LBL-14019

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAY 28 1982

LIBRARY AND
DOCUMENTS SECTION

ENERGY & ENVIRONMENT DIVISION

Presented at the Fourth Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, TN, May 11-14, 1982; and to be published in the Proceedings

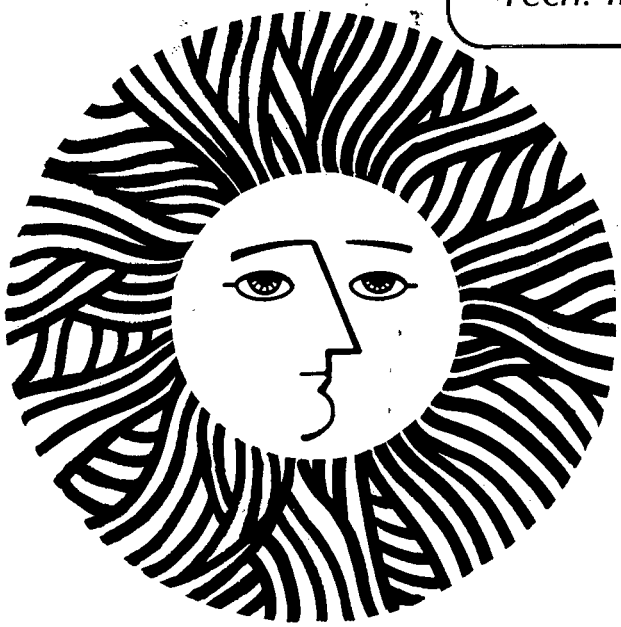
DIRECT LIQUEFACTION OF BIOMASS: RESULTS FROM OPERATION OF CONTINUOUS BENCH SCALE UNIT IN LIQUEFACTION OF WATER SLURRIES OF DOUGLAS FIR WOOD

Larry L. Schaleger, Carlos Figueroa, and Hubert G. Davis

May 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



LBL-14019 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-14019

DIRECT LIQUEFACTION OF BIOMASS: RESULTS FROM OPERATION OF CONTINUOUS BENCH SCALE UNIT IN LIQUEFACTION OF WATER SLURRIES OF DOUGLAS FIR WOOD

Larry L. Schaleger, Carlos Figueroa, and Hubert G. Davis
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Presented at the Fourth Symposium on
BIOTECHNOLOGY IN ENERGY PRODUCTION AND CONSERVATION
May 11-14, 1982
Gatlinburg, Tennessee

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Biomass Energy Technology Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and funded through Battelle Pacific Northwest Laboratory, Lead Laboratory for the U.S. Department of Energy, Biomass Energy Technology Division, Thermochemical Conversion Program under Contract DE-AC06-76LO-1830.

SUMMARY

The Lawrence Berkeley Laboratory's continuous liquefaction unit (CLU) has been successfully operated since July 1981. The operation has been single pass, feeding water slurries of prehydrolyzed Douglas fir wood (LBL process). Significant differences from results with the oil slurry, high oil and water recycle process (PERC process) tested at Albany, Oregon, have been found. The LBL process, at practicable temperatures and residence times, makes somewhat less wood oil and considerable more water-soluble product than does PERC. Consumption of carbon monoxide in LBL, other than by water gas shift reaction, is minimal, as opposed to several tenths of a mole per 100 grams of wood in PERC. Replacement of carbon monoxide with hydrogen as reactant gas makes little or no difference in yield distribution or product analysis.

Progress in characterizing the oil and water-soluble product, the overall stoichiometry of the LBL and PERC processes, and the role of formate ion is described.

Keywords: Biomass liquefaction; continuous biomass liquefaction unit; wood liquefaction.

INTRODUCTION

Wood, an underutilized, renewable energy resource that is virtually sulfur and nitrogen-free, can be converted to a dense, liquid fuel suitable for steam and power production by thermal treatment under a pressure of water and reducing gas in the presence of aqueous alkali [1]. Recognition of the role wood residues could play in the nation's long-term energy supply picture stimulated research by Appell and co-workers at the Pittsburgh Energy Research Center (PERC) [2] that led to the design and construction of a process development unit (PDU) for wood liquefaction at Albany, Oregon. During operation of the PDU from 1976-80, the technical feasibility of two different processes was demonstrated, resulting in the production of some 70 barrels of wood oil. However, work at Albany also revealed serious operational or economic flaws in both processes, demonstrating the need for further detailed investigation of basic process parameters.

In the original PERC recycle process that served as the design basis for the Albany PDU, wood flour was fed to the reactor as a slurry in anthracene oil or, as it became available, recycle oil [3]. Three major economic or operational difficulties became apparent: 1) drying and grinding required to prepare wood flour from chips is very energy-intensive; 2) wood solids could not be fed at concentrations greater than 10% without plugging; 3) excessive heat is required to sustain the process because of the need for oil recycle ratios as high as 19:1, plus substantial water recycle.

The need for a feasible, low recycle ratio process led to the development at LBL of a single-pass, water-based alternative [4]. In this process wood chips are prepared by chemical pretreatment (dilute acid hydrolysis) followed by mechanical refining. The resulting aqueous slurries have been found to be pumpable at concentrations in excess of 30%. However, experience at Albany suggested that low oil yields were the major shortcoming of the water-based process [5].

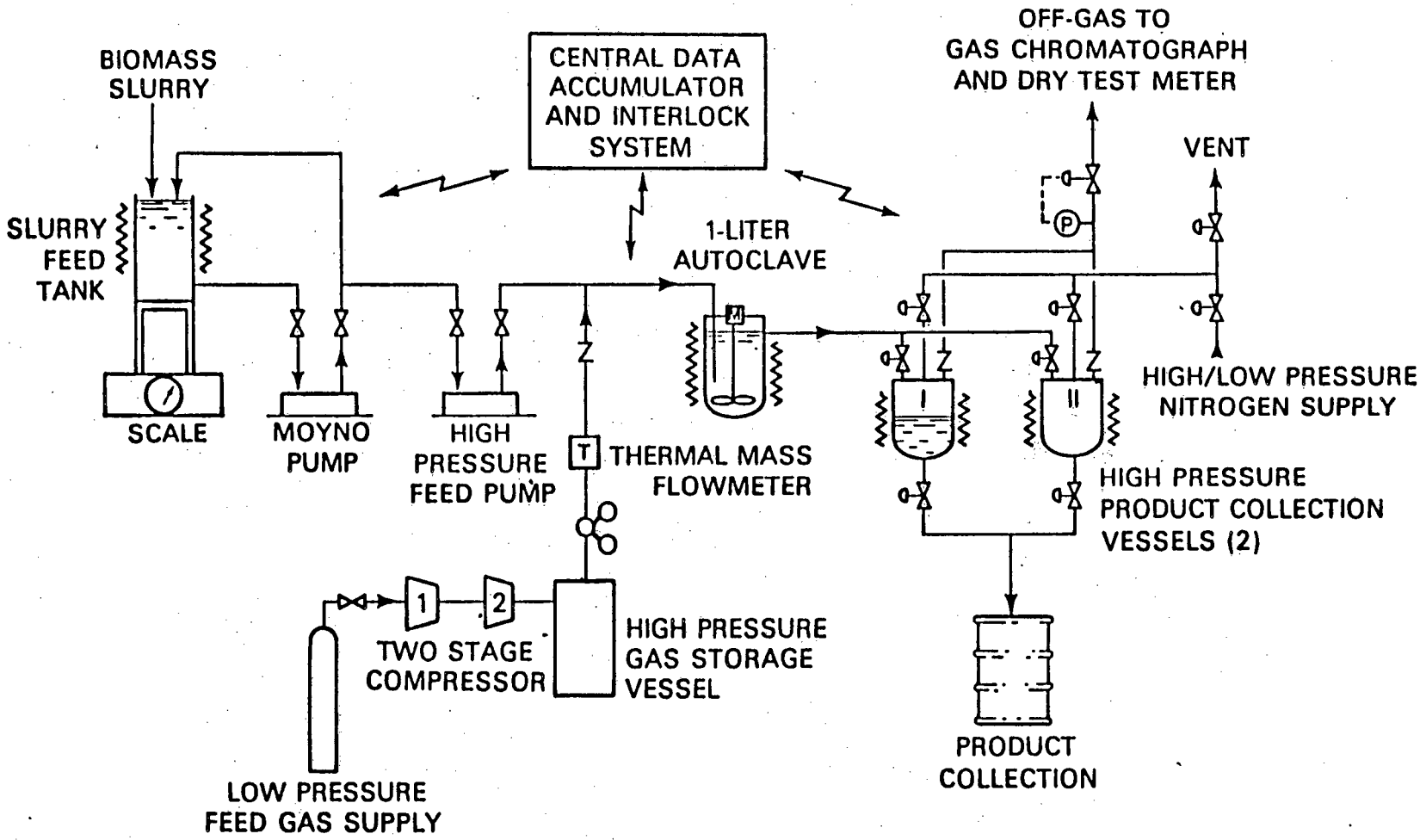
A bench-scale, continuous liquefaction unit (CLU) was designed and built at LBL to investigate the problem of yield and to further the development of a water-based process. This report summarizes the major findings of the first nine months of operation and their implications for the future of wood liquefaction.

GENERAL DESCRIPTION OF APPARATUS

A detailed description of LBL's continuous liquefaction unit has been given elsewhere [6]. Briefly, it consists of three sections: reactant gas and slurry feed system, reactor assembly, and product collection system (see Fig. 1).

The slurry feed assembly consists of a continuously weighed slurry hold tank fitted with a recirculation loop powered by a progressive cavity pump. Douglas fir wood slurry prepared by acid hydrolysis, neutralization with sodium carbonate and mechanical refining is passed through a colloid mill for rehomogenization, added manually to the hold tank and continuously recirculated. A portion is pressurized to 200-230 atm with a high-pressure reciprocating piston pump and fed to the reactor. Reducing gas is compressed to 300 atm and fed to the reactor from a one-gallon storage vessel.

FIGURE 1



BIOMASS CONTINUOUS LIQUEFACTION UNIT

XBL 817-1023

Schematic diagram of Lawrence Berkeley Laboratory's continuous liquefaction unit (CLU) for converting biomass to liquid fuel.

The reactor is a one-liter, stirred stainless steel autoclave equipped with an external electrical heater. The slurry-gas mixture is sparged toward the bottom of the reactor. The product stream exits near the top of the reactor and flows downward through an air-cooled line to one of two pressure let-down vessels. Product is alternately collected in one and then the other of these two vessels for periods of four hours.

Off-gases exit through a back-pressure control valve, are volumetrically metered and vented outdoors. Every 12 minutes or so a slipstream is diverted to an automatic gas chromatograph for separation and analysis of H_2, CO_2, N_2 and CO.

The entire system is made of 316 stainless steel. The maximum slurry feed rate is about 2 kg hr^{-1} although best operation has been achieved at 1.2 kg hr^{-1}. At a concentration of 20% by weight of wood solids and an oil yield of 40%, wood input and oil output rates are about 250 and 100 g hr^{-1}, respectively.

The product of four hours operation consists of about 400 g of a heavier, black oil phase and ca 4 kg of a lighter, green-yellow aqueous phase. The latter is decanted and the oil taken up in chloroform or chloroform-methanol and recovered by rotary evaporation of solvent under reduced pressure. A brittle, coke-like material (char) is recovered directly from the reactor after conclusion of a run.

The yield of char varies from < 1 to 10% and appears to be independent of the basic reaction variables. Although some dependence on reaction temperature can be inferred, efficiency of agitation (i.e., nature, number and placement of impellers on stirring shaft) and "smoothness

of run" appear to be more important variables. It is apparently formed at the hot walls of the externally-heated reactor and is probably due in part to incomplete dispersion of the multi-phase reaction mixture. Thus we believe char formation to be an operational problem rather than a chemical feature of the process, although this has yet to be demonstrated conclusively.

A detailed accounting of the first 12 runs conducted in the CLU has been given [6]. Several of the earlier runs had to be terminated prematurely due to plug formation in inlet and exit lines. These problems have been all but eliminated by better temperature control of the lines. Subsequently, premature shutdowns have been due to random equipment failures, gas leaks, stuck check valves and the like. Several runs have been voluntarily terminated after 24 hours of continuous operation. Operating parameters for some of the more informative runs are given in Table I. Table II gives raw yield and analytical data for the same set of runs.

CHARACTERIZATION OF PRODUCTS

Several methods for the characterization of wood oils have been developed and routinely applied. In addition to the estimation of number and weight average molecular weights by gel permeation chromatography (GPC) [7], chemical group separations are made by column chromatography [8]. Speciation and quantitation of the major carboxylic acids of the aqueous phase has been accomplished by high performance ion exchange chromatography (HPIEC) [8].

Crude wood oils are fractionated into chemical groups of increasing polarity/molecular weight by an adaptation of the SESC technique developed by Mobil Research for coal-derived fluids [9]. Nine solvent mixtures of

TABLE I

OPERATING PARAMETERS OF SELECTED RUNS

Run No.	8	10	11	12	13
Run time (hrs)	24	10	24	24	20
Temperature (°C)	330	350	340(A), 360(B)	340(A), 360(B)	340
Pressure (atm)	205	232	232	232	232
Slurry Feed rate (kg/hr)	0.9	1.1	1.2	1.2	1.04
Gas feed rate (L/min)	1.6	1.0	1.0	1.0	0.9
% CO[a]	50	100	100	0	0
Slurry, initial pH[b]	7.5	8.9	7.7	8.0	8.9

[a] Remainder H_2.

[b] Adjusted with sodium carbonate

TABLE II

PRODUCT YIELD AND ANALYTICAL DATA

Run No.	8	10	11 A	11 B	12 A	12 B	13
Oil yield (wt %)	32	27	33		27		33
% C	74.5	77	76	77	76	77	75
% H	6.8	7.5	7.2	7.3	7.0	7.3	7.1
% O	18.5	16	17	16	17.5	16	18
$\overline{M}_n$	282	272	323	254	271	246	295
$\overline{M}_w$	364	344	400	336	349	336	389
Char yield (wt %)	< 1	2	4		5		7
Soluble organics (wt %)	29	22	26		24		-
Final pH	4.1	5.1	4.3	4.5	4.2	4.5	5.0

increasing polarity or hydrogen donor/acceptor strength are used to sequentially elute distinct chemical groups from silica gel. After evaporation of solvent, the recovered fractions are weighed. Recovery is generally in the 85-100% range. Partial characterization of the recovered fractions by elemental analysis, GPC, infrared spectroscopy and solubility classification provides the structural information shown in Table III. A comparison of SESC profiles for the CLU runs of Table I and Albany runs TR-7 (LBL mode) and TR-12 (PERC mode) is made in Table IV.

Wood liquefaction results in the formation of a variety of water-soluble acids. This causes a drop in the pH of the aqueous phase from 6-9 to 4-5 and an increase in the concentration of titratable acid and anion from about 0.2 N to 0.4 - 0.6 N. Although a number of carboxylic acids have previously been identified by GC-MS [7], none save acetic proved to be major components of the acid fraction. The other major acids have now been shown by HPIEC to be glycolic (hydroxyacetic) and formic. The concentrations of these acids in slurry prehydrolysate and in effluent waters for the runs of Table I are given in Table V.

EFFECT OF PROCESS VARIABLES

The relative importance of two key process variables, temperature and the nature of the reducing gas, was investigated in runs CL-11 and CL-12. Both were conducted at 340°C for 12 hours and then at 360°C for another 12 hours at constant flow rates and system pressure. The reducing gases were pure CO and pure hydrogen, respectively. Reference to Table II shows that higher temperature resulted in an oil of somewhat lower oxygen content and lower molecular weight in both instances. Comparison of the SESC profiles

TABLE III

CHARACTERIZATION OF WOOD OIL SESC FRACTIONS[a]

Fract.	Wt %	Mol. Wt.	% O	Predominant Cpd Type
Liquids:				
1,2	0- 6	130	-	Aromatic hydrocarbons
3	1-10	175	11	Semipolar aromatics
4	5-30	190	16	Monomeric phenols
5	35-55	300	21	Dimeric phenols
Solids:				
6	10-25	540	23	Phenol oligomers
7	1- 3	590	-	-
8	5-20	560	-	-
9	0-10	-	-	-

[a] Dashed lines represent approximate dividing lines among oils, asphaltenes and preasphaltenes, as these terms are usually defined for coal-derived fluids.

TABLE IV

SESC PROFILES OF WOOD OILS

Fraction	CLU Run No.					Albany Run No.	
	8	10	11A	11B	12B	TR-7	TR-12[a]
1 + 2	1	3	1	4	3	1	6
3	2	18	1	16	15	16	12
4	5	8	6	20	25	39	21
5	37	50	53	41	39	19	34
6	26	14	19	12	12	14	14
7	2	1	1	0	0	1	-
8	10	3	19	1	2	6	2
9	-	2	-	6	3	3	-

[a] PERC mode. All other runs were conducted in the LBL single pass mode.

TABLE V

CONCENTRATIONS[a] OF WATER-SOLUBLE CARBOXYLIC ACIDS FORMED IN LIQUEFACTION OF DOUGLAS FIR

Run	Glycolic[b]	Acetic[b]	Formic[b]	Total[c]
Slurry Water	.04	.10	.11	.26
8	.26	.15	.09	.52
10	.30	.19	.06	.57
11A	.25	.16	.05	.50
11B	.21	.17	.04	.45
12A	.22	.12	.01	.40
12B	.18	.16	.01	.37

[a] Equivalents per liter. [b] Determined by HPIEC. [c] Measured by acid-base titration.

of Table IV for 11A and 11B shows a distinct shift from higher fractions (5, 6 and 8) to lower (1-4) as an apparent result of the increased temperature. This finding is in general agreement with a number of observations suggesting that the optimum temperature for wood liquefaction is in the 350°-360°C range [10].

On the other hand, changing from CO to H_2 reducing gas appears not to make a difference, at least not under the conditions and constraints of the LBL CLU. It is clear from the data of Tables II and IV that, at the same temperature, no distinctions between CL-11 and CL-12 are possible on the basis of elemental analyses, molecular weights, yields or SESC profiles. Somewhat higher carboxylate titers are obtained in CL-11 (Table V), but this is partly due to the production of excess formate by the reaction of CO and hydroxide ion.

The effect of pH on oil yield and quality has not yet been adeaquately defined. Slurries ranging in pH from 6.1 to 8.9 have given rise to aqueous effluents of pH 4.1 - 5.1. Since wood liquefaction is an acid-forming reaction, the buffering capacity of the slurry is as important a consideration as its initial pH.

STOICHIOMETRY AND YIELDS

The highest actual yield of oil obtained in CLU runs was 33%, based on 100 parts of wood organics fed. The highest combined yield of oil and char was 37%. However, there are material losses due to hold-up of heavy oil in downstream lines, valves and pressure letdown vessels and evaporation of volatiles upon solvent removal. Correcting for these losses on the basis of material balance considerations, i.e., carbon and oxygen

balances, leads to a consistent yield figure of about 40% oil plus char for the runs of Table I and others. The yield of water solubles is typically 25%. Carbon dioxide is formed in about 25% yield, exclusive of that derived from the water gas shift reaction. These results are summarized in Table VI.

Analysis of the amounts of oil collected in successive collection periods has shown that the initial collections are inevitably low. This is the direct result of hang-up on the walls of the receiver vessels. Thus in calculating yields, it is necessary to eliminate the first collection in each of the two vessels. Table VII shows the yields so calculated for the smoothest series of runs to date -- CL-10 through 13. The average yield of oil so calculated, 37.5%, is the best estimate of yields from the water-slurry process currently available. With an average coke yield of 5%, this gives 42.5% for oil plus char in reasonable agreement with the estimate from balances.

If, as we believe, the formation of char is an operational difficulty, then the maximum yield of wood oil obtainable by the LBL process using 20% wood slurries is 40 to 42%. About 53% wood oil was produced in Albany run TR-12 with the oil-slurry recycle (PERC) process. The difference is clearly due to the large fraction of product that goes into the aqueous phase in the LBL process.

Calculations show that the amount of CO consumed by other than the water gas shift reaction is 0.1 $\pm$ 0.1 mols per 100 lbs wood. Thus there is little if any reduction of wood by CO in the operation of the CLU; the dominant pathway for oxygen removal is decarboxylation. The conclusion is consistent with the conclusion that replacement of CO with H_2 or reducing gas makes little or no difference in the LBL process. It is in contrast to

TABLE VI

CORRECTED MASS BALANCE FOR CLU RUNS

	C	H	O	Total
Organic Feed				
Douglas fir wood	51	6	43	100
Products				
CO_2[a]	7	0	19	26
H_2O[a]	0	1	8	9
Water solubles[b]	14	2	9	25
Wood oil/char	30	3	7	40
Totals	51	6	43	100

[a] Based on oxygen balance. [b] Estimated from total organic carbon.

TABLE VII

OIL YIELDS BASED ON STEADY-STATE PORTION OF RUNS*

RUN	WT % OIL
CL-10	39
CL-11	41
CL-12	32
CL-13	38
AVERAGE	37.5%

* First two collection periods omitted.

the experience of Albany runs TR-8 and TR-12, where the corresponding figure for CO consumption was found to be 0.5 mols (ca. 14 lbs) per 100 lbs wood [11]. The major pathway for lowering oxygen content is still decarboxylation in these PERC runs, but chemical reduction by CO now competes with dehydration as the second most important mechanism. Unfortunately no comparable figure is available for Albany run TR-7 in the LBL process mode.

DISCUSSION

CLU Performance Evaluation

The full potential of the CLU has yet to be realized, but continuous operation using comparatively concentrated slurries of biomass under a range of operating conditions has been successfully demonstrated. Although several problems, such as char formation, remain to be solved, the major test, whether the results of the Albany PDU can be duplicated, seems largely to have been met.

The development of methods such as GPC and SESC fractionation now permit reasonably detailed comparisons between CLU and PDU wood oils. In Table VIII, CL-11B oil is compared with TR-7 and TR-12 oils. Although the temperatures of these runs were similar, the residence times were much greater in the case of the PDU runs. In TR-7 the residence time was on the order of several hours as compared to the 20 minutes of CL-11B; in TR-12 the average residence time was probably even longer than in TR-7 because of the high (19-1) recycle ratio. Nevertheless the similarities among these three product oils are more striking than their differences. Although it would be tempting to speculate on the effects of time, oil recycle and CO uptake on the basis of the data of

TABLE VIII

COMPARISON BETWEEN CLU AND PDU DOUGLAS FIR WOOD OILS

	CL-11B	TR-7	TR-12
T, °C	360	∿340	∿360
$\overline{M}_n$	254	215	240
$\overline{M}_w$	336	306	370
% O	16	13	13
ΣF 1-5[a]	81	75	73

[a] Sum of the volatile SESC fractions from Table IV.

Table IV and VIII, the main point is simply that the CLU apparently produces oil comparable in quality to that made by the Albany PDU. In other words, despite its small size and nonscalable reactor, the CLU appears to be a valid tool for process development.

There remains, however, one troublesome point. A truly continuous process cannot tolerate appreciable coking or char formation. Although run CL-8 produced almost negligible char, this result has not been duplicated in subsequent operation. Evidence from Albany is encouraging in this regard. In runs TR-10, 11 and 12, where a gas-fired, tubular reactor was employed under conditions of turbulent flow, virtually no coking occurred [5]. Both oil and water slurries were fed. This was a particularly significant observation since, unlike the stirred tank reactor of the CLU, a tubular reactor is scalable to commercial size.

In addition to the problem of coking, there is also a need to define the upper concentration limit of slurry feed. Although 30% slurry can be pumped through a small test loop, it remains to be seen whether continuous operation can be sustained at these concentrations.

Having established a reasonably firm data base for Douglas fir, another short-term project is to examine selected alternative biomass feedstocks under comparable conditions. Aspen or poplar species, known to be rather more reactive than Douglas fir in pulping, are of special interest because of the recent development of fast-growing hybrids [12]. A study of the liquefaction of aspen (Populus tremuloides) is in progress.

Further Process Development

The most significant finding of the present work is that 25% of the organic product is lost to the aqueous phase in the LBL process. So although the water-based process solves several major problems inherent in the PERC oil-recycle scheme, it does so only by paying an intolerably high price.

There are probably two major reasons for the high yield of water solubles. First, since there is some 10-12 times more water present per unit mass of oil in the LBL than in the PERC process, a much greater fraction of oil constituents is extracted into the aqueous phase. Second, since water as well as oil is recycled many times in PERC operation, a high percentage of the water solubles decompose, e.g., by decarboxylation of organic acids or reduction by formate, or condense with reactive constituents of the oil phase. For example, glycolic acid, the mose abundant component of the aqueous phase, may condense with reactive phenols upon continued recycling, resulting in a net transfer of mass from aqueous to oil phase.

Decreasing the yield of water solubles by recycling effluent water to the prehydrolysis step would not be economical because the need to alternately acidify (for hydrolysis) and neutralize (for liquefaction) would consume excessive amounts of sulfuric acid and sodium carbonate. While there are possibilities for double recycles -- hydrolysis water to hydrolysis and liquefaction water to liquefaction -- solving the problem almost certainly will require lowering the ratio of water to oil. Success in feeding 30% slurries would be a step in the right direction but may not be sufficient to rescue the process.

A clear answer to the question of which of the two processes, PERC and LBL, is the better can now be given: neither! However, a modified process concept, combining the best features of both, may provide the way to ultimate economic feasiblity. Several such ideas are under consideration. For example, prehydrolysis and oil recycle could be retained in separate loops, integrated by means of a phenomenon we call solvolysis. Solvolysis refers to the dissolution of wood solids effected by phenols, e.g., wood oil, that occurs at temperatures of 180-270°C [13]. The possibility that prehydrolyzed wood solids could be dissolved in wood oil at concentrations of 25-50% in the preheat stage of an oil-recycle process shows promise in preliminary investigations.

Upgrading Product Oil

Combustion tests conducted at the Pittsburgh Energy Technology Center have shown Douglas fir wood oil to be a satisfactory boiler fuel [5]. However, the hope that a higher quality fuel such as diesel could be made from wood simply by the action of alkali, carbon monoxide and heat now seems unlikely to be realized. The available evidence indicates that the formate ion mechanism, once thought responsible for effecting deoxygenation, plays a minor role at best. The liquefaction of wood under these conditions is better described as a controlled wet pyrolysis in which oxygen is lost primarily through the removal of carbon dioxide. Optimum conditions can be expected to make probably no more than a 10% yield of actual hydrocarbon and perhaps an upper limit of 20% of volatile nonphenolics. A good portion of the remainder of the product resulting from the optimum process can be expected to be monophenols, for which a number of potential uses as a chemical feedstock have been described [14].

It would seem, therefore, that the goal of converting wood to automotive fuel will be attained only be additional chemical processing. Experiments on hydrocracking by techniques reported to be applicable to coal-derived fuels, shale oil and tar sand oils are needed. Since hydrogen has proved as effective as carbon monoxide in our experiments, it may be feasible to integrate catalytic hydrogenation or hydrocracking within the existing process framework. Since CO feed reacts largely to form H_2 and CO_2 by the shift reaction anyway, the use of pure hydrogen would probably be economically advantageous, especially if, in conjunction with transition metal catalysis, a higher grade distillate fuel were produced. Calculations indicate that the hydrogen requirement should be less per unit volume of product than is needed for overall coal conversion.

CONCLUSIONS

- The LBL continuous liquefaction unit, employing a CSTR reactor, is operational on a scale of about 0.25 kg hr^{-1} of organic feed. While operated to date with aqueous slurries of prehydrolyzed Douglas fir wood, it should be able to process a wide variety of biomass forms and peat.

- The product wood oil made at this bench scale conforms closely in chemical and physical properties to that produced at the DOE's process development unit at Albany, Oregon.

- In runs to date, no significant differences resulting from operation with carbon monoxide, hydrogen or mixtures of these as reactant gases have been found.

- In the single-pass water-slurry process, yields of water-soluble organics amount to 25%, about half of which is carboxylic acids. The lower yield of wood oil in the water-based process as compared to the oil-recycle process (PERC) is entirely attributable to the larger amount of water soluble product made in the former process.

- The highest temperature of operation, 360°C, results in the highest quality wood oil in terms of oxygen content and molecular weight distribution.

- The major pathway for oxygen removal is decarboxylation; dehydration is the second most important route. In contrast to the oil-recycle process, no evidence for chemical reduction by carbon monoxide via intermediate formates can be discerned.

ACKNOWLEDGEMENT

The contributions of Pat Bronnenberg, Michael Eames, Mark Featherstone, Ray Gansley, and Rafael Zamora are gratefully acknowledged.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Biomass Energy Technology Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and funded through Battelle Pacific Northwest Laboratory, Lead Laboratory for the U.S. Department of Energy, Biomass Energy Technology Division, Thermochemical Conversion Program under Contract No. DE-AC06-76LO-1830.

REFERENCES

[1] F. Fischer and H. Schrader, Brennstoff-Chem., 2, 257 (1921).

[2] H.R. Appell, Y.C. Fu, S. Friedman, P.M. Yavorsky and I. Wender, "Converting Organic Wastes to Oil," Bureau of Mines Report of Investigations 7560, U.S. Department of Interior, Washington, D.C. 1971.

[3] Dravo Corporation, Blaw-Knox Chemical Plants Division, "Economic Feasibility Study for Conversion of Wood Wastes to Oil," prepared for Bureau of Mines, 1973; The Rust Engineering Co., "U.S. Bureau of Mines Wood-to-oil Pilot Plant -- Final Design Report," prepared for Bureau of Mines, 1974.

[4] L.L. Schaleger, N. Yaghoubzadeh and S. Ergun, "Pretreatment of Biomass Prior to Liquefaction," presented at the Third Annual Biomass Energy Systems Conference, Golden CO, 1979; S. Ergun, C. Figueroa, C. Karatas, and J. Wrathall, "LBL Continuous Biomass Liquefaction Process Engineering Unit," 1979 Annual Report, Lawrence Berkeley Laboratory, Energy and Environment Division, LBL-11650, October, 1980.

[5] P.L. Thigpen and W.L. Berry, Jr., "Liquid Fuels from Wood by Continuous Operation of the Albany, Oregon, Biomass Liquefaction Facility," presented at the 6th Annual Conference on Energy from Biomass Wastes, Lake Buena Vista, FL, 1982.

[6] C. Figueroa, L.L. Schaleger and H.G. Davis, "LBL Continuous Bench-Scale Liquefaction Unit -- Operation and Results," LBL-13709, presented at the 6th Annual Conference on Energy from Biomass Wastes, Lake Buena Vista, FL, 1982.

[7] H.G. Davis, D.J. Kloden and L.L. Schaleger, "Chemistry and Stoichiometry of Wood Liquefaction," Biotechnol. Bioeng. Symp., 11, 151 (1981).

[8] L.L. Schaleger and H.G. Davis, "Progress in the Characterization of the Products of Direct Liquefaction of Douglas fir," LBL-14017, presented at workshop/review meeting of the National Research Council, Saskatoon, Sask., Canada, February 1982.

[9] M. Farcasiu, "Fractionation and Structural Characterization of Coal Liquids," Fuel, 56, 9 (1977).

[10] H. Appell, "The Production of Oil from Wood Waste," in Fuels from Waste, L.L. Anderson and D.A. Tillman, eds., Academic Press, New York, 1977, pp. 121-140.

[11] H.G. Davis, C. Figuoeroa and L.L. Schaleger, "Liquid Fuels by Direct Liquefaction of Biomass,: LBL-14155, presented at KTI Fifth Annual High Temperature Processing Technology Symposium, Napa Valley, CA, May, 1982.

[12] H.W. Anderson and L. Zsuffa, Forest Research Report No. 101, Ontario Ministry of Natural Resources, Division of Forests, October, 1975.

[13] S.-M.G. Yu, Ph.D. thesis, University of California, Berkeley, CA, 1982.

[14] D.C. Elliott, "Description and Utilization of Product from Direct Liquefaction of Biomass," Biotechn. Bioeng. Symp., 11, 187 (1981).

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.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720