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Authors

Davis, H
Figueroa, C
Schaleger, L

Publication Date

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Submitted for the World Hydrogen Energy Conference
IV, Pasadena, CA, June 13-17, 1982

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February 1982

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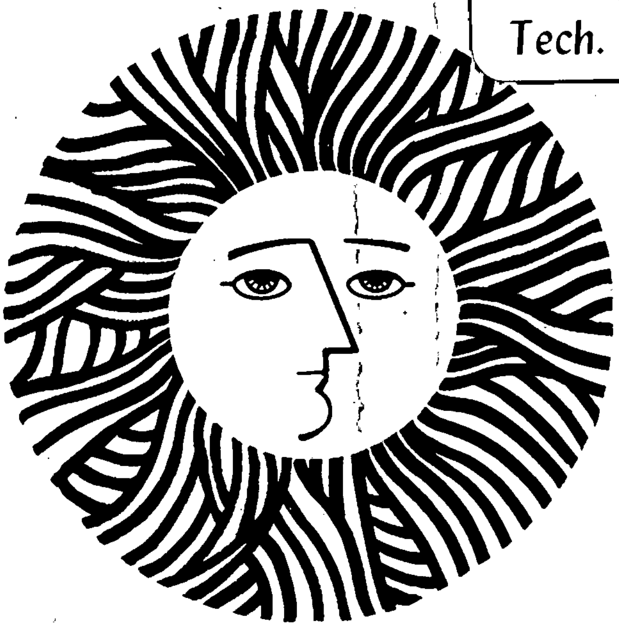

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Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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HYDROGEN OR CARBON MONOXIDE IN THE LIQUEFACTION OF BIOMASS

H. Davis, C. Figueroa, and L. Schaleger

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

The bench-scale continuous biomass liquefaction unit, in operation at Lawrence Berkeley Laboratory (LBL), is described. The feedstock is an aqueous slurry of partially hydrolyzed Douglas fir wood, but extension to other biomass types and peat is planned. The process has previously used carbon monoxide as reducing gas. Under the conditions employed at LBL, 330°-360°C, 200-270 BAR in an atmosphere of steam and reducing gas, no recycle, little or no reducing gas is consumed and it has been shown that hydrogen can be used as the reactant gas. Since large amounts of CO react by the water gas shift reaction, substitution of hydrogen gives a substantial economic advantage. It also opens the possibility of incorporating hydrogenation catalysts and integrating the liquefaction step with separate hydrocracking of crude product.

Yields and products are compared with those from the oil-recycle or PERC process. The water slurry process makes less of the desired crude wood-oil product (30-40 vs. 45-55 wt %) and more water soluble organics (about 25 vs. about 8 wt %). However, the most operationally successful PERC operations have achieved this product distribution at the expense of extremely high oil and water recycle and large CO consumption.

KEYWORDS

Continuous liquefaction of biomass; dewatering of biomass; hydrogen in biomass liquefaction; liquefaction of biomass; water-slurry process; wood-oil.

INTRODUCTION

The direct liquefaction process we describe here stems from efforts in the late 1960's at the Bruceton, Pennsylvania Station of the U.S. Bureau of Mines (Appell, 1971). In general terms, we may define it as a controlled pyrolysis of biomass under a moderately high pressure of steam and reducing gas. The reducing gas has been carbon monoxide or a mixture of carbon monoxide and hydrogen. Depending on the process conditions, there may or may not be a significant usage of reducing gas. For reasons which will be covered in the present paper, there are economic incentives for replacing carbon monoxide with hydrogen.

The objectives of liquefaction are to convert forms of biomass such as wood, agricultural or municipal wastes, and energy plants to liquid fuel. Biomass generally comes associated with percentages of water ranging from 30 to 90% of the total material. Even on a dry basis, biomass is oxygen-rich and has, therefore, a low heating value per unit mass. By achieving a phase separation from the associated water and a reduction in the elemental oxygen content, we can convert a material of net heating value in the range of 0 to 13 Mj/kg to a fuel oil in the range of 28 to 36 Mj/kg. The fuel "oil" is a dense, black, bitumen-like material which in general must be warmed to temperatures above ambient to make it pumpable. Boiler tests, however, were run at the Pittsburgh Energy Technical Center, on a sample stored in drums for nearly two years (Thigpen et al, 1982). It was concluded that the oil is an effective substitute for No. 6 fuel oil. Refining the crude biomass oil to higher grade fuels is a matter for future research.

Why are we interested in making fuel oil from biomass? The long range reasons, of course, stem from the fact that biomass is the ultimate organic feedstock and fuel, still available when most of the world's available fossil fuels are depleted. In many parts of the world, annual growth or potential growth of biomass greatly exceeds in heating value annual use of fossil fuels. This is not true in the more developed countries. In the U.S.A., for example, the heating value of all growth not used for food, lumber, clothing, pulp, etc., is only a few percent of our total consumption. On an absolute basis, however, the potential is considerable. If 15% of the U.S. land mass could be used to grow an average of 9 metric tons per hectare per year dry weight of biomass (say of poplar wood), the total gross heating value would be about 24 Exajoules--some 30% of present annual fuel consumption.

By making reasonable guesses as to the ultimate remaining recoverable reserves of oil, gas, and coal (I guessed 80 billion barrels, 500 trillion cubic feet and 250 billion tons respectively), we can estimate the situation 25 years from now. Even if we let oil and gas production gradually drop to about 44% of the present rate, their ultimate reserves will have dropped to about 21% of the present. Presumably coal production will have increased to replace the oil and gas, to absorb the inefficiencies of conversion of coal to more desirable fuels, and to permit small increases in coal exports and in electrical power production. This requires some 2.5 billion tons/year of bituminous coal equivalent. The recoverable reserve will be down to 150 billion tons and production will necessarily be declining if we plan to keep some conventional fossil fuel available during the 21st century.

We can hardly afford to pass up development of any biomass use process which offers possibilities of economical substitution for these fossil fuels.

A brief history of the Department of Energy's biomass liquefaction program is in order. On the basis of the work at Bruceton (Appell et al, 1971) DOE's predecessor, ERDA, decided, in 1974, to design and build a substantial process development unit (PDU) at Albany, Oregon. Since the Bruceton laboratories were known under ERDA as the Pittsburgh Energy Research Center (PERC), the projected process was termed the PERC process. The bench-scale process development work was far from complete, and several features of the original PDU design did not work well. As a result, the original operator, Bechtel Inc., and the later operator, the Rust Engineering Co., subsidiary of Wheelabrator-Frye Inc., had many difficulties. Several supporting efforts were set up. In particular, in 1978-79, the group at Lawrence Berkeley Laboratory (LBL) suggested an alternate procedure (Ergun et al, 1980; Schaleger et al 1980) which was termed the LBL process. Rust Engineering used this in their test run-7 (Ergun et al, Rust Eng. 1979) and succeeded, in 1979 in making the first sizable quantities of wood oil.

In 1979, it was decided to build a continuous bench scale liquefaction unit (CLU) at LBL. The purpose of this unit was to obtain chemical and engineering data on the process not possible in the larger, less flexible PDU. It was also felt that process improvements could be best identified at the smaller scale. The CLU was initially completed and tested in June-July 1980. Improvements in operability and safety were found to be necessary and the unit was rebuilt and ready for retesting in early 1981. Starting in June 1981, runs of increasing reliability have been carried out on a regular basis.

During 1980, Rust Engineering modified the original PERC process. They were able to operate the revised process at Albany and made many drums of wood oil in runs TR-8 and TR-9. They also made drums of oil by the LBL process in runs TR-10 and TR-11. In the latter two runs, Rust demonstrated the capability of heating slurries of wood in water to reaction temperature in a direct-fired tubular reactor. This was a substantial process achievement. The tubular reactor was also used successfully with slurries of wood flour in wet oil by the PERC process in run TR-12, February-March 1981 (Thigpen et al, 1982). From the viewpoint of smooth operation and material balance, this has been the best run to date. From TR-12 we can deduce, that if an economic process can be devised, a technically feasible engineering embodiment of it can almost certainly be designed.

A brief description of the PERC and LBL processes, as they are currently envisaged was given in a recent report (Davis et al, 1981), and is quoted here.

PERC process: wood is dried, ground to flour and slurried with a wet recycled product oil in a blender. It is also mixed with sodium carbonate catalyst (4 to 8% of the weight of wood) and additional water. The mixture is heated rapidly to a reaction temperature of 330 to 370°C in a directly fired tubular heater, with a flow of reducing gas (3 to 6 mols $CO + H_2$ per 100 kg wood), then passed through a tubular or standpipe reactor with volume sufficient to allow a space-time of 10 to 30 minutes. Reactor pressure is about 200 BAR. After cooling and pressure let-down, a portion of the existing wood oil is withdrawn as product and separated from the aqueous effluent. The remaining oil is recycled, without separation of water, to the wood-flour blender. In the absence of an existing stock of satisfactory wood oil, coal tar anthracene oil is used as the initial slurrying medium. Yields of wood oil from Douglas fir are in the range of 45 to 55%, depending on the severity of operation, i.e., on the degree of reduction of the oxygen content from the 40-45% level of wood. There are also substantial yields of water-soluble organics, largely carboxylic acids or their anions. The balance of the weight of wood is lost as carbon dioxide and water.

LBL process: Wood chips, with only incidental air drying, mixed with water, are brought to pH 1.7-1.8 with about 0.075-0.1% sulfuric acid. The mixture is heated at 180°C for 45 minutes to prehydrolyze the hemi-cellulose content and greatly weaken the structure of the wood. Sodium carbonate is added to bring the mixture to a pH of about 8 and it is homogenized by passage through a refiner. Slurries of total organic content in the range 20 to 30% or higher are obtained. Slurry is heated to reaction temperature with reducing gas in a direct-fired tubular heater as in the PERC process. Additional residence time is obtained by passage through a turbulent tubular reactor or other well-stirred reactor. The effluent mixture, after cooling and pressure let down, is separated into aqueous and oil phases. Total oil plus water-soluble product is about the same as in the PERC process, but there is a higher proportion of water-solubles, at least partly because of the lack of recycle.

The major deficiency of the PERC process is the need for an extremely high oil recycle. In the PDU, wood flour contents of 11% or more have caused plugging in blenders, lines, and pumps. In the most operationally successful run, TR-12, the average wood content of feed was only 7.5 (Thigpen et al, 1982). Since the feed slurry was approximately one part wood, 2.8 parts aqueous phase and 9.5 parts recycle oil, the new oil formed was only 5% of the total oil effluent and the oil recycle ratio was 19 to 1.

As a single-pass process, the LBL process avoids the oil recycle problem totally. Since the heat capacity of water is high, it is necessary to maximize the wood content of feed slurry, preferably to 30% or more. However, some heat can probably be recovered from the process. A major economic stumbling block of the PERC process is thus spoken to. Operational problems are, however, introduced and the products produced are not identical.

In this report we compare the results obtained by the Rust Engineering Co. in the PDU with results for the LBL process obtained by LBL in the bench-scale CLU. In particular, we consider the differences in consumption of reducing gas in the high recycle PERC operation and the single pass LBL procedure, and the effects, in the latter, of substituting hydrogen for carbon monoxide.

THE CONTINUOUS LIQUEFACTION UNIT

A flowsheet of the bench-scale continuous liquefaction unit, or CLU, is shown as Fig. 1. Separately prepared aqueous slurry is passed through a colloid mill and stored in the slurry feed tank. A progressive cavity pump circulates the slurry and supplies it at 2.4 BAR to a single piston high pressure pump. This elevates the pressure to 200 to 270 BAR. Reducing gas is sparged into the slurry before injection into the reactor. The reducing gas--carbon monoxide, hydrogen, or a mixed gas--is supplied from standard-sized cylinders, compressed to about 300 BAR in two stages and stored in a high pressure vessel. It is metered, at a constant preset rate, into the slurry supply line through a thermal mass flowmeter. The reactor is a stirred one-liter autoclave. It replaced a hot-air heated tubular reactor after efforts in 1980 and early 1981 showed that plugging problems were inevitable at the laminar flow conditions of the bench-scale unit. From the reactor aqueous, oil and gas phases flow together through an air-cooled 1/4 inch line to one of two product collection vessels, each of about 8 liters capacity, where the liquid product is collected. The gas flows through a back-pressure control valve and a dry test meter to the vent. The outlet gas is analyzed at regular intervals in a semi-automatic gas chromatograph. After about four hours of collection, or when a collection vessel is 50-75% full, product flow is switched to the alternate collector. The first collector is isolated and pressure is released to vent, slowly so as to avoid loss by foaming. Liquid product and water are then collected in weighed plastic bottles through an automatic valve kept warm enough to prevent plugging by the viscous oil.

In working up the product, most of the aqueous phase is decanted from the heavy oil. The oil is warmed to remove most of it from the receiver, but it is necessary to add solvent--generally a mixture of methanol and chloroform--to recover the balance. Removal of this solvent and of the small amounts of residual water results in some loss of the more volatile part of the product, probably as much as 3% of the feed biomass. Efforts to reduce or measure this are in progress.

The necessity that the heat requirement of the process be supplied through the wall of the reactor creates a coking problem. Actual amounts of coke formed during a run have varied, somewhat randomly, from as little as 0.3% of feed biomass to 10% or more. The amount may depend somewhat on the pH and the reaction temperature, but appears to be more closely related to the pitch and location of the agitator propellors and to operating upsets. Operations in the PDU showed that, under turbulent flow conditions, both water and oil slurries could be heated to reaction temperature in a direct-fired tubular heater without serious

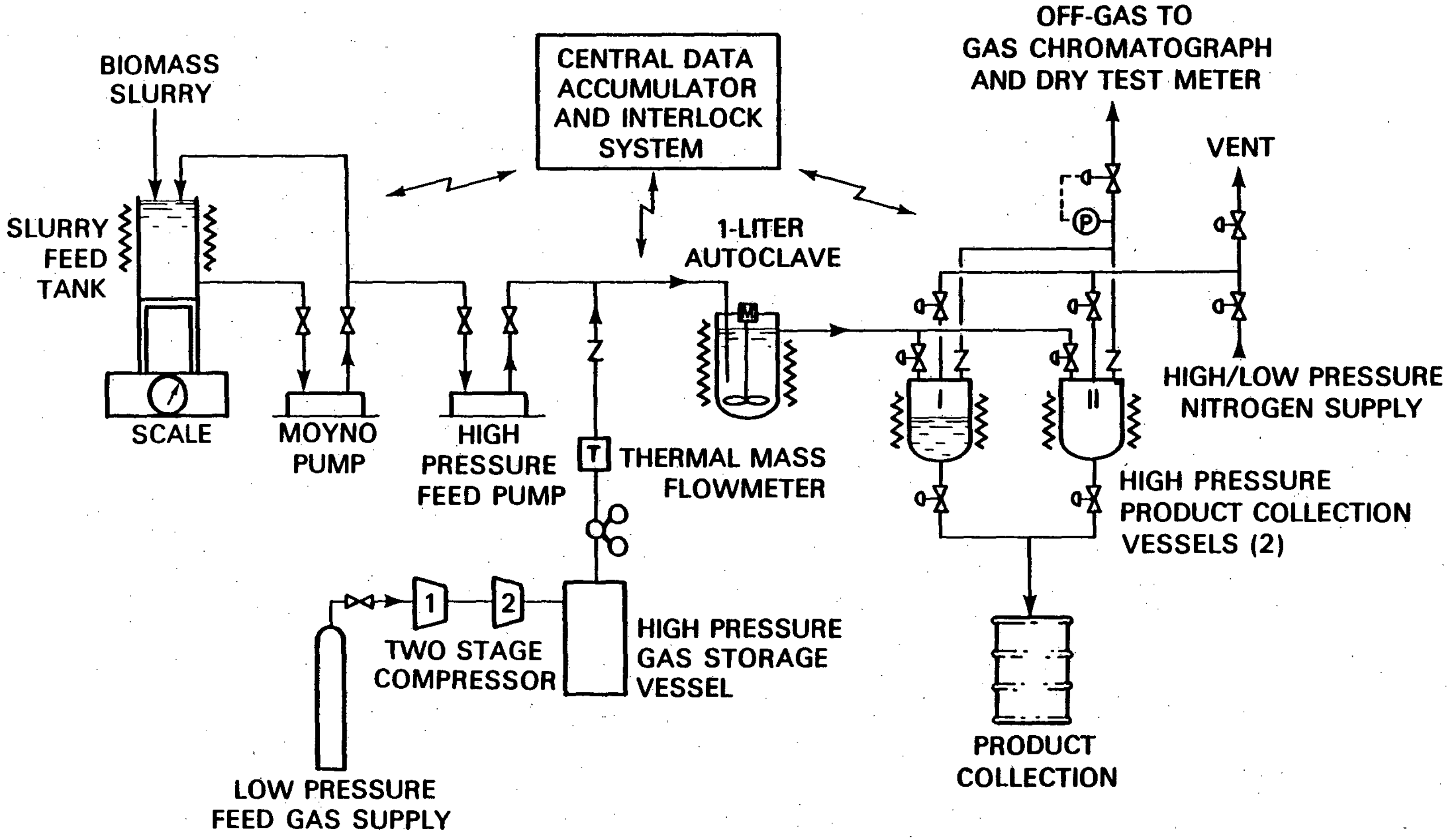
BIOMASS SLURRY
SLURRY FEED TANK
SCALE
MOYNO PUMP
HIGH PRESSURE FEED PUMP
CENTRAL DATA ACCUMULATOR AND INTERLOCK SYSTEM
1-LITER AUTOCLAVE
M
T
THERMAL MASS FLOWMETER
1
2
TWO STAGE COMPRESSOR
HIGH PRESSURE GAS STORAGE VESSEL
LOW PRESSURE FEED GAS SUPPLY
OFF-GAS TO GAS CHROMATOGRAPH AND DRY TEST METER
P
VENT
I
II
HIGH/LOW PRESSURE NITROGEN SUPPLY
HIGH PRESSURE PRODUCT COLLECTION VESSELS (2)
PRODUCT COLLECTION

FIGURE 1

BIOMASS CONTINUOUS LIQUEFACTION UNIT

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coking. This encourages us to believe coking is a specific operational problem.

In Table 1, we show typical results for CLU runs with carbon monoxide, hydrogen, and mixed feeds. The overall material recoveries in these runs were of the order of 97-100%. The accountability of wood products has generally been less because of the large water dilution. With a calculated 9% water yield included, it ranges from 80 to 100% for the runs shown in Table 1. As discussed above, the systematic losses are probably oil. If that is so, the true oil plus char yield is probably about 40% in each case. In the runs with highest and lowest product accountability, 7, 10, and 13 with 100, 86, and 99% respectively, oil plus char was 40, 29, and 40% respectively.

TABLE 1

YIELDS FROM DIRECT LIQUEFACTION OF DOUGLAS FIR WOOD SLURRY

			Yields wt %							
Run	Red. gas	Reac. temp. °C	Crude wood oil	Water Soluble	CO_2	H_2O est	Char	Oil + char from balance	Off gas Mol %	% O in oil
7	CO/H_2 1:1	350	31	25	25	9	11	41	N.A.	17
8	CO/H_2 1:1	330	32	29	23	9	0.3	39	N.A.	18.5
10	CO	350	27	22	25	9	1.6	44	H_2-32 CO-9 CO_2-59	16
11	CO	340-360	33	26	25	9	4	40	H_2-22 CO-22 CO_2-56	16.5
12	H_2	340-360	27	24	25	9	5	42	H_2-70 CO_2-30 CO-minor	16.8
13	H_2	340-360	31	27	24	9	9	40	H_2-75 CO_2-24 CO-1	17

Notes: H_2O and CO_2 yields are based on oxygen balance. Oil yield is recovered oil per 100 parts wood organics fed. Char is overall for run based on recovery from reactor. Water solubles are estimated from total organic carbon, see text.

Operation of bench-scale equipment with the type of feed and product described, is fraught with problems. Most of these have been solved (Figueroa et al, 1982) in the sense that runs of 24 hours or so duration can be mounted and acceptable data collected. There remain, however, two problems, perhaps related, to which we still seek solutions.

The dilute aqueous slurry feed yields a mixture which is over 90% aqueous and less than 10% oil, with the oil substantially denser than the aqueous phase. Despite the most violent agitation we have been able to achieve in the reactor, the oil appears not to be well-dispersed in the aqueous phase. We judge this from the observation that very little oil exits the reactor during the initial part of a run. The oil residence time evidently is much larger than that of the water-phase --perhaps as much as three hours vs. ten minutes. The phase separation problem must be related to the reactor coking problem. Possible solutions to one or both problems which we are still working on include use of a wall-scraper, addition of salts to the water layer to increase its density, and modifications of the type of agitation.

PRODUCT

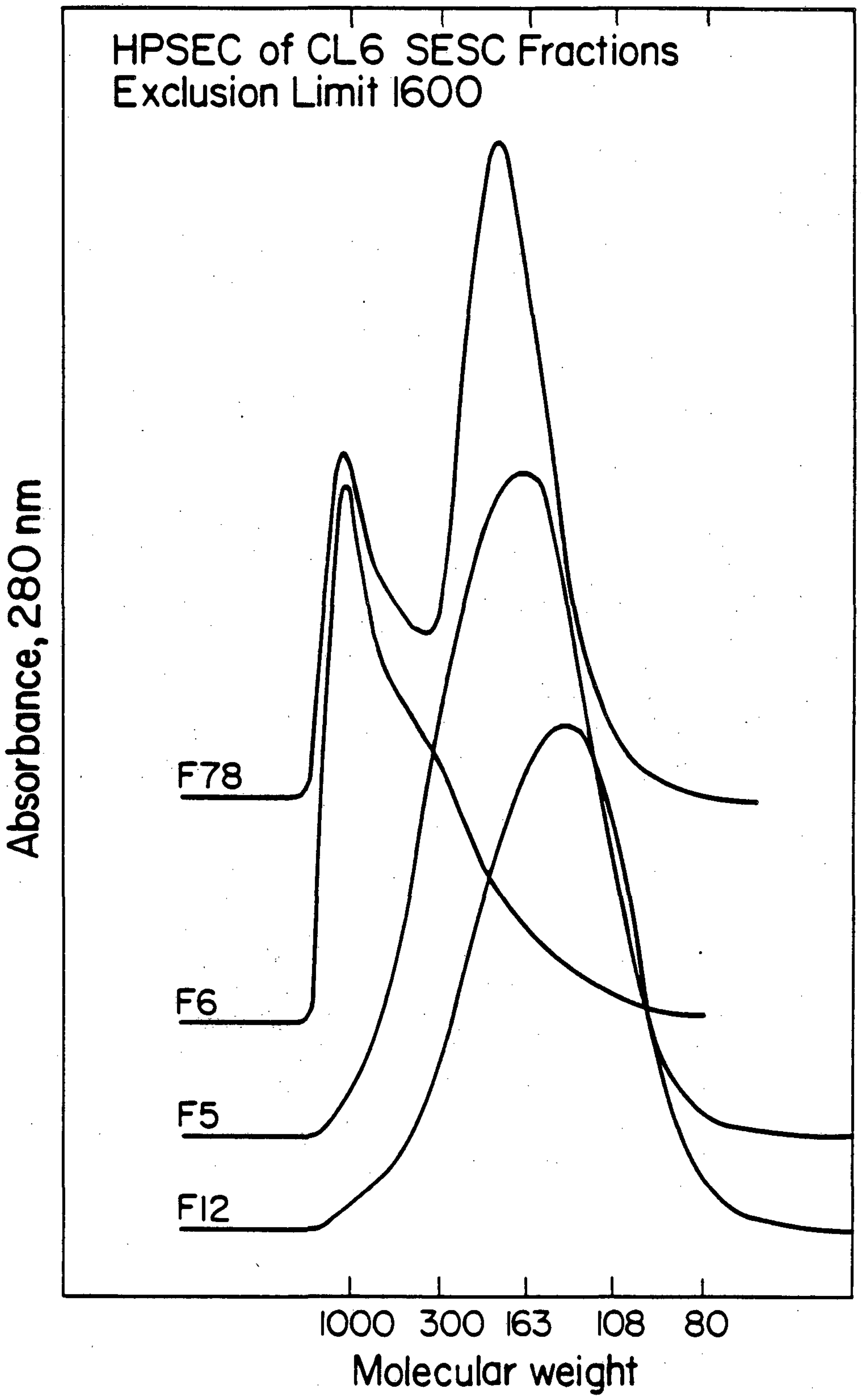
The crude oil product of direct wood liquefaction is a bitumen-like black material, which is liquid, but viscous, at slightly above ambient temperature. It has a specific gravity in the 1.1-1.2 range. We have characterized the oils by a variety of techniques (Davis et al, 1981) of which the most useful are elemental analysis, elution chromatography by a modified SESC, "sequential elution by solvent chromatography," technique (Farcasiu, 1977), GC-MS, and molecular weight distribution by high pressure size exclusion chromatography (HPSEC). A series of HPSEC chromatograms is given in Fig. 2.

The oil has been found to have oxygen contents in the range of 15 to 19%--typically 17%--hydrogen from 6.8 to 8%--typically 7.3%-- and carbon from 74 to 78%--typically 76%. The gross heating value is about 34Mj/kg (14,600 Btu/lb). Since the specific gravity is high, about 1.15, the heating value per unit value is about 39 Mj/l (140,000 Btu/gallon).

We plan to give details of the methods used in analysis and the results obtained in future papers and give only a brief summary here. The SESC technique has shown that the crude oil contains little or no true hydrocarbon. Over 95% of the molecules present contain at least one oxygen functionality-primarily phenolic hydroxyl, carbonyl and ether. Nevertheless, practically all of the oil can be eluted from silica gel with the series of SESC solvents used. Solvent extraction techniques show that 50 to 80% of the molecules are phenolic. GC-MS analyses of the more volatile portions confirm this. Of over 100 compounds identified in distillate fractions, about 80% contain one or more phenolic hydroxyl. The HPSEC studies show a broad molecular weight distribution with number average molecular weight in the range of 180-290 and weight average molecular weights of 300-500. The HPSEC tracings of Fig. 2 show that the sequential elutions of the SESC technique, which primarily separate on the basis of molecular polarity, also give fractions differing by molecular weights. The combined first two fractions (F12 in Fig. 2) have the lowest average molecular weight, fraction 6 has the highest, and the combined fractions 7 and 8 (F7, 8 in Fig. 2) show a bimodal distribution. In the sample used, recovery was effectively 100% after F8, and F9 and uneluted residue were insignificant.

The water-soluble products produced must at this point be considered a problem. They detract from the oil yield and, because of their low concentration in the aqueous phase, are not easily recovered or disposed of. Our analyses show that the product is roughly 50% carboxylic acids and their anions. About 35 have been identified, mostly by GC-MS as the methyl ester. These include single straight chain or branched acids--(formic acid homologs), dicarboxylic acids, keto acids and glycolic acid. Of all these, glycolic, acetic, and formic acids predominate, constituting roughly 90% of the total mass of acids. Among the neutrals, i.e., the compounds extractable at pH's of about 8, some 44 individual compounds have been identified with none really predominant. The major classes are phenolics, ketones--mostly cyclic--and substituted furans.

FIGURE 2



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DISCUSSION

In the present state of the art of direct liquefaction, the reasons for pursuing the process at all are limited: it produces a dense material, separable from water and feedable as a liquid to a boiler or gasifier, from a light, water-containing solid of low heating value. Under the circumstances, two objectives for research are clear. We must either greatly improve the quality of the crude product or we must modify the process until it is very simple and inexpensive to construct and operate.

Most of the ideas concerning improving the product involve some sort of catalytic treatment. Direct hydrogenation of product oils is currently being pursued by the Pacific Northwest Laboratory of Battelle Institute under a U.S. Department of Energy contract. From experience with such feedstocks as coal hydrogenation product and shale oil, removal of the bulk of the oxygen and reduction of the average molecular weight will require saturation of most of the aromatic rings. If the typical oil described above, with the average empirical formula of $CH_{1.15}O_{.167}$, is reduced with hydrogen to an average empirical formula of CH_2, the hydrogen consumption is 0.6 kg formula weight or 7.6 wt %. The yield from 100 kg oil plus 7.6 kg H_2 is 88.5 kg hydrocarbon plus 19 kg water. This allows for saturation of the liquid to monocyclic hydrocarbons but not for generation of significant amounts of paraffinic gas.

This is, of course, a large hydrogen consumption. However, comparison with the quantities required for coal hydrogenation and crude product upgrading puts it in perspective. For example, severe hydrocracking of crude SRC-II oil is reported (Sullivan et al, 1981) to require 4.75 kg H_2/100 kg oil. This removes oxygen, sulfur and nitrogen and largely saturates the liquids. Since the hydrogen requirement to produce the crude oil can be calculated to be over 7 kg/100 kg oil (Jackson, 1981), the total requirement for the sequence for coal is about 12 kg/100 kg oil. If the hydrogen or synthesis gas required for producing the crude wood oil is low, then the overall requirement for production of distillate fuels will compare favorably with that for production from coal. The naphtha, like coal-derived naphtha, will be an excellent reformer stock because of the higher content of naphthenes.

To determine the reducing gas requirement for wood oil, we look in some detail at two representative bench-scale runs, CL-11 and CL-12, and the most successful, operationally, of the Rust Engineering Co. runs in the Albany PDU, TR-12 (Thigpen et al, 1982). In CL-11 and CL-12, we used 100% carbon monoxide and 100% hydrogen, respectively, as reducing gas. In TR-12, Rust used synthesis gas.

From the typical data summarized in Table 2, it is clear that with CO or synthesis gas as the reactant, hydrogen is generated. This is by water gas shift reaction, probably with formate ion, always present to some degree, as an intermediate. The amount of CO used up by this route is large, about 0.5 kg mols/100 kg wood in CL-11 and 1.3 kg mol/100 kg wood in TR-12. This loss of CO is a serious economic problem, despite the generation of an equivalent amount of hydrogen, since the reverse shift reaction is not practicable.

CO_2 is generated by two other reactions--by simple thermolytic evolution from wood or intermediate products and by reaction of CO with oxygen in the intermediates. The amount of the latter reaction can be estimated from the net disappearance of synthesis gas. CO_2 not attributable to shift reaction or CO oxidation must then result from thermolysis.

TABLE 2

GAS COMPOSITONS FROM SELECTED RUNS

Run	Feed Gas, Mol %		Product gas, Mol %				Expansion ratio, dry gas, (Mols out)/(Mols in)
	H_2	CO	H_2	CO	CO_2	CH_4 etc.	
CL-11a	0.0	100.0	22.	22.	56.	tr	1.9
CL-12a	100.0	0.0	70.0	1.0	28.0	1.0	1.5
TR-12b	39.2	60.8	48.3	8.8	42.9	tr	1.52

a. This work
b. PDU run oil-recycle process at intermediate severity.

Calculations from the specific data of Table 2 give the following results.

TABLE 3

ANALYSIS OF GAS YIELD DATA

	kg Mols/100 kg wood		
Run	Shift reaction	CO oxidation	Pyrolytic CO_2
CL-11	0.5	0.2	0.6
CL-12	N.A.	(-0.1)*	0.6
TR-12	1.3	0.5	0.6

---

* Negative sign indicates a net production of synthesis gas, primarily hydrogen.

The difficulties of calculating gas yields from bench-scale data are such that the small net yield of hydrogen shown for CL-12 is not significant. The amount of CO shown as "oxidized" in CL-11 is barely significant at best. The value given for TR-12, is significant. Preliminary analysis of detailed data from the run shows the CO consumption by this route to lie in the range 0.2 to 0.8 kg mols/100 kg wood and to increase with temperature of operation. The value for pyrolytic CO_2, 0.6 mol/100 kg, is justified by a variety of runs in both PDU and CLU and is reliable to better than ± 0.1 mol/100 kg. The amount of shift reaction varies with run conditions. It increases with increasing CO concentration in the feed gas and with increasing pH of the aqueous phase.

It remains to determine whether we can account for a detailed atom balance compatible with the data from Table 4 for conditions at which a 16% O product oil is made. For the water-slurry process we assume a 40% yield of oil, based on ability to avoid coke formation. For the oil-slurry process we take the reported overall yield (Thigpen et al, 1982). Pyrolytic water yields are calculated from the hydrogen atom balance, since there are no reliable experimental data.

A reasonable balance can be reached.

TABLE 4

STOICHIOMETRY OF WOOD LIQUEFACTION

Feed: Douglas fir wood chips, maf
Basis: Nitrogen and sulfur (about 0.2 wt %) included in oxygen

A. Oil Recycle Process-- Based on Run TR-12 (Thigpen et al, 1982)

Wood, 100 kg ⟶	Oil, 53 kg, H/C = 1.31
C - 51.0	C - 39.9
H - 5.8	H - 4.4
O - 43.2	O - 8.7
	+ water solubles, 8 kg
+ CO, 13.2 kg (0.47 Mol)	C - 4.4
C - 5.6	H - 0.6
O - 7.6	O - 3.0
	+ H_2O, 7.2 kg (0.4 Mol)
Total input	H - 0.8
C - 56.6 kg	O - 6.4
H - 5.8	+ CO_2, 45.0 kg (1.02 Mol)
O - 50.8	C - 12.3
113.2	O - 32.7
	Total output
	C - 56.6
	H - 5.8
	O - 50.8
	113.2

TABLE 4 (continued)

B. Water Slurry Process--Based on CLU runs

Wood, 100 kg	→ Oil, 40 kg, H/C = 1.13
C - 51.0	C - 30.5
H - 5.8	H - 2.9
O - 43.2	O - 6.6
	+ Water solubles, 25 kg
Total input	C - 13.4
C - 51.0	H - 1.9
H - 5.8	O - 9.7
O - 43.2	+ H_2O, 9.0 kg (0.5 Mol)
	H - 1.0
	O - 8.0
	+ CO_2, 26 kg (0.50 Mol)
	C - 7.1
	O - 18.9
	Total output
	C - 51.0
	H - 5.8
	O - 43.2
	100.0

The chief element of uncertainty in the breakdown of Table 4, lies in the estimate of yield and elemental analysis of the water-soluble product. For the elemental analysis we use C-55, H-7.6, O-37.4 (wt %). This is based on elemental analyses on several extracted samples (Davis et al, 1981a). As many of the organic solubles are highly hydrophilic and also quite volatile, quantitative extraction has proved difficult. We have estimated the concentration from total organic carbon and the above assumed analysis. The resulting uncertainty is minor for TR-12 where the total yield of water solubles is relatively low, but it may be serious in our analysis of the water slurry stoichiometry.

Specifically, if our estimate of water-solubles yield is high there must be greater formation of pyrolytic water and of oil. Conceivably, 22% or 28% is a better estimate of water-solubles yield. If so, we can effect a balance by raising or lowering the oil and water yields to 42 and 10 or 38 and 8 to compensate.

It will be noted that the oil yield is higher in the oil recycle process (case A) than in the water-slurry process (case B) for two reasons. Most important is the difference in water-solubles. In addition, a little more of the carbon appears in the oil because some of the wood oxygen is removed by reaction with CO instead of by evolution of CO_2. The case A oil quality is slightly better in the sense that the H/C ratio is higher. This is related to the lower yield of water solubles. The H/C ratios of total oil plus water-soluble products are about 1.35 for both cases A and B. The oil-recycle process, however, picks up these gains in yield and hydrogen content at the cost of consumption of expensive CO and of an inordinately high oil recycle.

CONCLUSIONS

We conclude that it is operationally feasible to convert wood and other forms of biomass to a crude fuel oil by either an oil recycle (PERC) process or a single-pass water slurry (LBL) process. The PERC process gives higher yields, but so far has required very high oil and process water recycles and consumes expensive CO. The LBL process avoids the recycle problems. It is capable of producing an oil with oxygen content in the range of 15 to 18% without significant consumption of CO. Hydrogen therefore can be used instead.

The ability to substitute hydrogen has several advantages. Most obviously, it bypasses the loss of carbon monoxide from the reactant gas cycle resulting from the shift reaction. If an appropriate expendable or recoverable hydrogenation catalyst can be found, it offers the chance to do some reduction catalytically. Catalysts, probably not fitting the above limitation, have been reported previously and there is currently active Canadian interest (Boocock et al, 1980). Finally, if the crude oil should be subjected to the type of hydrocracking proposed for shale oils and coal-derived oils, integration of the hydrogen supply for liquefaction and hydrocracking offers benefits.

Many areas remain for investigation. The hydrogenation catalysts referred to need to be studied. Modifications of process which increase the oil yield at the expense of water-solubles are being sought. In any case, recovery or disposal of the water-solubles is an important problem. An extension of the continuous liquefaction effort to other feedstocks, other woods, agriculture wastes, "energy" plants, peat, etc., is also important and is being studied as limited time and funds permit.

Low severity variations of the basic process offer possibilities as a dewatering process. Naturally dilute, wet feedstocks are converted to a material feedable as a liquid and of much higher net heating value.

The amount of work remaining to devleop a viable process is great. The incentive for the future, as world fossil fuel supplies are depleted, is equally great. The successes at Albany and Berkeley make us believe operability, at least, can be achieved.

The objective of the R and D program is to extend and modify the present processes, so that when the need is there, commercial operability will prove possible.

ACKNOWLEDGEMENT

The contributions of Patricia Bronnenberg, Mark Featherstone, Raymond Gansley, Dieter Kloden, and Rafael Zamora are gratefully acknowledged.

This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry, Biomass Energy Systems Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 and by Battelle Pacific Northwest Laboratory, Lead Laboratory for the U.S. Department of Energy, Biomass Energy Systems Division, Thermochemical Conversion Program under Contract No. DE-AC06-76LO-1830.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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