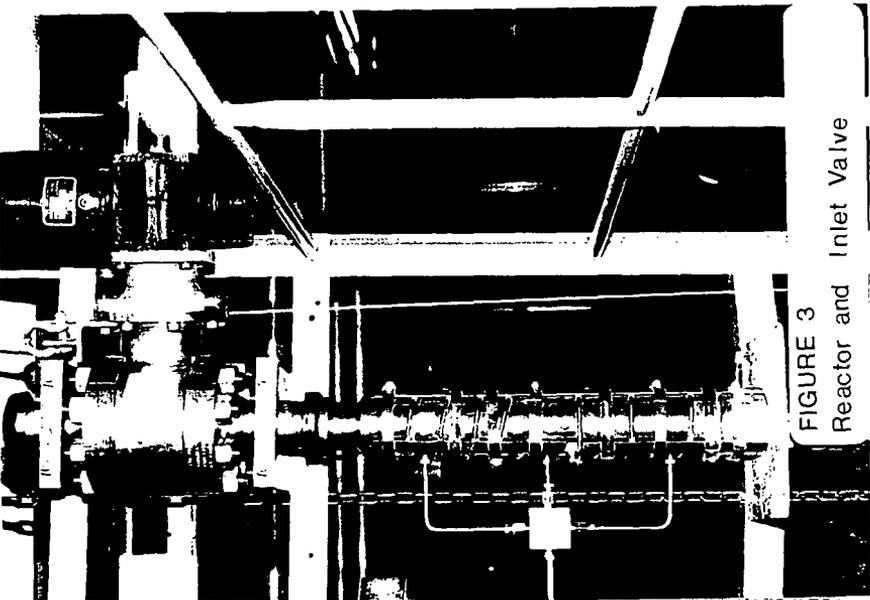


FIGURE 2
Reactor and Steam Vessel

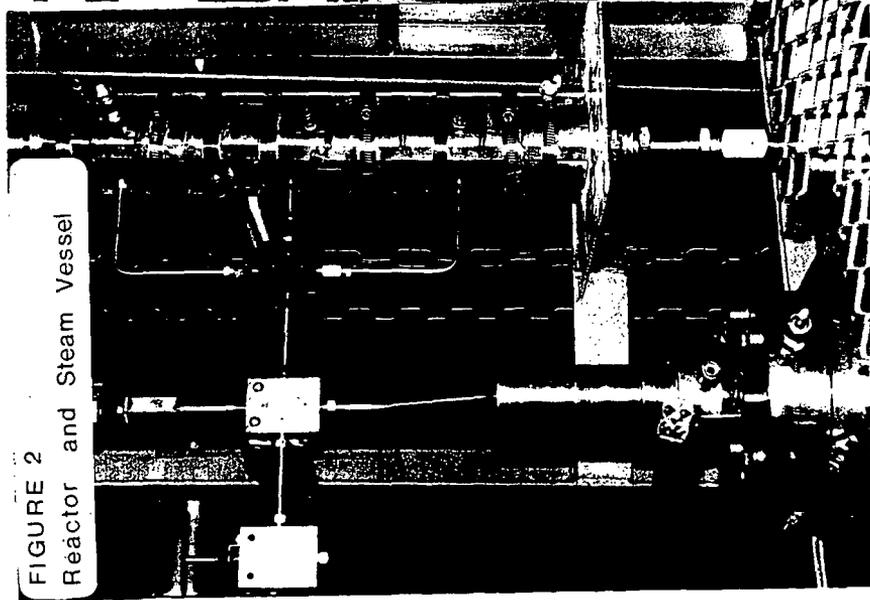


FIGURE 3
Reactor and Inlet Valve

FIGURE 1
CASCADE UNIT FOR
WOOD CHIPS LIQUEFACTION

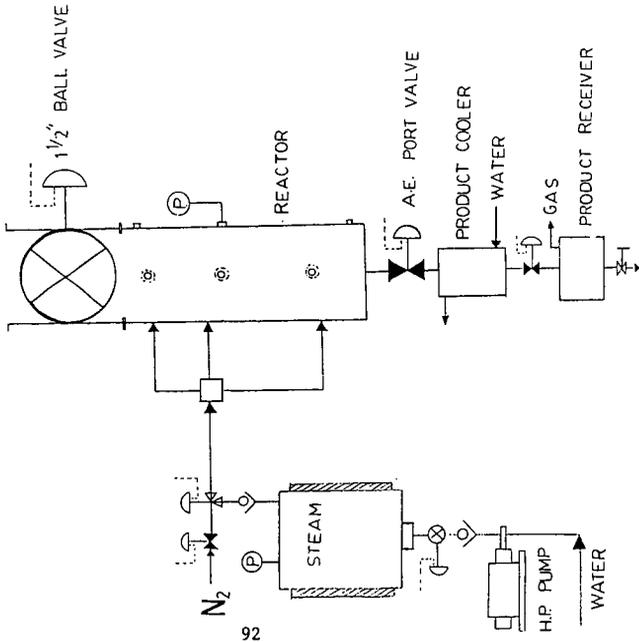
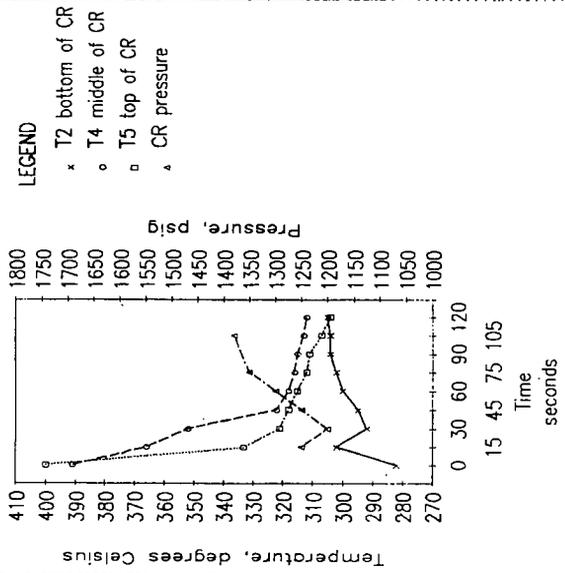


FIGURE 4
Temperature, Pressure Profiles

Steam for 7 Seconds
340 C, 2100 psig
1.0 L Water in SG



The Reactor

The reactor (Figures 2 and 3) was designed by THP Inc. according to ASME Code, Section VIII, Div. I., 1984 addenda. The rating was set at 24.1 MPa (3500 psi) at 350°C which allowed for 7.6 MPa (1100 psi) gas overpressure above the vapour pressure of water 16.5 MPa (2400 psi) at that temperature. A single ingot of TP 316 stainless steel was used for machining the reactor which has an internal diameter of 1.5 inches (3.8 cm) and an external diameter of 3.0 inches (7.6 cm). The length is 19 inches (48 cm) and the internal diameter is 600 mL which allows for a feed of 100 g of dry wood chips. At the top end an Oteco hub (Figure 2) is threaded and seal welded to the reactor body. A 1 inch Autoclave Engineering (AE) slim-line connector is threaded to the base of the reactor. A total of 9 holes are drilled in the reactor body to take 1/4 AE inch-slim connectors. The three on the left side of the reactor are for steam inlet lines. On the front face the top hole is for a rupture disc (20.67 MPa, 3000 psi). The middle hole is for a 1/8 inch thermocouple, and the bottom hole is for a vent line. On the right hand side, the upper and lower holes are for 1/8 inch thermocouples, and the middle hole is for a pressure gauge.

The reactor is clamped near its base by a split ring which is spot welded to a bracket bolted to the reactor frame. The split ring also supports a steel plate on which insulation, in the form of ceramic brick, (not shown in Figures) is stacked to the neck of the reactor. The brick is cut and fitted to the external contours of the reactor. A rectangular steel case is fitted outside the brick.

Heating is supplied to the reactor by two, 6 feet long (1.8 inch O.D.) heaters joined in parallel. These are coiled around the reactor as shown in Figures 2 and 3, and held close to the reactor by four longitudinal steel strips and eight circlips. The maximum power drawn by the heaters is 4 kw. The coils are operated through a temperature controller and with all the lagging in the place, the reactor can be brought to 365°C in 70 minutes.

Inlet Valve and Feed Basket

The inlet valve and its relationship to the reactor can be seen in Figure 3. The valve (Mogas Industries Inc.) is a 1.5 inch (3.8 cm) ball valve (ANSI 2500 series) rated at 24.8 MPa (3600 psi) at 370°C. It is joined to the reactor by a matching Oteco hub and supported on the frame by two brackets. The controller is air operated via solenoid valves. Failure of air pressure closes the valve. The valve is insulated by three layers of 1.5 inch thick glass wool, thus preventing excessive heat losses. The valve and controller together weigh 68 Kg and are attached to a pulley system to facilitate removal from the reactor when this is necessary.

The cylindrical feed basket is made of stainless steel mesh and is spot welded. The basket, besides facilitating feed addition, prevents contact of chips with the reactor walls and allows recovery of unconverted wood.

Outlet Valve

Another 1.5 inch ball valve was originally planned for the reactor outlet. However, because of initial cost considerations, this was replaced with a Crosby 0.5 inch ball valve (ANSI 1500) rated at 18.4 MPa (2665 psi) at 370°C. Special hubs were made by THP for connection to the reactor and the cooling lock. Considerable leaks were encountered with this system, probably because of misalignment of the hubs with the reactor body. Therefore, the system was replaced with a 0.5 inch AE seat and cone (port) valve rated 17000 psi at 350°C. The products thus had to negotiate two right angle turns before entering the product cooler. However, this was not considered a problem, because only water, oil and finely divided material would be exiting the reactor. The Crosby valve may be retested in the future after modification of the hubs.

Let-Down Lock and Collection Vessel

The cooling lock is a 20 inch long AE nipple, having an internal diameter of 0.688 inches (1.7 cm). The internal volume is 122 mL. An external copper jacket allows for use of a coolant, although at this time air cooling appears to be sufficient. Indeed excessive cooling is not desirable as the oil may not flow easily to the product collection vessel. At the time of writing, we are planning the installation of a larger lock (300 mL), since the total liquid discharge often exceeds the volume of the present lock.

The products discharge from the lock into a pyrex cylindrical vessel, approximately 5 inches in diameter and about 8 inches deep. Another smaller container such as a beaker can be placed inside the vessel if necessary. The collection vessel is sealed except for an outlet for the product gases which pass to a brine displacement vessel for volume measurement.

Steam Vessel and Injection

The top of the steam generator is visible at lower left in Figure 2. It is a 2 L AE autoclave equipped with a pressure gauge and thermocouple. The magndrive stirrer has been left in place but is not used. The steam transfer line can be seen passing upward from behind the magndrive to a two-way valve. When the steam line is closed, nitrogen flush gas can be passed from the transfer line on the left hand side to the reactor. Steam and nitrogen enter the reactor at three locations on the reactor as shown (Figure 2). If necessary, the hot generator can be charged with make up water using a Milton Royal high-pressure pump.

Control Panel and Safety Systems

The control panel is located in a room directly adjacent to that containing the unit. The panel contains main switches as well as switches to open and close the various valves. A digital readout and/or chart indicators allow the monitoring of thermocouple temperatures.

The major hazard of this type of equipment is the accidental release of steam to the atmosphere with subsequent injury to personnel. The equipment does contain an electrical override, in that the steam inlet valve can not be electrically operated, unless closure of the reactor inlet valve is initiated. However, this is not sufficient, since the reactor inlet valve takes 3-4 seconds to close, whereas the steam inlet valve opens in about 1 second. Thus if the switch for the steam inlet valve is moved to the open position immediately after the switch for the reactor inlet valve is moved to the closed position, then the contents of the steam vessel could discharge through the inlet valve. The system has, therefore, been provided with an extra safeguard in that the shaft of the inlet valve actuator now carries an extension arm. When the valve is fully closed, the extension arm activates a microswitch which only then allows the steam inlet valve to open. The equipment is also designed such that the main inlet valve cannot be opened if the steam valve is open. This is a purely electrical override but is sufficient, since the steam valve operates faster; i.e., it closed much faster than the reactor inlet valve can open. This, however, does not prevent the accidental discharge of the reactor contents to the atmosphere. To avoid this possibility, the reactor inlet valve has a keyed switch. The operator, after manually loading the wood, then inserts the key to close the reactor inlet valve. He then removes the key rendering the switch inoperable.

Polymethylmethacrylate sheet is installed around the equipment in locations where sudden steam leaks could otherwise injure the operators.

Operation of the Unit (Experimental)

Figure 4 shows typical temperature and pressure profiles (340°C steam injected

for 7 s). Before steam injection, the top and middle of the reactor had temperatures close to 400°C whereas the bottom of the reactor, where heat losses are greater, was at 300°C. After steam injection, the temperatures shown by the upper two thermocouples dropped over a period of about 2 minutes and came close to the temperature of the bottom thermocouple. Condensed steam was present in the base of the reactor, and the internal pressure of the reactor was controlled by the temperature of the surface of this water plus nitrogen and product gas overpressure. As might be expected, the pressure in the reactor is slightly higher than the equilibrium steam pressure corresponding to the temperature of the thermocouple at the base of the reactor (i.e., at the bottom of the water layer).

The following procedure is typical for a liquefaction experiment. The reactor was preheated and flushed with nitrogen with the inlet valve open. The stainless steel basket was loaded with wood chips (100 g, 8 per cent moisture) and then quickly lowered through the inlet valve. The nitrogen valve was closed, as was the inlet valve. Immediately the steam line was opened--usually for about 7 s. After 2 minutes, the products were discharged into the cooling lock, and after a further 30 s the valve to the collection vessel was opened. The gas separated and its volume was measured by displacement of water. Temperatures and pressures in the reactor and steam vessel were monitored throughout this procedure. The basket was retrieved through the inlet port after venting of the reactor.

The oil solidified and could be physically separated from the water by filtration (acetone free oil). The aqueous layer was centrifuged to yield a small insoluble fraction (aqueous-phase solids) most of which was acetone-soluble. An acetone flush of the reactor yielded further oil (acetone-wash oil). A small amount of acetone-insoluble material stuck to the walls of the basket (insolubles). The moisture content of the acetone-free oil was about 20%. However, heating the oil to 70°C for half an hour lowered the water content to less than 3%. This is a rather dramatic, and unexpected reduction in water content, but remelting the oil allows the separation and evaporation of water that was trapped when the oil originally solidified. This semi-dry oil softened around 50°C.

RESULTS AND DISCUSSION

The results from one typical run are discussed here. A steam temperature of 355°C was used, and the wood chips in this instance were soaked for 20 minutes with water for 20 minutes prior to addition. A further 51 g of water was added to the reactor in this way. The presoaking, which was intended to prevent charring, has no advantages and has now been discontinued.

A reasonable, overall mass balance was obtained, but this was not very meaningful, given the relatively large amounts of water involved in the reaction. Approximately 250 g of water were discharged in this run, and no particular effort was made at that time to limit the amount of condensate. A more important aspect is the carbon balance, and in this run slightly more carbon (45.6 g) was accounted for in the products than was in the feed (44.4 g). Figure 5 shows the distribution of carbon in the various product phases. The insoluble fraction is a composite of those acetone insolubles left on the basket and those in the oils. No aqueous phase acetone-insoluble solids were obtained with 355°C steam, and they only become significant when using steam below 340°C. The fraction of total carbon in the gas phase was close to 10 per cent. As in previous runs, about 90 per cent of this gas was carbon dioxide--the balance being mostly carbon monoxide. The total mass of gas was 18.6% of the wood mass. From our previous work on single chip (0.64 x 0.64 x 7.6 cm) liquefaction (7) this is approximately the percentage that would be produced at a water/wood ratio of 1.0 when the steam is generated internally. In that case, however, the oil chars due to the lack of water, so the mechanism for the increased gas production is probably different.

The elemental composition of the oil are also very similar to those obtained in

FIGURE 5
Wood Chips Liquefaction
 Carbon Distribution in Products

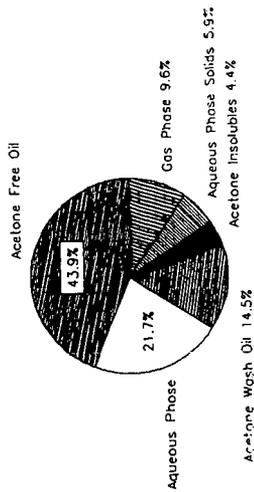
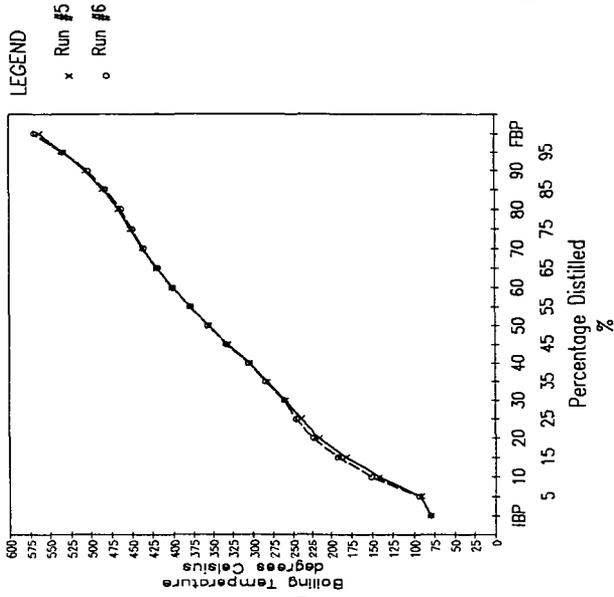


FIGURE 6
Boiling Point Distribution
 of Acetone Free Oils
 by ASTM Method D2887-73



Data provided by DC Research

the previous study, the carbon percentage being close to 70.0 and the hydrogen being around 6.5. The oxygen percentage (by difference) is thus in the low 20 per cent range. If complete oxygen removal was required by hydrotreating, then the viable oxygen limit in the substrate from an economic standpoint is about 20 per cent (11).

A distillation curve for the oils is shown in Figure 6. Approximately 60 per cent of the oil distills below 405°C, which is at the upper end of the range for heavy gas oil in petroleum distillation. Although the average molecular weight of the oil is not known at this time, it can be estimated from Goring's work (10) on the softening point of lignins that the value is less than 1000. The distillation results and the polar nature of the oil (which would increase boiling points relative to alkanes of similar molecular weight) support this estimation.

Continuing Work

Experiments are continuing to define the optimum temperatures and residence times for maximising oil yield and quality. In addition, the effect of water content and chip size are being investigated. Further results from these studies will be reported in the near future.

ACKNOWLEDGEMENTS

The construction and operation of the cascade autoclave system is contract supported by Energy, Mines and Resources, Canada, through the Bioenergy Development Program. We thank the Natural Sciences and Engineering Research Council of Canada for financial support to Stephen Allen through an Undergraduate Summer Research Award.

REFERENCES

1. H.O. Bergstrom and K.N. Cederquist, U.S. Patent 2177557, 1937.
2. H.R. Appell, Y.C. Fu, S. Friedman, P.M. Yavorsky and I. Wender, U.S. Bureau of Mines Technical Report of Investigation #7560 (1971).
3. H.R. Appell, Y.C. Fu, E.G. Illig, F.W. Steffgen and R.D. Miller, U.S. Bureau of Mines Report of Investigation, #8013 (1975).
4. D.G.B. Boocock, D. Mackay, M. McPherson, S.J. Nadeau and R. Thurier, Can.J.Chem.Eng., 47, 98 (1979).
5. D.G.B. Boocock, Final Report of Contract File #24SU.23216-3-6143 for Renewable Energy Division, Energy Mines and Resources, Canada, 1984.
6. D. Beckman and D.G.B. Boocock, Can.J.Chem.Eng., 61, 80 (1983).
7. D.G.B. Boocock and F. Porretta, J.Wood Chem. and Technol., 6, 127 (1986).
8. D.G.B. Boocock, F. Agblevor, A. Chowdhury, L. Kosiak, F. Porretta and E. Vasquez in Energy from Biomass and Wastes X, IGT Symposium, Washington D.C., April, 1986, in press.
9. D.G.B. Boocock and L. Kosiak unpublished results.
10. D.A.I. Goring, Pulp and Paper Canada, 64, T517 (1963).
11. M.J. Van der Burgt and H.P. Ruyter, Shell International Petroleum, Private Communication.

OIL PRODUCTION BY HIGH-PRESSURE THERMAL TREATMENT
OF BLACK LIQUORS: AQUEOUS-PHASE PRODUCTS

P. J. McKeough and A. Å. Johansson

Laboratory of Fuel Processing and Lubrication Technology
Technical Research Centre of Finland
02150 Espoo, Finland

ABSTRACT

Liquid-phase treatment of black liquors, from alkaline pulping, at 300 - 350 °C in a reducing atmosphere results in the formation of an oil-like product, which separates out from an aqueous phase containing the inorganic constituents. The process has several potential forms of application. This study was conducted in support of the development of one such application: a new recovery system for the kraft pulping process. Thermal treatment experiments were performed using different reactant gases. On the basis of analyses of the resultant gaseous and aqueous phases, the main reactions leading to aqueous-phase products were elucidated. This information was used to advantage in the compilation of a process scheme for the recovery of the cooking chemicals from the aqueous phase.

INTRODUCTION

A process producing liquid fuels from the organic matter of the black liquors from alkaline pulping is being developed at the Laboratory of Fuel Processing and Lubrication Technology, Technical Research Centre of Finland (VTT). The central operation in the process is the liquid-phase thermal treatment of black liquor at 300 - 350 °C under a reducing atmosphere (1). The treatment results in the formation of a hydrophobic oil which separates out from an aqueous phase containing the inorganic constituents (Figure 1).

The process can be applied in either of two basic ways:

- as a method to produce oil in conjunction with the kraft pulping process,
- as an entirely new system for recovering the cooking chemicals and energy from kraft spent liquors.

The first type of application exploits the favourable properties of black liquor as a feedstock for high-pressure conversion. In comparison to solid biomass, the advantages of black liquor as a feedstock include:

- no pretreatment required. Black liquor can be directly pumped into the reactor at dry solids concentrations as high as 60 %.
- black liquor contains alkaline compounds known to catalyze conversion reactions,
- cellulose, the most valuable component of wood, is not subjected to the conversion process.

In this type of application, the kraft cooking chemicals are recovered using the traditional method which is centred around the Tomlinson recovery boiler. Additional plant fuel (wood waste, peat, coal) is needed. Preliminary economic evaluations have indicated that this type of oil production process would be economic if oil prices were at their 1985 level.

In the second type of application, the Tomlinson recovery boiler is replaced by a safer and thermally more efficient recovery system, in which the oil produced by thermal treatment is used as plant fuel. This type of process is, in many respects, similar to the Hydrolysis Recovery Process developed by the St.

Regis Paper Company, USA (2), the essential difference being the use of a reducing atmosphere in the VTT process. The experiments described here-in were undertaken in support of the development of this second type of process.

The specific objectives of the present study were to elucidate the main reactions leading to aqueous-phase products, and, by applying this knowledge, to establish process schemes for the recovery of the cooking chemicals from the aqueous phase. Because the composition of the aqueous phase is dependent upon the composition of the reactant gas, several different gases were employed in these experiments.

It should be mentioned that research on conversion of black liquors is but a part of a wider biomass conversion program being undertaken at our laboratory. Other major parts to this program are:

- development of fixed-bed and fluid-bed gasification processes, including combined cycle power generation applications,
- supportive research for the first synthesis-gas plant using peat or wood as feedstock (the peat-ammonia plant of the Finnish company, Kemira),
- basic research on direct liquefaction processes for peat and wood (high-pressure liquefaction and flash pyrolysis),
- development of low-waste technologies.

EXPERIMENTAL

The kraft black liquor, employed in the experiments, originated from a laboratory cook of Scots pine (Pinus sylvestris). An analysis of the liquor is given in Table 1.

Table 1. Analysis of kraft black liquor¹.

	% of dry solids
Organic matter	78.9
Total Na	18.4
NaOH	3.0
Na ₂ S	5.5
Na ₂ SO ₄	0.04
Na ₂ CO ₃	1.1

¹ dry solids content of 30 %

A later batch of liquor, prepared in a similar way, was also analyzed for volatile acids (formic and acetic acids) and lactic acid, which are present as sodium salts in the liquor. On the basis of the analyses it can be concluded that the contents of these acids in the feed liquor used in the present experiments were approximately 6 % om, 4 % om, and 4 % om respectively, where % om denotes the percentage of black liquor organics.

The experiments were conducted in a 1-litre autoclave. In a typical experiment 500 ml of black liquor was placed in the autoclave and reactant gas was charged at sufficient pressure (5 - 9 MPa) to result in a total pressure of about 20 MPa at the reaction temperature. The autoclave was then heated at a rate of about 5 °C/min. A fixed time-at-temperature of 45 min was chosen for these experiments.

At the end of the reaction period, the autoclave was rapidly cooled, after which gases were released, measured, and analyzed. The organic phase and the aqueous

phase were separately recovered from the autoclave and weighed. The pH of the aqueous phase was measured. In many of the experiments the aqueous phase was also analyzed for formic, acetic, and lactic acids (present as sodium salts) and for CO₂ (chemically bound in sodium carbonate or bicarbonate). The former were analyzed by gas chromatography as their benzyl esters (3), the latter by measuring the amount of CO₂ liberated upon acidification with excess mineral acid.

The primary experiments were those employing either carbon monoxide or hydrogen as reducing gas. Two temperatures, 300 °C and 350 °C, were investigated. Experiments employing non-reducing carbon dioxide were also conducted in order to assess whether alkali neutralization by the reactant gas plays an important role in the thermal treatment process. One experiment was performed with a reactant gas of composition similar to that of a typical low-calorific fuel gas (producer gas) generated by gasification of biomass with air.

RESULTS AND DISCUSSION

The main experimental results are presented in Table 2.

Table 2. Results of autoclave experiments. Time-at-temperature: 45 min.

Experiment	1	2	3	4	5	6	7	8
Reactant gas	CO	CO	H ₂	H ₂	H ₂	CO ₂	CO ₂ /H ₂ ¹	Producer gas ²
Temperature, °C	300	350	300	350	350	350	345	350
Pressure, MPa	20	26	18	22	22	24	26	26
Yields, % of black liquor organics (% om)								
oil ³	24.9	26.9	0	23.2	22.6	0	22.1	20.2
bitumen ⁴	35.1	25.6	80.7	36.5	33.4	81.4	34.1	36.5
CO ₂ ⁵	30.1	32.1	0.4	2.4	2.4	0.6	5.2	3.9
H ₂	0.5	0.7	- 0.5	- 0.3	- 0.2	0	- 0.3	- 0.1
CO	- 31.8	- 28.6	0	0	0	0	0	- 3.8
CH _x -gases	0.4	0.6	0.1	0.7	0.8	0.7	1.0	0.7
H ₂ S	1.4	1.1	0.3	0.5	0.4	1.0	ND	0.4
CO ₂ /aqueous ⁶	2.0	19.0	10.0	ND	18.0	ND	19.0	ND
formic acid ⁷	35.7	10.6	6.2	ND	4.6	1.6	ND	ND
acetic acid ⁷	4.5	3.9	4.1	ND	3.8	3.9	ND	ND
lactic acid ⁷	1.3	0.3	1.5	ND	0.3	0	ND	ND
Aqueous-phase pH	8.5	8.5	10.2	9.5	9.4	8.9	8.4	9.1

¹ 60 % CO₂, 40 % H₂

² 14 % CO₂, 51 % N₂, 17 % H₂, 18 % CO

³ organic product as oil layer

⁴ heavier organic product

⁵ in gaseous phase

⁶ in aqueous phase as HCO₃⁻ or CO₃⁼

⁷ present as sodium salts

ND: not determined

Formation of oil phase

In this experimental program, complete separation of the organic product as a single oil layer was not achieved, even when reaction conditions were apparently similar to those successfully employed in other types of reactor in earlier development work (CO/300 °C) (1). In experiments in which an oil layer was

formed, part of the organic matter was also converted into a bitumen-like material. It was assumed that this separation of the organic product into two phases was dependent on certain physical parameters of the reaction system. This assumption has since been confirmed. In this study, concerned with reactions of aqueous-phase constituents, efforts were not expended in optimizing physical conditions for oil-layer formation. In Table 2, the yields of "oil" and "bitumen" are reported separately.

The oil yield data of Table 2 indicate that, at 300 °C, CO was effective in producing a distinctly oil-like product but H₂ was not. At 350 °C, H₂ was also an effective reactant gas, as were mixtures of CO and H₂ with other gases (for example, "producer gas"). CO₂, on the other hand, was not effective, confirming that the most important function of the reactant gas is to reduce organic matter in the liquor.

Interactions between gaseous and aqueous components

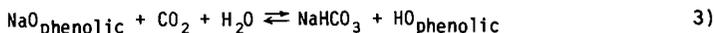
In all experiments the thermal treatment led to a decrease in the black liquor alkalinity, the final pHs being in the range 8 - 10 (Table 2). The chief neutralizing agents were the gases CO and CO₂. The decrease in alkalinity was least extensive in experiments employing hydrogen as reactant gas, but it was nonetheless quite significant, particularly at 350 °C (Expts. 4 and 5). In these cases, the neutralizing agent was CO₂, a product of the thermal decomposition of the organic matter (decarboxylation).

The electrolyte systems of kraft black liquor are well known (4). In principle this data can be applied to the product mixture of the thermal treatment process, allowing the following conclusions to be drawn:

1. In all cases, sulphur is present as HS⁻ in the aqueous phase, the final pHs (8 - 10) being lower than the pK_a for HS⁻ (~ 13.5) and higher than the pK_a for H₂S (~ 7). Very little H₂S should be formed.
2. HCO₃⁻ predominates over CO₃⁼²⁻, particularly at the lower end of the observed pH range. pK_a for HCO₃⁻ is ~ 10.
3. The phenolic hydroxyl groups of the lignin molecules are largely in an unionized condition, i.e. not bound to the sodium ion (pK_as: 9.5 - 11).
4. The carboxyl groups, which do not decompose during the thermal treatment, remain ionized (pK_as: 3 - 5). The three main fractions of the organic matter of the black liquor are lignin, aliphatic acids, and extractives. The aliphatic acid fraction contains the bulk of the carboxyl groups, but some are also encountered in the other fractions (5).

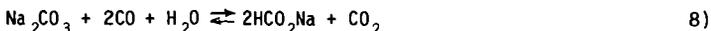
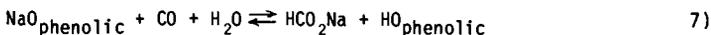
However, it should be noted that, because of mass transfer limitations, equilibrium between the gas and liquid phases is not necessarily established during all phases of the treatment process. For example, considerable amounts of H₂S were evolved during the treatment, the lower the pH the more H₂S (Table 2), indicating a higher pK_a value at the reaction temperature, and, after the rapid cool-down, lack of equilibrium between H₂S in the gas phase and H₂S in the aqueous phase.

When the neutralizing agent is CO₂, the main neutralization reactions can be written as follows:





When CO is the neutralizing agent, the equations become:



The results in Table 2 indicate that, at 350 °C, Reactions 1 to 4 occurred to a significant extent in all atmospheres. In the CO atmosphere, a significant amount of formate was also produced (Reactions 5 to 9). At 300 °C, the aqueous-phase composition in the CO experiment was considerably different from that in the H₂ experiment. In the CO atmosphere, a very large quantity of formate was formed. The increase compared to the CO/350 °C experiment was presumably due to a shift in the equilibria of Reactions 8 and 9. In the H₂ atmosphere at 300 °C, carbonate formation, although still significant, was less than at 350 °C (less decarboxylation of organic matter).

Stability of organic acid salts

A large fraction of the organic material of black liquor is comprised of aliphatic acids (5). In addition to the acids analyzed, there are significant quantities of less volatile aliphatic hydroxy acids. The acids, present as sodium salts in black liquor, are formed from wood polysaccharides during pulping. At the present time, the fate of the hydroxy acid components, other than lactic acid, during the thermal treatment process is not known with certainty. A recent study of cellulose conversion in alkaline solution suggests, however, that these components will not be converted into water-insoluble product, that is, oil, under these conditions (6). This is consistent with the energy yields of organic phase (oil and bitumen) observed in the present experiments. The yields are what one would expect if the organic phase were to originate almost entirely from the lignin fraction of black liquor. Forthcoming experiments will aim at confirming the origins of the oil product.

The present results (Table 2) indicate that sodium acetate was rather stable under the conditions of the thermal treatment, while sodium lactate decomposed to a large extent. Sodium formate decomposed in the CO₂ atmosphere, presumably due to a shift to the left of the equilibria of Reactions 8 and 9. In the H₂ atmosphere, formate was fairly stable. In this case, the decomposition of formate to carbonate was probably prevented by the following reaction (7):

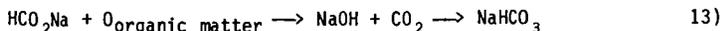


Consumption of reducing gas

From the point of view of oil formation, the most important reactions of CO or H₂ are the reduction reactions:



Sodium formate can also function as a reductant in a similar way (8):



However, the results of the $\text{H}_2/300^\circ\text{C}$ experiment suggest that the formate present in the black liquor feedstock (at 6 % om concentration) is not an effective reductant.

In addition to its being consumed as a reductant, CO is consumed in partial neutralization of black liquor alkalinity (Equations 5 to 9) and in production of H_2 by the water-gas-shift reaction:



From the data of Table 2, it has been possible to establish the consumption patterns of CO at 300°C and 350°C (Table 3).

Table 3. Consumption of CO.

		% of black liquor organics (% om)	
		CO/300 °C	CO/350 °C
I	Neutralization	18	3
II	Reduction	7	16
III	Shift	7	10
	Total	32	29

The total level of CO consumption, about 30 % om, is equivalent to a H_2 consumption of 2.1 % om, which is a much higher value than that observed in H_2 experiments: 0.3 - 0.5 % om (Table 2).

IMPLICATIONS FOR PROCESS DEVELOPMENT

The aqueous phase leaving the thermal treatment reactor contains the following compounds:

- NaHS ($\rightleftharpoons \text{Na}_2\text{S}$)
- NaHCO_3 ($\rightleftharpoons \text{Na}_2\text{CO}_3$)
- Sodium salts of aliphatic acids, with formate and acetate as two main components. The formate content is considerable when the reactant gas is CO.
- Other organic compounds in smaller amounts.

The organic acid salts and other organic compounds cannot be recycled, in their entirety, to the cooking stage. If not purged from the system, they will quickly build-up in concentration in the cooking liquor and retard the delignification reactions. Furthermore, particularly if the formate concentration is high, there may be insufficient sodium for binding to the hydroxide ion. In fact, various possibilities of converting sodium formate directly into sodium hydroxide were investigated in this study, but none of these proved to be technically feasible.

One example of a workable scheme for the recovery of chemicals is depicted in Figure 2. A part of the aqueous phase leaving the thermal treatment stage is recycled through a wet oxidation reactor where organic matter is oxidized to carbonate, CO_2 , and H_2O . The heat produced is employed in heating the feed

stream to the thermal treater. The rest of the aqueous phase is recausticized in the conventional way. In addition to the normal components of kraft green liquor, this liquor contains NaHCO_3 and some organic matter. The presence of organic matter should be an advantage because, according to the literature, a small but significant increase in pulp yield can be expected (2). The presence of NaHCO_3 will lead to a higher lime requirement in the recausticizing stage.

Wet oxidation is quite an economic process step in this scheme because the feed stream to it is already at the required temperature and pressure. Sulphide will be oxidized to sulphate, but it should be reduced again to sulphide in the subsequent heat treatment stage. This latter reaction will be investigated experimentally in the near future. For reasons of low gas consumption and low gas cost, producer gas is the reducing gas proposed for the scheme of Figure 2.

Preliminary economic evaluations of this scheme have indicated that it would be more economic than the conventional recovery process, particularly if a higher pulp yield were obtained. This process would also have a higher thermal efficiency than the conventional process.

CONCLUDING REMARKS

The black liquor treatment process being developed at VTT has several promising forms of application. The work described in this paper has furthered the development of one such application: a new recovery system for the kraft pulping process. Current research is being directed at gaining a better understanding of the oil-forming reactions occurring during thermal treatment.

ACKNOWLEDGEMENTS

This work was sponsored by the Energy Department of the Finnish Ministry of Trade and Industry. The authors particularly wish to acknowledge the contribution of Paula Ylinen, M. Sc., who undertook the study of the conversion of sodium formate into sodium hydroxide. Thanks are also due to the following staff members of the Laboratory of Fuel Processing and Lubrication Technology: Dr. Raimo Alén, Virve Tulenheimo, M.Sc., and Anja Oasmaa, M.Sc.

REFERENCES

1. Johansson, A. Biomass 4(1984)155-160.
2. Adams, W. S., & Maples, G. E. AIChE Symp. 76(1980)200, 114-119.
3. Alén, R., Jännäri, P., & Sjöström, E. Finn. Chem. Lett.(1985)190-192.
4. Rydholm, S. A. Pulping processes. New York 1965, John Wiley & Sons.
5. Sjöström, E. Appl. Polym. Symp. 37(1983)577-592.
6. Krochta, J. M., Hudson, J. S., & Drake, C. W. Biotech. & Bioeng. Symp. 14(1984)37-54.
7. Anon. Gmelins Handbuch der anorganischen Chemie. System-Nummer 21, Verlag Chemie, 1967.
8. Appell, H. R. et al. Conversion of cellulosic wastes to oil. U.S. Bureau of Mines, RI 8013, 1975.

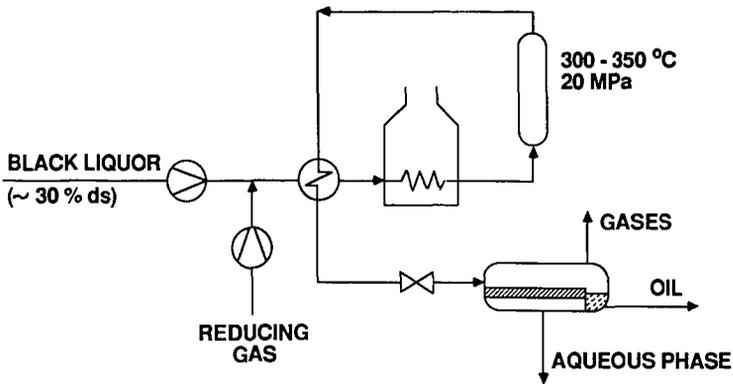


Figure 1. The thermal treatment process for black liquors.

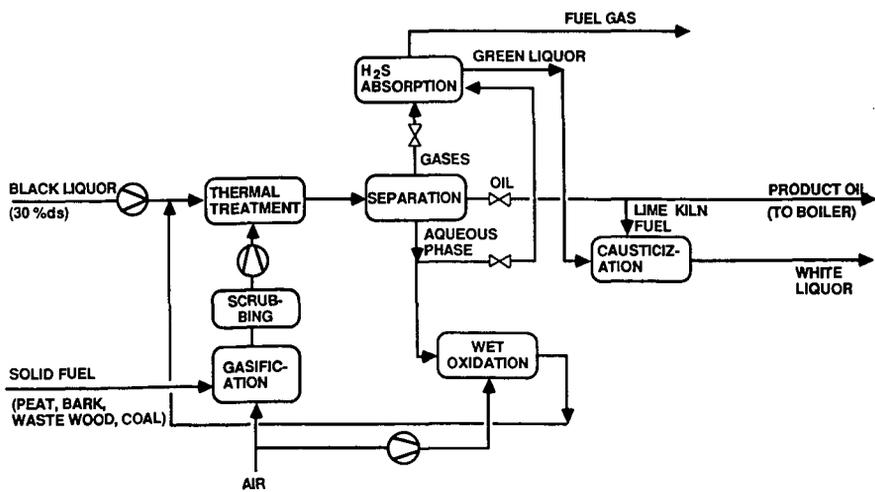


Figure 2. Preliminary scheme for a new kraft recovery process.

BIOMASS LIQUEFACTION UTILIZING EXTRUDER-FEEDER REACTOR SYSTEM

Don H. White, D. Wolf and Y. Zhao

Department of Chemical Engineering, University of Arizona, Tucson, Arizona 85721

ABSTRACT

Biomass including wood could provide liquid fuels on a regional basis if an economic liquefaction process can be developed. Through research sponsored by the U.S. Department of Energy (DOE), under its Thermochemical Conversion Program managed by Battelle PNL, the University of Arizona has developed a unique method of pumping concentrated, viscous biomass slurries, characteristic in biomass direct liquefaction systems. A modified single-screw extruder has now been shown to be capable of pumping solid slurries as high as 60 wt. % wood flour in wood oil derived vacuum bottoms. Preliminary experimental runs showed that a low-oxygen crude wood oil could be produced over a wide range of temperatures, pressures, with or without carbon monoxide and with or without a sodium carbonate catalyst.

INTRODUCTION

The modified extruder has now been shown to be capable of pumping slurries as high as 60 wt. % wood as compared to only 10-20 wt. % in conventional systems. The ability to handle such concentrated slurries which are in solid form at normal temperatures is expected to improve direct liquefaction wood oil quality and process economics. Various preliminary process design and economic studies indicated that the utilization of this newly-developed extruder-feeder in biomass direct liquefaction processes could lead to one or more of the process improvements listed below.

1. Elimination of recycle wood oil (or dramatically reducing it), which should result in less coke formation and better quality wood oil. In fact, even the reduced recycle will be wood oil vacuum bottoms, a heavy residue that might be decomposed further to a lighter oil.
2. Attainment of reactor temperature almost instantaneously, by the mode of adding heat (some by extruder-feeder preheater and remainder by superheater steam).
3. Attainment of near-plug flow in the reactor when using static mixers. This means that all biomass solids with nearly the same residence time in the reactor, have better control of conversion per pass and more uniform wood oil quality should be attained.

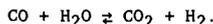
The extruder-feeder acts simultaneously as both a feed preheater and a pumping device into a 3,000 psi pressure reactor in the biomass liquefaction process. It could prove to be of importance in other processes where high concentration of solids in liquids are to be handled, like in the pulp and paper industry, hydrolysis of wood or other cellulose, other biomass liquefaction processes, coal liquefaction processes and some biomass gasification processes.

EARLY BUREAU OF MINES RESEARCH

In the early 1970's the Bureau of Mines showed that cellulosic materials, all other carbohydrates, wood wastes (largely cellulose and lignin), urban wastes (mostly cellulose plus other carbohydrates, proteins, fats, and small amounts of other organic materials), sewage sludge, agricultural wastes, and bovine manure can be converted to oil with carbon monoxide and water. Some plastics depolymerize and dissolve in the product oil; some remain as part of the unconverted residue (1,2).

Effect of Carbon Monoxide

Carbon monoxide and water react to form hydrogen and carbon dioxide in the following water-gas shift reaction:



Because some hydrogen adds to cellulose during its conversion to oil, it seemed at first reasonable to suppose that the hydrogen gas formed in the water-gas shift was responsible for converting cellulose. But when hydrogen was added to the reactor, it had little effect; an equivalent molar amount of carbon monoxide was much more effective. Early work showed that carbon monoxide consumption at lower temperatures (250°C) was low.

Effect of Water

The original experiments by the Bureau of Mines with carbon monoxide on low-rank coal (lignite) were successful without added water, because this coal has a large amount of moisture. However, addition of water was beneficial. It served as a vehicle (solvent) for the reaction. Cellulose forms water on being heated and the added water plus carbon monoxide improves the oil yield. However, added water also shifts the water-gas reaction in the direction of more carbon dioxide and hydrogen (more carbon monoxide is consumed); this side reaction may or may not be desirable.

The critical temperature of water is 375°C; above this temperature all the water is in the gaseous state. There were indications that the presence of liquid water is desirable. This may be accomplished by adding enough water so that some liquid is always present. The temperature must of course be below 375°C. If insufficient water is added, most of it will be in the gas phase, even below 375°C.

Nature of Conversion Reactions

The Bureau of Mines speculated on the possible chemical reactions in 1971 as follows:

"Cellulose, starch, and other carbohydrates can undergo a large number of reactions on treatment at elevated temperatures and pressures with carbon monoxide, water, and sodium carbonate or other alkaline salts. Since almost every carbon atom in a carbohydrate is bonded to an hydroxyl group (-OH), some dehydration will take place. Hydrolyses of the polysaccharides to glucose will also occur; glucose and the smaller units formed from it are soluble in water. Hydrolysis of the fats in the refuse to long-chain palmitic and stearic acids will also occur. Probably the most important overall reaction in converting cellulose to oil is the splitting out of oxygen to form molecules with high hydrogen-to-carbon ratios. Cellulose and other carbohydrates lose water and carbon dioxide just on being heated. Oxygen can also be lost by reaction with the added carbon monoxide to form carbon dioxide, by hydrogenation, by various disproportionation reactions, and by combinations of these reactions".

Later Bureau of Mines Research

Further research work in the early 1970's by the Bureau of Mines resulted in data on the reaction parameters (1). In general, the more readily hydrolyzable forms of cellulose, especially those containing pentosan units can be readily converted to a bituminous oil at temperatures as low as 250°C. Lignin and high-molecular-weight cellulose, containing crystalline cellulose, required higher reaction temperatures of about 350°C.

Wood is considerably more difficult to convert to oil than other biomass sources, but good oil yields were obtained by the Bureau of Mines in the presence of organic solvents as shown in Table 1 during wood liquefaction at 275°C. It was believed that some carbon monoxide was evolved during the decomposition of the wood and was apparently about equal to the amount of carbon monoxide consumed.

Table 1. - Effect of Water and Solvent on Wood Liquefaction

(50 g softwood sawdust, 1 hr at 275°C, 300 psig CO)

Cresol solvent, (g)	Water, ml	Catalyst		Pressure, psig	Conversion pct	Yield, pct	CO used g/100 g wood
		Type	Amount				
50	200	HCO ₂ Na	5	1,900	99.9	48	6
50	50	Na ₂ CO ₃	2	1,780	99.3	60	4
75	10	None	0	1,470	99.0	58	0
75	10	HCO ₂ H	1	1,500	99.3	58	0
75	10	HCO ₂ Na	1	1,560	99.8	60	0

The Bureau of Mines did considerable work at pressures below 2,000 psig and at 250°C. However, the products obtained at these mild conditions were pitches instead of oils. The lowest temperature at which a suitable oil could be produced was 300°C, at which temperature the combined water vapor and carbon monoxide pressure exceeded 2,000 psig.

The Bureau of Mines conducted some interesting experiments using formic acid or sodium formate in place of carbon monoxide. This lowered the operating pressure at 250°C to the range of 1,000 - 1,100 psig, and still gave good oil yields, as shown in Table 2 below. This technique would be less successful above 250°C because the formates decompose too rapidly.

Table 2. - Liquefaction of Wood in Absence of Carbon Monoxide

(50 g softwood sawdust 50 g Cresol solvent, 1 hr at 250°C)

Water, ml	Catalyst, g		Pressure, psig	Oil yield pct	Conversion pct
	Type HCO ₂ Na	Amount HCO ₂ H			
100	1	5	1,070	60	99.6
100	5	1	1,040	55	99.0
100	2.5	2.5	1,050	55	99.8
50	2.5	2.5	1,040	41	90

The unstabilized crude wood oil is very reactive to continued exposure to temperature. The Bureau of Mines studied the effect of recycling wood-derived oil. When using an initial carrier oil, such as mixed cresols, it was calculated that after 6 runs, using the product as recycle oil carrier, the original carrier oil would be reduced to about 9 percent. A series of runs at 250°C to 275°C showed that the product became too thick to use after only four cycles. A temperature of at least 300°C and pressures of 2,700-3,000 psig were needed to obtain a product with acceptable softening point.

OTHER RESEARCH ON BIOMASS LIQUEFACTION

There has been other research on biomass liquefaction by high-pressure, liquid-phase systems, but it appears to be fragmented and scattered. Remarkably, many of the concepts presented by the Bureau of Mines in the early 1970's appear to remain to some extent the "state-of-the-art" in biomass liquefaction, compared for example, with the extensive technology developed for coal liquefaction by Mobil, Exxon, Gulf and others, largely supported by the DOE and some by EPRI.

Battelle Pacific Northwest Laboratories

A fundamental study using pure cellulose (Solka-floc) was performed at Battelle, sponsored by the Division of Chemical Sciences, Processes and Techniques Branch, DOE (3). A series of 129 autoclave experiments analyzed by statistical methods indicated that carbon monoxide, while it promotes the attainment of high yields as claimed by the Bureau of Mines, is not necessary for the reaction to proceed. Analysis of the products by ^{13}C -NMR, GC/MS, and gel permeation chromatography indicated that the non-volatile fraction of the oil consists of 44% aromatic carbon and 7% aromatic hydrogen, corresponding to a benzenoid polyaromatic with a substitution ratio of 5:1. However, the oxygen content of the non-volatile fraction and distillable oil is approximately the same. Since the oil contains a series of polyalkylated furans, this suggests that the char is a poly-furan rather than a conventional apaltene derivative. Volatile products from the oil fraction consists of furans, cyclic ketones, linear and branched alkenes, and phenolics. The high proportion of phenolics relative to normal crude oil could explain the observed highly corrosive nature of the biomass-derived oils.

Albany Biomass Liquefaction Facility

The Albany facility operated on the basic PERC process, so designated because the original work was conducted at the Pittsburgh Energy Research Center. It was operated initially by the Bechtel Corporation, followed by the Rust Engineering Company (the latter for prime contractor, Wheelabrator Cleanfuel Corporation). The process involved reacting biomass in an oil slurry with carbon monoxide and hydrogen at temperatures up to about 380°C and pressures up to 4,000 psig.

The final Albany test run, Test Run No. 12, prior to shutdown and phaseout on June 30, 1981, produced over 11,000 pounds of wood oil is a sustained and controlled run. The oil had characteristics closely approximating the original design basis as shown below in Table 3.

Table 3 -- Summary of Properties of Albany Crude Wood Oil

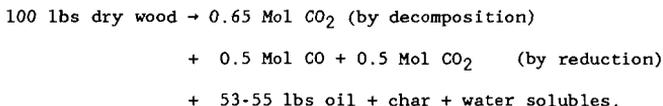
	<u>Design Basis</u>	<u>Run 12 Product</u>
Specific gravity	1.1	1.11
Viscosity	515 cp at 140°F	135 cp at 210°F
Heating value	13,390 Btu/lb (Calculated)	14,840 Btu/lb (measured)

Crude Wood Oil Analysis:

Carbon	72.62	78.9
Hydrogen	7.05	8.51
Nitrogen	0.13	0.5
Sulfur	0.14	0.08
Oxygen	20.05	12.3

Lawrence Berkeley Laboratory (LBL)

This laboratory provided technical assistance to the Biomass Facility at Albany, Oregon. For example, during the earlier period of Albany operations, it provided useful guidance from material balances on what chemical reactions might be occurring (5). It deduced that Douglas Fir wood converted to oil plus small amounts of water-soluble products and char at about 52-55 wt % efficiency. Based on an approximate stoichiometric analysis, the following changes occur.



Carbon monoxide used is about 200 SCF/100 lbs wood or 370 SCF 100 lbs product or 1300 SCF/bbl product. The yield of non-gaseous product can be less than 51% only if carbon monoxide is generated by decomposition of wood or by reaction of wood or its products with water. This appeared to be contrary to observations.

LBL researchers focused their attention on the prehydrolysis of wood to cut down swelling so that wood/water slurries containing up to 25 wt % wood could be pumped (6). This was done at 180°C, 45 min, with 500 ppm sulfuric acid. They used moist chips, water content of 75 wt.% and operated at about pH of 2 in a stirred autoclave. The wood chips disintegrated into fine particles and some courser but friable particles. When the resultant sludge passed through a disc refiner, a pumpable slurry was obtained.

LBL constructed a bench-scale liquefaction unit based upon the above water/oil/wood slurry concept. It was operated with limited success, but ran into plugging problems, possibly due to the small diameter of process tubing. Also, considerable wood oil product dissolved in the large water phase, and the economics of recycling this large water phase or treating it for disposal did not look attractive from the limited experimental data.

Crude Wood Oil Fuel-Burning Tests

Test runs were also made in the Albany facility to simulate the conditions proposed by LBL for its water/oil/wood slurry system, and in fact was the technique that produced the first significant quantities of wood oil. Combustion tests were conducted in a commercial boiler on oils produced by both LBL and PERC process modes at the Pittsburgh Energy Technology Center (PETC). Two barrels, approximately 100 gallons of wood oil from each process, were burned in a 20 Hp Johnson three-pass fire tube boiler designed to transfer 670,000 Btu per hour, with results as follows:

Table 4. Comparison of Heavy Liquid Fuels

	Test Run No. 8 PERC Distillate Oil	Test Run No. 7 LBL Crude Oil	Fuel Oil No. 2	Fuel Oil No. 6
Carbon %	84.5	78.1	87.3	87.0
Hydrogen %	9.5	7.7	12.5	11.0
Nitrogen %	0.2	0.1	--	0.3
Sulfur %	0.2	0.1	0.21	0.70
Ash %	0.2	0.2	--	0.10
Oxygen %	8.4	13.8	--	1.0
Heating value Btu/lb	19,840	17,360	18,610	14,940

Upgrading Crude Wood Oil by Hydrotreating

Currently, Battelle Pacific Northwest Laboratory has a major effort on the development of a hydrotreating process for wood oil product upgrading (7,8). Individual components from the product of direct liquefaction of biomass have been subjected to hydrogenation with a number of transition metal oxide catalysts. Sulfided cobalt-molybdenum has been found to be effective for the hydrodeoxygenation of phenolics. The product of choice from hydro-treating would be the aromatic product which maximizes oxygen removal and minimizes hydrogen consumption.

Other Interest in Biomass Liquefaction

This paper emphasized direct biomass liquefaction in the United States, but would be remiss if it did not point out the high interest in biomass liquefaction in other parts of the world, especially Canada and Europe. Low pressure pyrolysis is being investigated at the University of Sherbrooke, Canada (9). At the Royal Institute of Technology, Sweden, a research project in progress compares the dissolution of coal, peat and biomass in hydrogen donor solvent - tetralin at 350°C to 400°C, cold pressure of nitrogen 5.0 MPa and reaction time 15 to 120 minutes (10). At the University of Saskatchewan, Canada, the liquefaction of aspen poplar wood to produce a proto-oil was investigated (11). In the batch reactor studies, the water to wood ratio emerged as the most important parameter affecting yield and quality of oil. The Department of Scientific and Industrial Research, New Zealand, believes that biomass liquefaction has several inherent advantages over other processes for obtaining liquid fuels (12). The process is rapid and it does not require the production of reducing gases. This should allow smaller scale processing than other processes. Biomass is much less abrasive, and it is softer than coal.

CURRENT BIOMASS LIQUEFACTION RESEARCH AT ARIZONA

The advanced extruder-feeder biomass liquefaction reactor system was designed to experimentally convert wood flour to liquid wood oil fuels by direct liquefaction. The extruder-feeder system developed at the University of Arizona is incorporated into the system to develop 3,000 psig pressure at its discharge and preheat the slurry prior to entering the vertical reactor. As the wood flour slurry enters the reactor it is mixed with superheated steam and carbon monoxide. Gas dispersion as well as heat and mass transfer will be attempted by the use of static mixer elements inside the tubular reactor. The superheated steam is used to heat the wood flour slurry up to the reaction temperature of 350°C almost instantaneously, which is then maintained by the use of electrical band heaters surrounding the reactor. Steam and carbon monoxide also react via the water-gas shift reaction to provide hydrogen for the liquefaction. The liquefaction products are split into the vapor and liquid

fractions, condensed, cooled down and brought to atmospheric pressure by means of the let-down system. Computer control and real-time data acquisition have been implemented for the unit.

The University of Arizona in its limited experimental runs over the past year has consistently produced a low-oxygen crude wood oil, namely, in the 6-8 wt % oxygen range. A few samples of this oil are currently being evaluated for upgrading by hydrotreating by Battelle Pacific Northwest Laboratory (13). This may prove to be a good candidate of wood oil for upgrading to a petroleum-like transportation fuel.

Experimental data for some of the initial runs made at the University of Arizona over the period of August 29, 1985 through July 2, 1986 are shown in Tables 5, 6 and 7. These experimental runs were purposely planned to cover several extremes of operating conditions, namely, pressure, with and without reactant carbon monoxide, and with and without sodium carbonate catalyst. Experimental runs showing effects of residence time, temperature and various feedstock treatments have not yet been performed.

Table 5 -- Continuous Biomass Liquefaction Experimental Conditions

Run No.	Wood Four	Wood Oil Vacuum Bottoms	Feedstock H ₂ O, wt. %	Na ₂ CO ₃ Catalyst, pp hr.	Temp. °C	Press. psi	Feed Rate lb/hr	Residence Time Minutes
1	40	60	8	10	375	3,000	10	72
2	38	62	12.2	2	400	800	6	120
3	38	62	8.8	0	400	1,000	8	90
4	38	62	15	0	400	1,200	7	103
5	40	60	19.7	0	400	2,300	10	72
6	38	62	15	2	400	3,000	3	240
7	40	60	15	0	400	3,000	8	90

Table 6 -- Elemental Analysis of Crude Wood Oil Obtained by Liquefaction

Run No.	Crude Distillate, wt. %	Crude Distillate Analysis, wt. %			
		C	H	O	N
1	24.8	82.71	9.07	6.52	0.13
2	24.7	84.72	9.03	9.03	0.22
3	39.0	84.51	8.66	8.66	0.22
4	27.0	84.12	8.67	8.67	0.34
5	23.4	82.00	8.81	8.81	0.21
6	30.0	81.64	8.46	8.90	0.10
7	27.0	80.00	8.40	10.02	0.00

Table 7 -- Properties of Crude Wood Oil Obtained by Liquefaction

Run No.	Viscosity, C.S., 30°C	Heat of Combustion Btu/lb.	Water Content mg./mol	Aromacity (NMR)	
				Aromatic	Aliphatic, C H
1	86	16,300	3.08	0.60	0.22
2	135	16,960	3.19	0.68	0.32
3	164	16,510	5.51	0.68	0.30
4	155	16,450	7.71	0.66	0.27
5	100	16,200	5.43	0.69	0.37
6	120	16,020	5.48	0.88	0.31
7	103	15,000	8.69	0.99	0.36

The crude distillate was obtained by vacuum distillation of the reactor effluent at 2-3 mm/Hg absolute pressure and temperatures starting at about 300°F and going up to 550°F. As can be seen it has a reasonably low viscosity at 30°C and a heat of combustion of about 16,000 BTU/lb. The aromatic content as determined by nuclear magnetic resonance is about 40 percent. Most important, the oxygen content has been reduced during liquefaction from about 42 wt.% in the white birch feedstock to about 6-7 wt.%, such that hydrotreating to a transportation fuel should be facilitated.

Even though the extruder-feeder has demonstrated the ability to feed 60 wt.% wood flour/sawdust feedstocks, these initial experimental runs were made with feedstocks ranging from 35 to 42 wt.% white birch wood flour. Thus, if one assumes the heavy vacuum bottoms are essentially inert as a carrier of the feedstock, then one would expect to generate 35 to 40 wt.% (less losses due to oxygen reduction) of crude wood oils in the once-through liquefaction system. Some results to date on the vacuum distillation of the reactor effluent, which contains the Albany vacuum bottoms carrier are as follows:

Table 8 -- Vacuum Distillation of Liquefaction Reactor Crude Product

Run No.	Run Date	Feedstock W.F., wt. %	Reactor Pressure psi	Percentage of Reactor Product Distilled, wt. %	Percentage of Reactor Product Condensed, wt. %
2	2/19/86	36	800	24.7	17.5
3	3/19/86	38	1,000	39.0	25.5
4	4/19/86	38	1,200	27.0	19.0
5	5/29/86	40	2,300	23.4	16.0
6	6/30/86	36	3,000	30.0	20.0
7	7/02/86	40	3,000	27.0	23.9
8	7/30/86	33	600	19.0	9.0
9	7/31/86	33	600	20.0	11.0

The liquefaction of wood to a crude wood oil having a much lower oxygen content and essentially little change in the hydrogen content means that for even a 100% of theoretical conversion to wood oil, there is a large loss of weight of product compared with the feedstock weight. Under certain liquefaction conditions, the elimination of oxygen from wood can occur by about 60 percent as water and 40 percent as carbon dioxide (14). Under other liquefaction conditions, the elimination of oxygen from wood is claimed to occur by about five percent water and 95 percent carbon dioxide (15). The off-gas of the above experimental runs were analyzed, but due to the water present from the steam injection, the ratio of water/carbon dioxide evolved from white birch wood has not yet been determined. Assuming a 50/50 ratio of

water/carbon dioxide evolving in these data, the theoretical loss of weight of wood going from 41.26 wt. % oxygen to 7.0 wt. % oxygen is 48 percent. Thus, 100 pounds of dry white birch biomass can theoretically produce about 52 pounds of crude wood oil, under the above assumption of liquefaction conditions. If one were to apply this theoretical yield to the amount of condensed distillate obtained as listed in Table 8, then yields greater than 100 percent theoretical are obtained. Even changing the assumption on the ratio of water/carbon dioxide rejection from the biomass over a range consistent with known H/C ratios of crude wood oils can only partially account for the high quantities of crude oil distillates obtained. One other conclusion that could be drawn (assuming the experimental data is reasonably correct) was that the Albany black vacuum bottoms are not inert at the liquefaction temperature of 375-400°C. Consequently, the thermal stability and possibility of obtaining distillable products from the Albany black vacuum bottoms were investigated.

The Albany black vacuum bottoms used at the University of Arizona came in drum lots from Albany, Oregon, where it was obtained by fractionating Douglas Fir wood oil in a fairly large vacuum fractionator. This material was used during the period August 29, 1986 through July 2, 1986 until essentially exhausted. A second lot of Albany vacuum bottoms, a brownish-black in color, was used in a "long run" of 52 hours duration conducted July 29-31, 1986. The elemental analysis of these two Albany vacuum bottoms and some related data are as follows:

Table 9 -- Elemental Analyses Related to Feedstocks and Carrier Oils

	Wt. % C	Wt. % H	Wt. % O	Wt. % N	Total CHON
Black Vacuum Bottoms	78.96	6.71	12.05	0.26	97.98
Brown Vacuum Bottoms	81.58	6.25	9.22	0.37	97.42
Distillate Black V.B.	85.21	7.60	5.32	0.23	98.36
White Birch Wood	46.98	5.61	41.26	0.04	93.89

First, to test the thermal stability of black vacuum bottoms, a series of three samples were heated in the absence of other reactants to 400°C for 2, 3 and 4 hours, respectively, in a pressure autoclave. The autoclave was cooled, all products except gases collected, and analyzed. Whereas the fresh Albany black vacuum bottoms were 99-100% soluble in THF, all three of the samples heated to 400°C for 2 to 4 hours showed that in all three cases 50 percent of the original samples were insoluble in THF, indicating a further cross-linking, polymerization, oxidation or carbonization of some type. Equally important, the other 50 wt. % of the original sample appeared to represent about 7 wt. % off-gas at 400°C and about 43 wt. % remaining as a "vacuum bottoms" containing some crude wood oil.

Secondly, when the fresh Albany black vacuum bottoms are further distilled at 2-3 mm/Hg absolute pressure, a total of 22.5 wt. % distilled as the temperature gradually was raised to 550°F, at which point no additional distillate was observable. A total of 16.3 wt. % of the original feed was condensed with 70°F cooling water with the balance being non-condensables at 70°F.

Yields of crude wood oil appear to be from 80 to 100 percent of the theoretical when all of the above data are used in the calculations. The weakest assumptions involve how much additional crude wood oil is derived from the Albany black vacuum bottoms carrier fluid. Another indication of the near-theoretical yield of crude wood oil is the low methane, ethane and hydrogen content of the off-gas, despite the liquefaction temperature being on the high side at 375-400°C.

CONCLUSIONS

A reasonably low-viscosity, low-oxygen crude wood oil can be obtained in the once-through, near-plug flow high-concentration solids vertical reactor system. Experimental conditions to date are on the high side of temperature and residence time, and on the low side with respect to pressure, quantity of steam, quantity of sodium carbonate catalyst, quantity of carbon monoxide reactant and quantity of superheated steam. The experimental unit exhibits good operability and has begun to provide good material balances, such that it appears that future runs can evaluate the many parameters affecting conversion, yield and quality of the crude wood oil.

REFERENCES

1. Appell, H.R. et al., "Converting Organic Wastes to Oil", BuMines RI 7560 (1971).
2. Appell, H.R. et al., "Conversion of Cellulosic Wastes to Oil", BuMines RI 8013 (1975).
3. Molton, P.M. et al., "Mechanism of Conversion of Cellulosic Wastes to Liquid Fuels in Alkaline Solution", Presented at Third Energy from Biomass and Waste Symposium, Sponsored by IGI, Held at Alexandria, Virginia (August 1978).
4. Berry, W.L. and P.L. Thigpen, "Operation of the Biomass Liquefaction Facility, Albany, Oregon", Presented at 13th Biomass Thermochemical Conversion Contractor's Meeting, Arlington, Virginia (October 1981).
5. Davis, H. et al., "Catalytic Biomass Liquefaction Quarterly Report" LBID-272, Lawrence Berkeley, Berkeley, California (April-June, 1980).
6. Ergun, S. et al., "Catalytic Biomass Liquefaction Quarterly Report", LBL-11019, Lawrence Berkeley Laboratory, Berkeley, California (February 19, 1980).
7. Elliott, D.C., "Bench Scale Research in Biomass Direct Liquefaction", Presented at the 14th Biomass Thermochemical Conversion Contractor's Meeting, Arlington, Virginia (June 1982).
8. Elliott, D.C., "Hydrotreating Biomass Crude Oils", Proceedings Annual Biomass Thermochemical Conversion Contractors Meeting, Minneapolis (October 1985).
9. Roy, C. C. et al., "The Pyrolysis under Vacuum of Populus Tremuloides and its Constituents", Presented at Fundamentals of Thermochemical Biomass Conversion: An International Conference, Estes Park, Colorado (October 1982).
10. Hornell, C. et al., "Dissolution of Peat and Wood in Tetralin compared with Coal", Presented at Fundamentals of Thermochemical Biomass Conversion: An International Conference, Estes Park, Colorado (October 1982).
11. Eager, R.G., et al., "Liquefaction of Aspen Poplar to Produce an Oil and Chemicals", Presented at Fundamentals of Thermochemical Biomass Conversion: An International Conference, Estes Park, Colorado (October 1982).
12. Miller, I.J., "Biomass Liquefaction as a Potential Process", Presented at Fundamentals of Thermochemical Biomass Conversion: An International conference, Estes Park, Colorado (October 1982).
13. White, D.H., Personal Communication with D.C. Elliott (August 1, 1986).
14. Espenscheid, W.F., "Liquefaction of Solid Carbonaceous Materials", U.S. Patent 4,052,292 (October 4, 1977).

15. Chen, N.Y. et al., "Liquefaction of Solid Carbonaceous Materials", U.S. Patent 4,247,384 (Issued January 27, 1981).

ACKNOWLEDGEMENT

This research was supported by Department of Energy Contracts DE-AC06-76RLO-1830 (Subcontract B-96249-A-Q from Battelle Pacific Northwest Laboratories) and DOE Contract EW-78-S-05-5679. Special thanks are given to M. Chehab, A. Homaidon, A. Lezzar, D. Joshi and B. Reyes, who performed much of the experimental work. We also appreciated the assistance of Professor N.R. Schott, while on Sabbatical at the University of Arizona. Many undergraduate students too numerous to list have also contributed to this research project and their help is greatly appreciated.

Characterization of Products Formed During
Coliquefaction of Lignin and Bituminous Coal at 400°C

by

Paul Altieri

and

Robert W. Coughlin

Department of Chemical Engineering
University of Connecticut
Storrs, Connecticut 06268

Abstract

The filterable solids from coliquefaction were about 30% benzene soluble compared to about 10% soluble when the same amounts of coal and lignin were reacted individually. In the case of coliquefaction, far more of the benzene-soluble material was also pentane-soluble oil. As a result of coreaction, significant amounts of nitrogen from the coal appeared in the liquid product in contrast to no observable nitrogen in the liquefaction product of coal alone under comparable conditions. Gaseous products were significant and contained CO₂ as a major component. More carbon-14 from the lignin got incorporated into the liquid product during coliquefaction of coal and lignin than in the case of liquefaction of lignin alone under comparable conditions.

Introduction

Recent reports (1, 8) have shown that liquefaction of bituminous coal can occur at temperatures as low as 300°C when the potentially abundant, renewable raw material, lignin, is present in the reaction mixture. Previous processes²⁻⁵ have generally required temperatures above about 400°C in order to rupture carbon-carbon bonds, a necessary step for depolymerization of coal. Lignin degrades thermally at temperatures as low as 300° with the production of substituted phenoxyl radicals. Heredy and Neuworth⁶ and Larsen et al⁷ reported that the presence of phenolic components in the reaction mixture aids the depolymerization of coal resulting in substantial coal liquefaction.

Thus it was hypothesized,⁽⁸⁾ that phenoxy radicals produced by lignin at temperatures ordinarily too low for depolymerization of coal abstract hydrogen from carbon-carbon bonds of coal molecules thereby making them more susceptible to thermal scission.

This paper reports the characterization of the liquid and solid products recovered after co-liquefying coal and lignin in the presence of the hydrogen donor solvent, tetralin. Products were investigated from three separate reactions:

1. Lignin and coal reacted together in tetralin
2. Lignin reacted in tetralin
3. Coal reacted in tetralin

Experimental

Materials And Reagents

Lignin

The lignin used was a "caustic" type obtained from autohydrolysis of aspen. It was purchased from Stake Technology LTD, Ontario, Canada. The lignin was dried in a vacuum oven at 85°C under low pressure (10 torr) for 24 hours and then stored in a dessicator for later use without any further purification.

Coal

Illinois No. 6 bituminous coal (particle size 74-105 micrometers) was obtained from the Pittsburgh Energy Technology Center. This coal has been found to have a 13.6% ash content which was accounted for when computing results on a moisture and ash free basis (maf basis). Crushed coal was sieved to the 74-105 micrometer particle size range, then dried and stored in the same manner as the lignin.

Reagents

All solvents were "Baker analyzed grade" from J. T. Baker Co. except guaiacol which was obtained from Pfaltz and Bauer Co. and tetralin which was obtained from Eastman Kodak Co. Hydrogen and nitrogen gases (98%) were supplied by AERO-All Gas Co.

High Pressure Liquefaction

Tetralin (200 ml), lignin (25 g), coal (25 g), and catalyst were mixed in an inner cylindrical vessel of sheet stainless steel. This was inserted in a one-liter 316 s.s. Magna-drive autoclave manufactured by Autoclave Engineers Inc. The bomb was sealed, pressure tested, flushed with hydrogen, and then pressurized with 1000 psig hydrogen. The system was then heated with agitation at 1500 rpm to 400°C for 1 hour. Approximately 45-60 minutes were required during which time the pressure rose from 1000 psi to 1900-2400 psi. After one hour at the desired reaction temperature, the system was cooled to around 40°C by flowing water through the internal coil for about two hours. Pressure in the cooled reaction vessel ranged

between 700-1000 psig. After venting gases the product material in the liner was removed and transferred to a tared container. Any liquid that remained in the bottom of the autoclave was removed with a pipette and added to the products together with liquid from rinsing the autoclave and liner with known amounts of fresh tetralin.

The product mixture consisting of both insoluble residue and liquid was weighed and then filtered through a tared glass fritted filter (ASTM 10-15). This insoluble, filtered residue was dried at 85°C under vacuum to constant weight.

Determination of Benzene and Pyridine-Soluble Fractions

The filtered residue material was extracted in a tared Soxhlet extraction thimble using benzene until the extract became clear (about 24-48 hours). The thimble was then dried at 85 C under vacuum to constant weight. The weight loss is reported as material which is benzene soluble.

The thimble containing the benzene-extracted solid residue was then extracted with 150 ml pyridine for 24-48 hours. Material soluble in pyridine was computed as weight loss.

Determination of Asphaltenes and Oil

The benzene extract was evaporated and the residue dried to constant weight, then redissolved in a minimum amount of fresh benzene with gentle warming. Then n-pentane (100 ml) was added to precipitate asphaltenes which were filtered and dried to constant weight. The filtrate remaining after asphaltene precipitation was evaporated to recover the "oil" (benzene and pentane soluble).

Carbon-14 Analysis

Various liquid product fractions were analyzed for carbon-14 by New England Nuclear Laboratories using a liquid scintillation spectrometer.

Analysis of Nitrogen Carbon and Hydrogen

Various liquid product fractions were analyzed for nitrogen, carbon and hydrogen content by the American Cyanamid Company. Oxygen content was obtained by difference. Two trials were performed for each sample.

GC/MS Characterization of Evolved Gases

Lignin (25 g), coal (25 g), and tetralin (300 ml) were reacted at 400 degrees centigrade for one hour at 2200 psi in a rocking autoclave (Parr #4021). The procedure was otherwise as discussed above.

After reaction the autoclave was cooled and then connected to the sampling valve of a Hewlet Packard #5985 GC/MS equipped with a stainless-steel column packed with Carbowax. The autoclave vessel was held at $\sim 200^{\circ}\text{C}$ while a small flow of gas was released and periodically sampled for GC/MS analysis. Temperature programming of the GC column from 20°C to 225°C over a time span of 60 minutes permitted adequate separation of components.

Results And Discussion

Table 1 summarizes mass balances for four experiments. The amount of gas formed was computed by difference.

Characterization of Solid Products of Reaction:

Figure 1 summarizes the work up and fractionation of the solid and liquid products of reaction. The individual fractions, P1 through P7 are further identified in Table 2.

Characterization of coal liquids as benzene-soluble and pentane-soluble goes back to Pelipetz et al (9) who viewed solubility in benzene as a measure of the extent to which coal has been hydrogenated; unreacted or partially reacted coal remains insoluble in benzene. Solubility in benzene and pentane is a measure of the "oil" produced. The portion that is soluble in benzene but insoluble in pentane (i.e. precipitated by pentane) is called asphaltenes. Asphaltenes are high-molecular weight intermediate products in coal liquefaction. The presence of asphaltenes in coal-derived liquids has been reported by both Pelipetz (9) and Weller (10). Stern (11) showed that both the quantity and the molecular weight of the asphaltenes present in the coal-derived liquid product affect its viscosity. These methods are also described by Mimal (12). As evident from Figure 1, we also employed pyridine solubility which was used by Whitehurst (13) to represent the extent to which coal is converted to liquid products (13).

The mass of solids filtered from the products of the reactions are plotted in Figure 2 (see Table 3 for experimental conditions). Figure 2 compares the solids from experiment 4-A (in which lignin and coal are co-liquefied) to the sum of the solids filtered in experiment 4-B (in which only lignin is used) plus experiment 4-C (in which only coal is used). The cross-hatched area of each bar graph represents benzene-soluble material (P4) which is greatly increased (by about a factor of four) when lignin is present in the reaction mixture.

Further characterization of the benzene-soluble solids (P4) is shown in Figure 3. Figure 3 shows that when lignin and coal are co-liquefied the production of asphaltenes

(benzene-soluble but pentane insoluble, (P5)) is increased more than the corresponding production of "oil" (soluble in benzene and pentane, (P6)).

The benzene-insoluble residue was partially soluble in pyridine in every case. Co-reacting lignin with the coal does not cause any substantial change in pyridine solubility of the benzene insoluble residue.

Three control experiments (5A, 5B and 5C) were conducted at room temperature but with all other aspects identical to experiments 4A, 4B and 4C. The results shown plotted in Figure 4 indicate essentially no liquefaction took place since the mass of filtered solid product was equal to the mass of coal and/or of lignin charged to the reactor. Benzene soluble solids are only about 2.5g in the case of the control experiments vs about three g for coal and lignin reacted separately at 400°C and about 11 g for the coreaction of coal and lignin at 400°C.

Characterization of Liquid Products:

Liquid products from reactions 4A and 4B were further characterized by analysis for carbon-14 and nitrogen. Because coal contains significant nitrogen but lignin contains very little, nitrogen analysis of liquid products indicates the relative contribution of coal. Because lignin contains significant carbon-14 but coal does not, the carbon-14 content of the liquid indicates the relative contribution of lignin. The half life of carbon-14 is 5730 years and coal was formed from biomass millions of years ago; therefore the carbon-14 remaining in coal is unmeasurable. Any detectable carbon-14 in the liquid must be contributed by the lignin which contains carbon-14 comparable in isotopic abundance to that in carbon dioxide in the atmosphere because the lignin was prepared from wood cut within recent years. Tetralin used as the solvent in the experiments contributed negligible carbon-14 because it was produced from petroleum formed millions of years ago.

Table 4 reports carbon-14 contents of the liquid products for the case when lignin and coal are present in the reaction mixture as well as when only lignin was present in the reaction mixture. The greater concentration of carbon-14 observed when lignin and coal are co-liquefied suggests ruptured coal molecules may incorporate lignin fragments. Coal may also catalyze the liquefaction of lignin or more lignin may get incorporated into the liquid because it reacts with coal fragments rather than self-polymerizing into a solid.

Table 5 shows the elemental analysis of the coal and Stake lignin used in the experiments. Table 6 shows that the liquid filtrate obtained from experiment 4-A when coal and lignin are coreacted contains 0.1% nitrogen compared to no detectable nitrogen in the liquid formed by reaction of coal alone.

The absence of nitrogen in liquid products from coal reacted alone at 400°C (experiment 4B) indicates that the nitrogen-containing portions of the coal molecules were not depolymerized. During co-reaction with lignin under the same conditions (experiment 4A), however, nitrogen does appear in the liquid products indicating more extensive depolymerization of coal molecules. The content of nitrogen (0.1%) indicates a rather uniform disintegration of the coal to form liquid because this value is close to what one would compute using the original nitrogen content of the coal and the apparent fraction of coal that was liquefied. Table 6 also shows the nitrogen content of three distilled fractions of the liquid obtained from experiment 4A. The lowest-boiling fraction is tetralin and contains no nitrogen. It appears the nitrogen is concentrated in the non-distillable residue as might be expected if the nitrogen occurs in the larger molecular fragments contributed by the coal.

Characterization of Gaseous Products

Mass balances (see Table 1) suggest the formation of significant amounts of gases during the reaction. An experiment was performed in which coal and lignin were reacted as in experiment 4-A and the reactor then cooled under pressure. Later, the reactor was heated to about 200°C and the product gas was sampled from the reactor at this temperature and analyzed by GC-MS. Table 7 shows the mass balance for this experiment and the components detected in the vented gas.

Based on the respective peak heights of the GC chromatogram, carbon dioxide was the most abundant gaseous product with water vapor being next. The gases estimated in Table 1 by difference from mass balances contain only a small contribution from water vapor, however, because liquid and solid products were collected and weighed after the reactor was opened at room temperature. The reactor was sampled for gas analysis by GCMS at 200°C, however, at which temperature the gas phase would contain considerably more water vapor than at room temperature.

Acknowledgement

The authors are grateful for support from the National Science Foundation under Grant No. CPE 8303505 and for nitrogen assays performed by the American Cyanamide Company.

References

1. Couglin, R. W., F. Davoudzadeh, *Nature*, 303, 5920, pg. 789-91, (1983)
2. Thorogood, R. M., C. L. Yeh and S. M. Morris, "Scaleup of the SRC-I Coal Liquefaction Process", paper presented at 3rd Annual Conference Coal Gasification and Liquefaction, University of Pittsburgh, August 3-5, 1976.
3. Schmid, B. K. and D. M. Jackson, "The SRC-II Process", paper presented at 3rd Annual Conference Coal Gasification and Liquefaction, University of Pittsburgh, August 3-5, 1976.
4. EDS Coal Liquefaction Process Development, U. S. DOE Report No. EE-2353-2, October 1977, Contract No. Ex-76-C-01-2353.
5. H-Coal Integrated Pilot Plant Phase I-Final Report, U. S. ERDA, No. HCP/T-1554/ (Vol. II) UC-90d, November 1977, Contract No. EX-76-C-01-1544.
6. Heredy, L. A. and M. B. Neuworth, *Fuel*, 41, 221 (1962).
7. Larsen, J. W., T. L. Sanis, B. R. Rodges, *Fuel*, 60, 335 (1981).
8. Coughlin, R. W., and F. Davoudzadeh, *Fuel*, Vol. 65, pg. 95-106 (1986).
9. Pelipetz, J., *Ind. Eng. Chem.* 40, 1259-64 (1948).
10. Weller, S. and J. Pelipetz, *Fuel* 29, 208-11 (1951).
11. Sternberg, W., *ACS Symposium Series*, Vol. 20, 111-122 (1975).
12. Mima, M. J., Analytical Methods for Coal Products, Vol 1, Ch. 19, (1979).
13. Whitehurst, D., Coal Liquefaction Fundamentals, ACS, Washington, D.C., (1980).

TABLE 1
Mass Balances For Liquefaction Experiments

Expt # (1)	Initial Mass Charged (g)			Total Mass Charged (g)	Liquid and Solid Pdts (g)	Gaseous(3) Pdts, % of Total
	Lignin	Coal	Solv.			
2-B(2)	25	25	223.0	277.0	241.6	12.8
4-A	25	25	190.8	240.8	215.3	10.6
4-B	25	0	190.8	215.8	186.2	13.7
4-C	0	25	191.0	216	203.0	6.0

- (1) Reactions run at 400°C for one hour in tetralin and 1000 psi hydrogen initial pressure.
 (2) Reaction run at 300°C for 3 hours in guaiacol.
 (3) Gaseous products are computed by difference.

TABLE 2
Definition of Quantities Used for
Characterization of Reaction Products

- P1 = Mass of Liquid Filtrate (g)
 P2 = Mass of Solid Filtered (g)
 P3 = Mass of Benzene-Insoluble Solids (g)
 P4 = Mass of Benzene-Soluble Solids (g)
 P5 = Mass of Benzene-Soluble Solids
 Precipitated by Pentane (g)
 P6 = Mass of Benzene-Soluble Solids that are
 Pentane Soluble (g)
 P7 = Mass of Benzene-Insoluble Solids that are
 Pyridine Soluble (g)

TABLE 3
Experimental Conditions

Expt #	Mass of Lignin (g)	Mass of Coal (g)	Volume of Tetralin (ml)	Reaction Temp. (C)	Reaction Time (hr)
4-A	25.0	25.0	200	400	1
4-B	25.0	-	200	400	1
4-C	-	25.0	200	400	1
5-A*	25.0	25.0	200	25	100
5-B*	25.0	-	200	25	100
5-C*	-	25.0	200	25	100

* - Control experiments

TABLE 4

Carbon 14 Analysis of Liquefaction Product

<u>Expt #</u>	<u>Reported Activity</u> (1)	<u>Experiment Description</u> (2)	<u>Lignin Molecules/ml</u>	<u>Carbon-14 Atoms/ml</u>
4-A	4.56*	Coal/lignin	4.58×10^{20}	1.98×10^{10}
4-B	3.30*	Lignin	3.82×10^{20}	1.65×10^{10}

- (1) Carbon-14 activity determined by liquid scintillation spectrometry, performed by New England Nuclear Company.
 (2) Reactions performed at 400 C for 1 hour with tetralin used as the solvent.

* Represents value obtained after background count of 2.5 dpm/ml has been subtracted.

TABLE 5

Elemental Analysis of Unreacted Lignin And Coal
(maf basis)

	<u>Stake Lignin</u>	<u>Illinois No. 6 Coal</u>
% C	60.58	82.20
% H	5.30	5.20
% O	34.11	6.81
% N	-	1.38
% S	-	4.15

TABLE 6

Results of Nitrogen Analysis of Liquid Filtrate Products⁽¹⁾

<u>Experiment</u>	<u>% Carbon</u>	<u>% Hydrogen</u>	<u>% Nitrogen</u>
4-A*	76.6	5.9	0.1
4-B**	76.3	6.1	-

Atmospheric Distillation of Liquid Product From Experiment 4A

<u>Fraction #</u>	<u>Boiling Range (°C)</u>	<u>Volume of Fraction (ml)</u>	<u>% Nitrogen</u>
1	188 - 190	130	-
2	192 - 195	5	.04
3	> 195	-	.34

* Coal and lignin co-liquefied at 400 C.

** Coal alone reacted at 400 C.

(1) Nitrogen analysis was performed by American Cyanamid Co.

TABLE 7

Characterization of Vented Gas for Experiment # 6-A

Expt# (1)	Initial Mass			Total Mass Charged (g)	Liquid and Solid Prod. (g)	Gaseous (2) Products,% of Total
	<u>Lignin</u>	<u>Coal</u>	<u>Solv.</u>			
6-A	24.8	25.0	220.8	270.6	244.0	9.98

- (1) Reaction run at 400C for 1 hour in tetralin and 1000 psi hydrogen initial pressure.
 (2) Gaseous products computed by difference.

Components detected in gas:

Major: CO₂, H₂O, CH₃OH

Minor: bicyclo(7,1,0)decane
 naphthalene
 1-nonyne
 tetralin
 methyl thiofurate

Figure Captions

- Flow diagram of treatment and characterization of solid and liquid products.
- Benzene solubility of solids filtered from products of experiments 4A, 4B and 4C. P3-benzene-insoluble portion. P4-benzene-soluble portion.
- Pentane solubility of benzene-soluble material extracted from solid products of reaction. P5-pentane-insoluble portion. P6-pentane-soluble portion.
- Benzene solubility of products from control experiments conducted at room temperature. Compare to Figure 2.

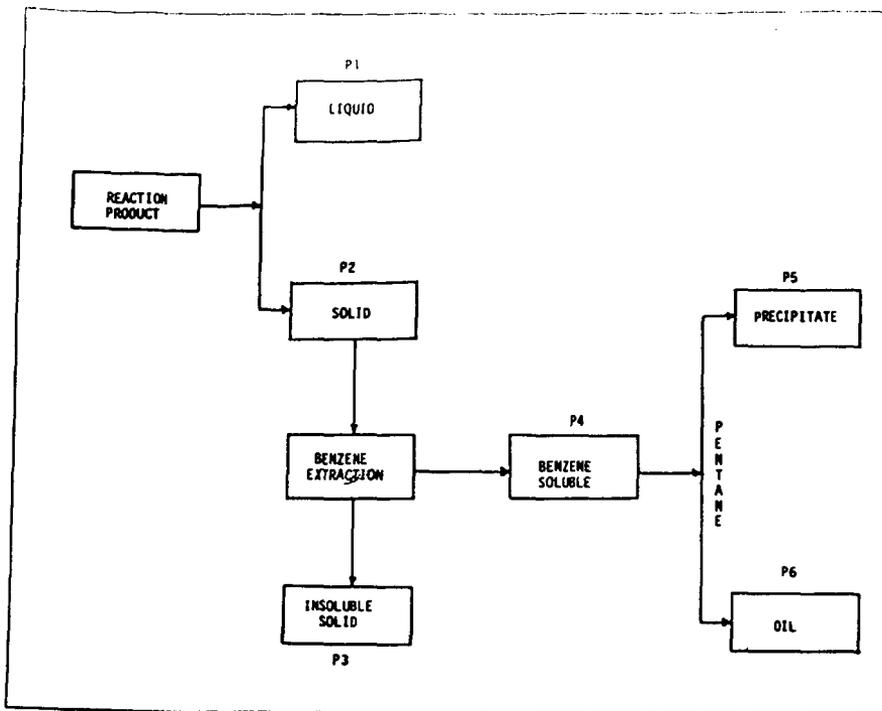


FIGURE 1

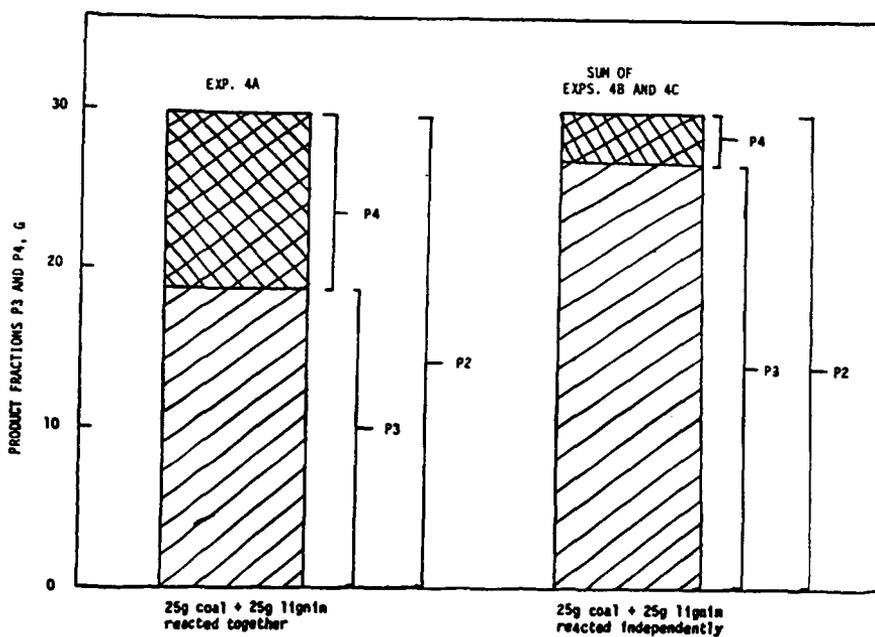


FIGURE 2

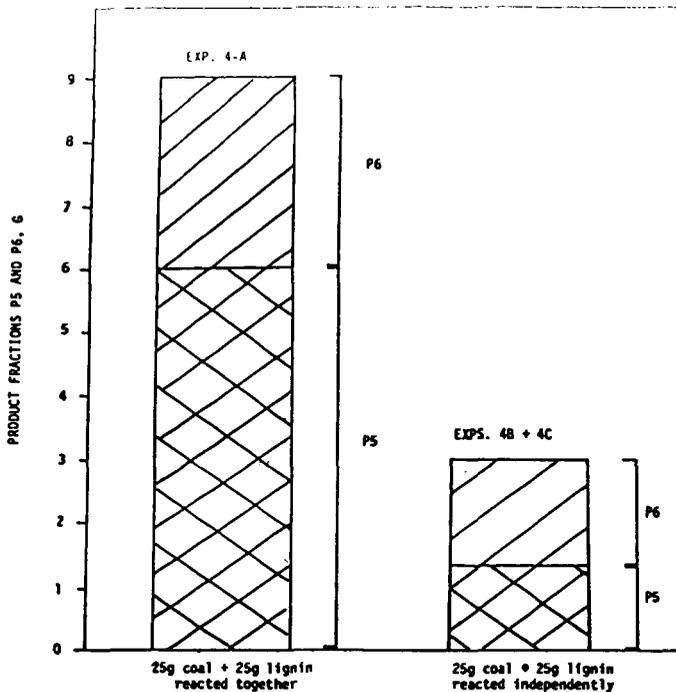


FIGURE 3

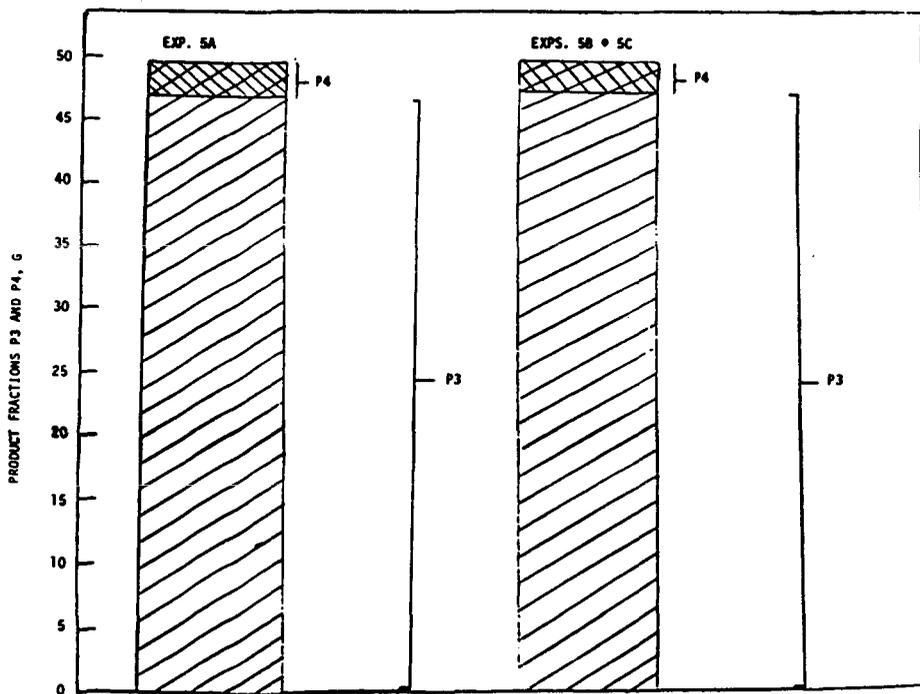


FIGURE 4