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LBL CONTINUOUS BENCH-SCALE LIQUEFACTION UNIT, OPERATION AND RESULTS

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## ENERGY & ENVIRONMENT DIVISION

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Carlos Figueroa, Larry L. Schaleger,  
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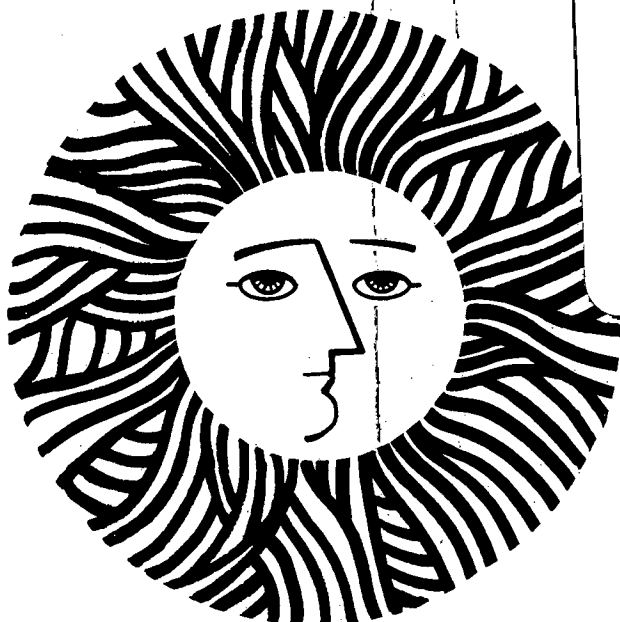
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LBL CONTINUOUS BENCH-SCALE LIQUEFACTION UNIT,  
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## ABSTRACT

A bench-scale continuous liquefaction unit (CLU) is now fully operational at the Lawrence Berkeley Laboratory. The CLU is a flexible system capable of examining feedstocks introduced in slurry form by various liquefying techniques. It is the only continuous biomass liquefaction unit currently in use.

Emphasis has been on the liquefaction of aqueous slurries (about 20% organics) of prehydrolyzed Douglas fir wood, without recycle, under the following conditions:

- 330-360°C
- 3000-3400 PSIG
- pH 6-9 ( $\text{Na}_2\text{CO}_3$ , 5-10% of wood)
- CO-H<sub>2</sub> ratios in reactant gas 1:0, 1:1, 0:1
- Experiment duration 10-24 hours.

Results show about 30% of feed organics is converted to CO<sub>2</sub> plus H<sub>2</sub>O, with crude wood oil yields 20-35% and water-soluble organic products 20-30%. Atom balances and difference calculations indicate that the estimates of oil yield are low. The ratio of water-solubles to oil is higher than in the oil recycle, or "PERC" process. Direct reduction by CO and usage of feed gas are less than in PERC.

A variety of analytical techniques is used to characterize both wood-oil and water-solubles. The SESC technique, developed by Mobil for coal liquefaction products, combined with size exclusion chromatography, is especially useful for showing effects of process variable changes on product oil.

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# LBL CONTINUOUS BENCH-SCALE LIQUEFACTION UNIT, OPERATION AND RESULTS

## INTRODUCTION

The recent history of the direct biomass liquefaction effort dates from efforts in the late 60's at the Pittsburgh Energy Research Center (PERC).<sup>(1)</sup> The Department of Energy's process development unit (PDU) was completed in 1976 at Albany, Oregon. Operation of the PDU between 1976 and early 1980, demonstrated a need for further detailed investigation of basic process parameters. To address this need, a bench-scale continuous liquefaction unit was designed and built<sup>(3)</sup> at Lawrence Berkeley Laboratory (LBL). Successful operation of the CLU was achieved in 1981 and is the subject of this report.

The Albany PDU was originally designed to feed dry wood flour slurried in recycle product oil, with coal-derived anthracene oil used for start-up. This procedure was termed the PERC process. It involved drying and grinding Douglas fir wood chips, slurrying the resulting wood-flour in anthracene oil or recycle oil as it became available, adding 10% aqueous sodium carbonate as catalyst, preheating in a scraped-wall vertical preheater, reacting in a 120-gallon autoclave at 330-350°C and 3000 PSIG, pressure let-down, and phase separation. During the 1976-1979 period, there were many operational difficulties. As an alternative, a single-pass water-slurry process was suggested.<sup>(9)</sup> The PDU, as designed and constructed, was not particularly well-adapted to this water-slurry or LBL process. Nevertheless, it was tried in 1979, and the first sizable quantities of wood-oil product were made by it.<sup>(6)</sup>

During 1980 and early 1981, the operators of the PDU, the Rust Engineering Division of Wheelabrator Clean Fuels, made three runs with a modified PERC process and two with the LBL process. Substantial quantities of product oil were made by both procedures. There were operability problems with the LBL process, and again it appeared that the PDU, even with some modification, was not well-adapted to handling water-slurry feeds. Operations with the modified PERC procedure were much smoother, especially during the final run, TR-12<sup>(7, 10)</sup> in February and March of 1981. Excellent material balances and good oil yields were obtained.

Perhaps the most significant accomplishment of the last three runs at the PDU was the finding that both water and oil slurries can be preheated to full reaction temperature in a direct-fired tubular preheater. It should be noted that the flow regime at Albany was turbulent. Under laminar conditions attempts to heat water slurries at LBL have resulted in coking problems.

Smooth operation in the PERC process required feeding a very dilute slurry of wood flour in recycle oil, recycle water and catalyst solution.<sup>(7, 10)</sup> The recycle ratio of oil was very high -- we estimate about 19 to 1 -- and there was also a large water recycle. Thus, there remains a strong incentive to develop a viable single-pass, or low recycle ratio, process. Operation of the CLU in 1981 and 1982 is aimed at obtaining sufficient data on the effects of variables on the water-slurry process, or a modification thereof, so that a viable single-pass procedure can be recommended for scale-up.

Primary biomass-derived oils do not lend themselves to easy characterization by conventional analytical or separation techniques. In order to follow the effects of process variables on the product, we have developed several chromatographic or solvent elution methods of characterization. We find an adaptation of the SESC technique, developed by Farcasiu(4) of Mobil, when combined with size exclusion chromatography, to be especially useful. A significant part of the overall product of liquefaction is water-soluble and exits the reaction system in effluent water. We have characterized these products by gas chromatography, acid-base titration and by extraction. The analytical and characterization techniques are described further below.

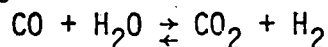
## GENERAL DESCRIPTION OF THE WATER SLURRY OR LBL PROCESS

Our CLU operations have emphasized the water-slurry or LBL process, as applied to Douglas fir wood chips. The sequence of processing events follows (see Figure 1).

The first step is a partial hydrolysis. This is an explicit step -- prehydrolysis -- in the LBL process, but probably occurs in the early stages of reaction in any case. Prehydrolysis is carried out at 180°C in dilute sulfuric acid, at pH about 1.8. Passage through a disc refiner or colloid mill produces a slurry which is pumpable at total solids concentration of 30% or more.

During prehydrolysis, carboxylic acids are formed, but the pH rises. Elements in the wood (e.g. calcium carbonate, calcium oxalate, basic nitrogen compounds) neutralize the excess acid. The final pH, typically about 2.4-2.5, is approximately what would be expected from the organic acids alone. Under the conditions of hydrolysis the hemicelluloses are essentially completely hydrolyzed, but hydrolysis of cellulose should be 5% or less. The water phase contains reducing sugars, formic, acetic, and other acids, and other organics.

The water slurry is pumped into a reactor, tubular or back-mixed. There it is heated to about 350°C under an atmosphere of steam and carbon monoxide or hydrogen or synthesis gas at about 3000 PSIG and maintained at temperature for a residence time of the order of 10 to 60 minutes. The original wood components lose oxygen as water and carbon dioxide, and are thereby converted into a heavy oil soluble in such organic solvents as acetone and chloroform. The water gas shift reaction occurs

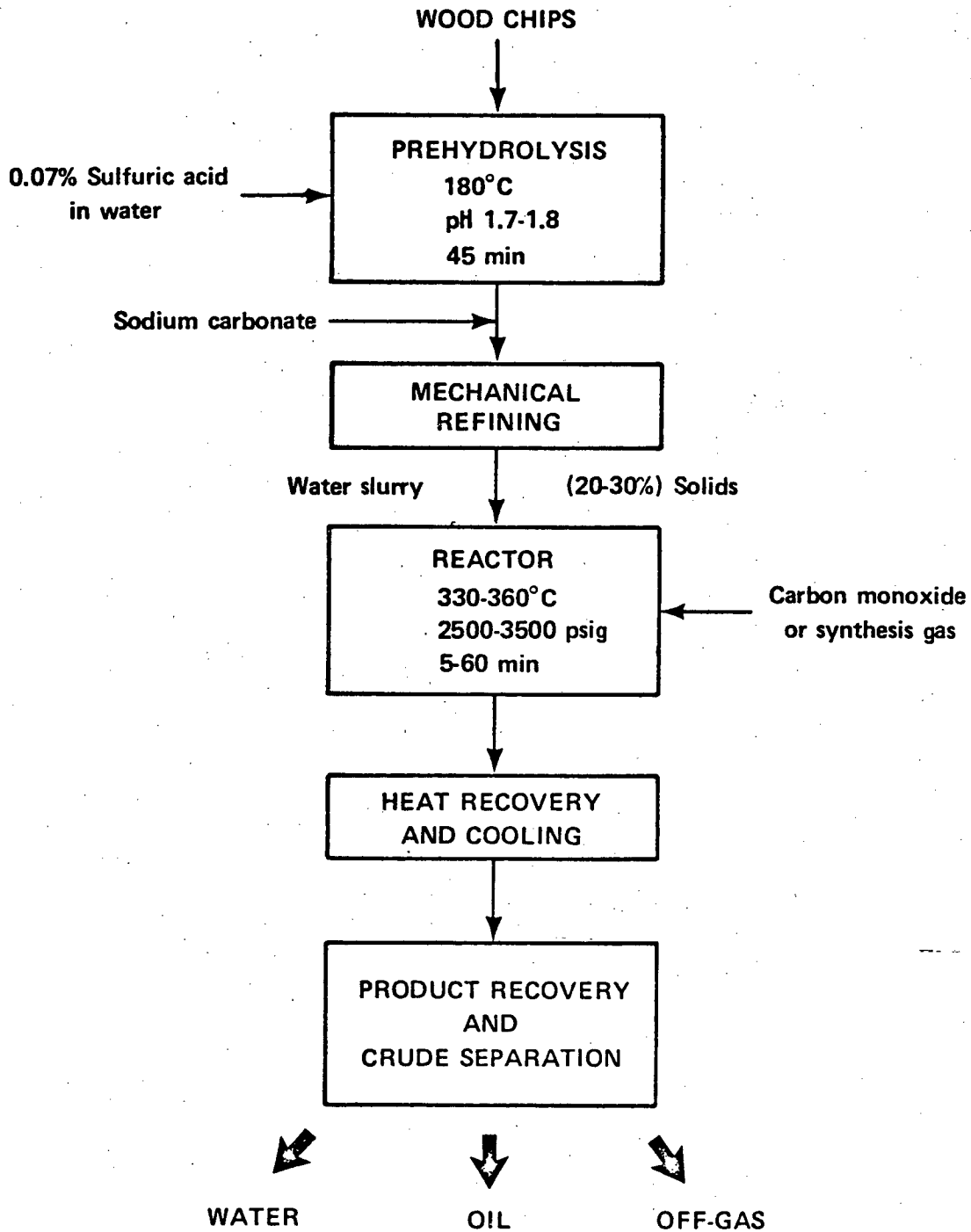


so that, with a CO-containing reactant gas, there is a net gain of hydrogen in the gas phase. Carbon dioxide is formed by pyrolytic decomposition, by reaction of carbon monoxide with oxygen in wood conversion products, and by shift reaction.

The water-soluble product includes carboxylic acids, a small amount of phenolics and low molecular weight oxygenated compounds such as cyclic ketones. Depending upon the amount of sodium carbonate or other alkali added as "catalyst," the acids will be present in the aqueous product phase as anion or acid in various ratios.

FIGURE 1

LBL LIQUEFACTION PROCESS



XBL 8111-1529

The elemental analysis of the wood-oil product derived from the above sequence includes anywhere from 12 or less to 17% or more O, depending upon the severity of liquefaction; i.e., upon the temperature and reaction time. The oil is highly polar, the predominant fraction being phenolic, and contains little actual hydrocarbon.

## EXPERIMENTAL

### General Description

The biomass liquefaction unit (CLU), as shown in Figure 2, is highly instrumented and was designed in a mechanically simple configuration to avoid plugging by small extraneous particles. There are three major process sections making up the CLU: reactant gas and slurry feed system, reactor assembly, and product collection system. Auxiliary equipment includes a central data processor for continuously monitoring temperature and pressure points as well as providing operating system interlocks.

Douglas fir wood chips (2-inch industrial hogged wood) have, to date, been the source of raw material for the liquefaction experiments. Several barrels of acid-hydrolyzed wood slurry were prepared at the Albany, Oregon PDU for use at LBL.

Prior to each experimental run, 30 kg batches of slurry are re-homogenized by continuous recirculation through a colloid mill. This is done to prevent dried slurry particles or clumps, which form upon storage, from plugging lines, check valves, or other restrictions in the slurry feed system.

### Reactant Gas and Slurry Feed System

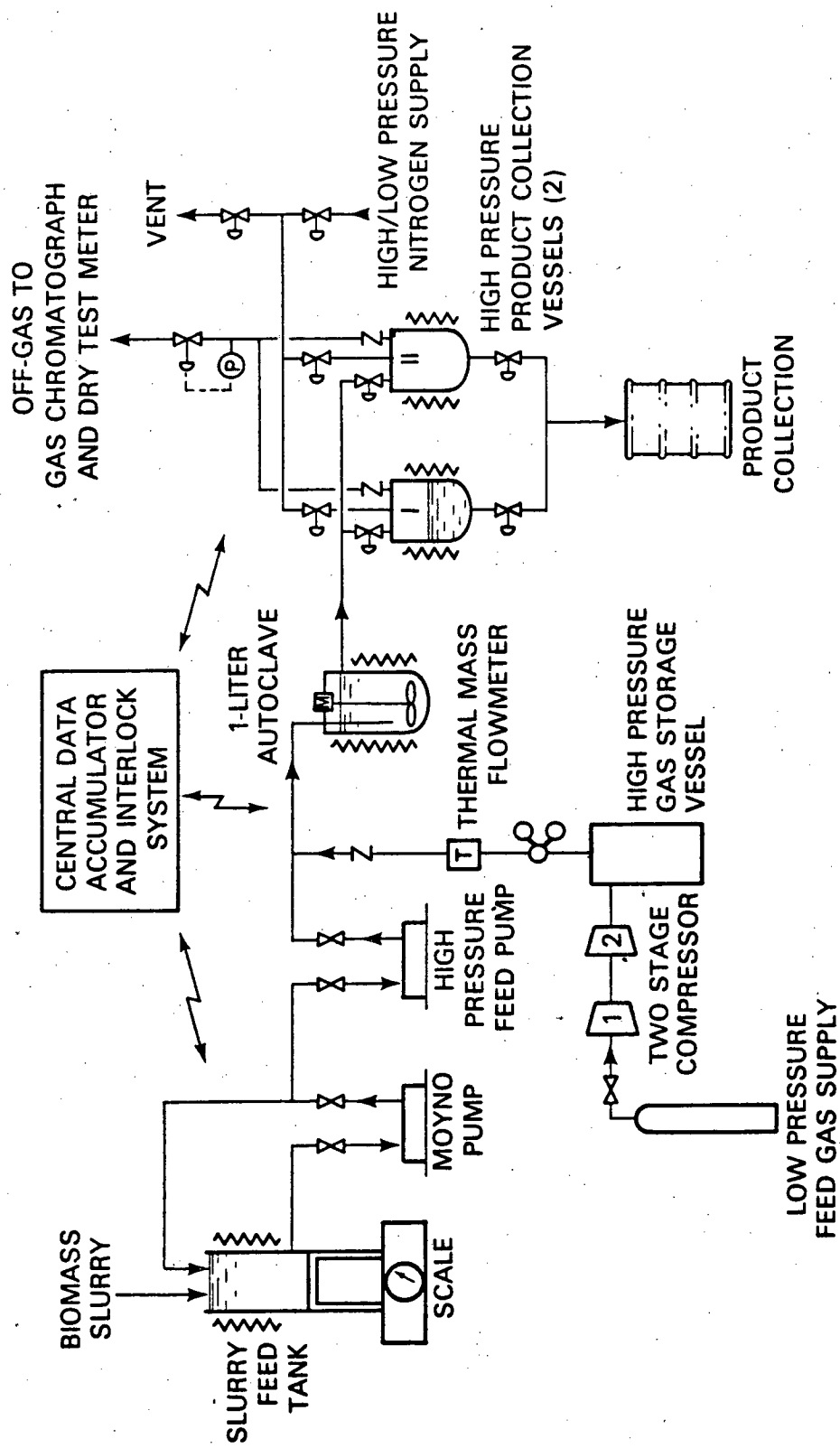
The slurry feed assembly consists of a continuously weighed feed tank with a recirculation pump loop. A progressive cavity pump is used as the recirculation pump to maintain the slurry pressure at 20 psi. This is necessary as the following high pressure feed pump requires sufficient suction pressure to operate. A single piston high pressure pump elevates the slurry pressure from 20 psi to 3000-3400 psi. Before the reactor, reactant gas is sparged into the slurry.

Reactant gas, carbon monoxide, or hydrogen, or mixtures of both, is compressed from standard-size gas cylinders through two compressors to 4500 psi and stored in a one-gallon surge vessel. After the vessel, a pressure regulator supplies gas to the thermal-mass flow meter at 4000 psi. This high performance flow meter accurately and reliably meters gas to the reaction section.

### Reactor Assembly

Slurry and gas reactant are sparged together into a magnetically stirred, electrically heated, one-liter autoclave. Separate visual observations indicated that a single upward pitched propeller operated at 1000 rpm is sufficient to insure proper solid-liquid-gas contacting. The resulting oil/water/gas stream exits near the top of the reactor and flows through a downward sloping air-cooled line to the product collection section.





**BIOMASS CONTINUOUS LIQUEFACTION UNIT**

Figure 2

XBL 817-1023

## Product Collection System

The combined oil/water/gas product stream is diverted downward to one of two 2-gallon liquid receiver vessels. These vessels can be independently isolated, depressurized, discharged of product, and re-pressurized with nitrogen so as not to significantly affect the overall system pressure or flows.

Off-gases exit from the top of either receiver vessel, through a check valve, to the main back-pressure control valve where the gas pressure is reduced to atmospheric. The off-gas volumetric flow is measured via a gas meter. Finally, a slip stream of gases is diverted to an automated gas chromatograph for analysis. The remaining off-gases are vented.

The total liquid is separated manually into oil and water fractions. The oil, which tends to stick to receivers, is dissolved in an organic solvent, generally a chloroform-methanol mixture. Solvent and small residual amounts of water are evaporated in a rotary vacuum evaporator. Some of the most volatile organic product is lost in this procedure. The water layer is titrated to determine total acid and carboxylate anion and analyzed for total organic carbon. Other analyses applied to the oil product are described in a later section.

## CLU OPERATING EXPERIENCE

Following very limited success with indirectly heated small bore tubular reactors during 1980 and early 1981, the reactor section of the CLU was replaced with a stirred one-liter autoclave as shown in Figure 2. This converted the previous plug-flow reactor to a CSTR (continuous stirred tank reactor), effectively a 400 to 1 scaledown of the Albany PDU. As operating problems other than reactor tube plugging have proved to be solvable, acceptable operation has been achieved, starting with run CL-5, July 16, 1981. Minor improvements in stirring, slurry injection, pressure let-down, and reactor hardware have been made during the summer, and run CL-6 turned up a special problem which is discussed below. Runs from CL-7 on are based on our overall plan for a study of operating variables to be completed in 1982.

Operating conditions of runs 2-12 are summarized in Table 1. Some additional yield and analytical data are given in Table 2.

### CL-2 to CL-4

In these runs we mainly learned to cope with mechanical and other operating problems which arose with the revised reactor system. "Plugs" developed in feed lines from over-preheating, in take-off lines from congealed liquid product, or in valves from overheating. Once identified, these problems were controllable. Mass recoveries were poor because run times were short. However, oil samples were obtained, and it was possible to make comparisons with oil products made in the PDU or in the tubular reactor runs.

### CL-5

The overall run time was about 16 hours. Good samples were ob-

TABLE 1 CIU: SUMMARY OF RUNS WITH BACK MIXED REACTOR

Run No.	Date '81	Run Time (hours)	T °C	P (atm)	Reactor Time (min)	Slurry Feed (kg/hr)	Gas Type (Ratio)	Gas Feed (L/min)	% Mass Recovery	Oil Yield (wt %)	Reason for Termination	Operating Equipment Modifications	Comments
2	6/28	1.5	350	205	13	1.8	CO/H <sub>2</sub> 1:1	1.8	-	-	Plug	Slurry preheater installed	Poor temperature control on inlet and outlet reactor lines. Better control of line temperatures improved operation in later runs.
3	7/1	1	350	205	13	1.8	CO/H <sub>2</sub> 1:1	1.8	-	-	Plug	-	-
4	7/7	2	350	205	17	1.4	CO/H <sub>2</sub> 1:1	1.6	80	24	Plug	Lowered slurry preheat temperature to 100 °C	-
5	7/16	15	345	205	18	1.3	CO/H <sub>2</sub> 1:1	1.6	92	20	Plug	-	-
6	8/4	5	354	205	29	0.8	CO/H <sub>2</sub> 1:1	1.6	~100	15	Gas leak	Installed air reactor outlet line cooler on reactor outlet line to replace water cooled exchanger.	High water vaporization rate noted
7	8/24	10	350	205	15	1.6	CO/H <sub>2</sub> 1:1	2.2	91	31	Off-gas line plugged.	-	Oil foams upon depressurization.
8	9/2	24	330	205	26	0.9	CO/H <sub>2</sub> 1:1	1.6	~100	32	Voluntary	Installed separate off gas vent line	New gas line avoids common vent pressure surges.
9	9/25	4	350	232	23	1.0	CO	1.0	-	-	Check valve failure	Replaced all viton o-rings with silicone	-
10	9/29	10	350	232	21	1.1	CO	1.0	95	27	Feed sparger plugged.	Feed sparger line shortened to reduce effect of coking in line	Off gas composition: 32% H <sub>2</sub> , 9% CO, 59% CO <sub>2</sub>
11	10/15	24	340, 360	232	20	1.2	CO	1.0	98	33	Voluntary	-	Off gas composition: 22% H <sub>2</sub> , 22% CO, 56% CO <sub>2</sub>
12	11/4	24	340, 360	232	20	1.2	H <sub>2</sub>	1.0	98	27	Gas leak	KO.pot installed to collect foam.	Off gas composition: 70% H <sub>2</sub> , 30% CO <sub>2</sub>

TABLE 2  
 CLU RUNS — ADDITIONAL YIELD AND ANALYTICAL DATA

Run No.	Elemental Analysis of Oil (maf)			Average Molecular Weight Recovered Oil <sup>a</sup>		Estimated Yield Soluble Organic, wt %	Aqueous Phase		Char Estimated Yield wt %
	C	H	O	$\bar{M}_n$	$\bar{M}_w$		Slurry	Effluent	
4	74	7.5	19	271	483	26	6.1	4.5	7.1
5	77	7.9	15	213	319	23	6.1	5.0	9.0
6	78.5	8.2	13	176	232	20	6.1	3.9	3.9
7	76	7.4	17	242	384	27	7.5	4.5	11.3
8	74.5	6.8	18.5	-	-	33	7.5	4.1	0.3
9	-	-	-	-	-	26	8.9	4.5	-
10	77	7.5	16	-	-	22	8.9	5.1	1.6
11A	76	7.2	17	-	-	28	7.7	4.3	3.7
11B	77	7.3	16	-	-	25	7.7	4.5	
12A	76	7.0	17.5	-	-	25	8.0	4.2	5.0
12B	77	7.3	16	-	-	23	8.0	4.5	

<sup>a</sup>  $\bar{M}_n$  and  $\bar{M}_w$  are number and weight average molecular weight, respectively.

tained and the overall material balance was fair (about 92%). It was found that letting down the pressure from the product recovery vessels too rapidly leads to a loss of oil product by a foaming mechanism. Hence, in CL-5, a disproportionate amount of oil was contained in the 8% overall loss, and the real oil yield is higher than the 20% shown in Table 1. A series of improvements in the let-down procedure corrected the loss problem, especially from run 8 on.

#### CL-6

While CL-6 was a short run, aborted because of a system gas leak, there were interesting results. The aqueous effluent was found to be very low in titratable anion and, therefore, in sodium salts in general. This suggested that little or no water had exited from the reactor as liquid -- on the contrary, that it had left almost totally as vapor, leaving the sodium salts behind. As a result of this observation, the total system pressure was increased from 3000 psig to 3400 psig to insure minimal water vaporization in later runs. Further, the small amount of oil product obtained in this run had the lowest molecular weight and was the most fluid of any wood oil we have seen. Presumably, we were primarily recovering the vaporized lighter ends.

#### CL-7

This was a good run at 350°C with synthesis gas and a moderate ratio of gas to slurry input (1.72 Moles per 100 g wood or wood hydrolysate).

#### CL-8

This was the best run to date. It showed us that at the reaction times available in the CLU -- the liquid space-time was 60 minutes and the residence time about 30 minutes -- the 330°C product is heavy, viscous and probably under-reacted. If these are undesirable qualities, the range of temperatures which should be studied is fairly narrow, about 340-360°C. Because of the problem of vaporization, it is best at the higher temperature to limit the flow of reactant gas and to raise the total pressure somewhat. These two steps reduce the ratio of fixed gas flow at reaction conditions to water flow and, therefore, the percentage of water which exits the reactor as vapor.

#### CL-9, 10

A single upward thrust propeller was used for stirring in these runs and the feed gas was 100% CO. Shortly after the start of CL-9, the check valves on the gas product line were found to be stuck open. The run was stopped, double check valves in series were installed and run CL-10 was started. With 100% CO as gas feed, it was immediately apparent that the water gas shift was occurring to a considerable extent. Also, substantial amounts of formate ion were formed in the aqueous layer. The molar gas compositions became constant, shortly after start-up, at 9% CO, 32% H<sub>2</sub>, and 59% CO<sub>2</sub>. The pressure ratio (H<sub>2</sub>.CO)/H<sub>2</sub>O.CO at 350°C is estimated to be about 1, as compared to an equilibrium constant of 20, so that the water gas shift equilibrium is approached but not reached.

The potential for feed line plugging was reduced by shortening the inlet line into the CSTR. Through run CL-10, this brought the feed almost to the bottom of the reactor. Starting with CL-11, the line ends just below the expected level of the liquid during operation.

### CL-11, 12

These were both successful runs with two reaction temperatures (340 and 360°C) explored in each. Product gas flow measurements and analyses for CL-11 showed that little or no carbon monoxide was used up except by shift reaction. We therefore replaced carbon monoxide with hydrogen for CL-12.

CL-12 demonstrated no observable operating differences with pure hydrogen as the reactant feed gas. Preliminary analytical results from the oil produced also suggest no significant differences caused by the change in reactant feed gas.

## CHARACTERIZATION OF WOOD OILS

Several methods for the detailed characterization of oil product have been developed and applied. These include the fractionation of crude oil according to polarity and molecular weight through the use of an adaptation of the SESC (sequential elution by solvents chromatography) technique<sup>(4)</sup> and estimation of number and weight average molecular weights by HPSEC (high performance size exclusion chromatography). We have also used GC-MS (capillary gas chromatography-mass spectroscopy) to identify key compounds and compound types present in both oil and water phases.<sup>(5)</sup> A solvent extraction method designed to partition the oil into a neutral (non-phenolic) fraction and phenolic fractions of two molecular weight ranges has been described elsewhere.<sup>(2)</sup>

The SESC technique, originally developed by Farcasiu<sup>(4)</sup> at Mobil for coal-derived liquids, has been especially useful in showing up differences among the various wood oil samples. The method as we have adapted it, employs a specially prepared silica gel column. A sample (~2g) of oil, suspended with silica gel in benzene, is added to the top of the column.

Sequential washings with nine solvents remove portions of the oil according to increasing polarity. After evaporation of solvent, the recovered fractions are weighed and a reasonably good material balance can be obtained. Generally, the recovery is 85 wt % plus, and recoveries of less than about 80% indicate the presence of fractions of extremely high polarity and/or of molecular weight above about 1500-2000. Solvents used and properties of typical eluted fractions are shown in Table 3. The weight distribution of SESC fractions from various wood oils, including those from Albany runs TR-7, TR-10, and TR-12, are shown in Table 4.

TABLE 3

## CHARACTERIZATION OF WOOD OIL SESC FRACTIONS.

<u>Fraction</u>	<u>Solvent</u>	<u>Description (Molecular Wt. Range)</u>
1	Hexane	Aliphatic hydrocarbon
2	Hexane - 15% Benzene	Aromatic hydrocarbons (130-170)
3	Chloroform	Aromatic ethers, 11% oxygen (150-200)
4	Chloroform - 4% Ether	Monophenols (150-200)
5	Ether - 4% Ethanol	Diphenols, 20% oxygen (180-300)
6	Methanol	Dark solid, 23% oxygen (300-650)
7	Chloroform - 4% Ethanol	Polyhydric phenols (160-210) Polyphenols (> 600)
8	Tetrahydrofuran	
9	Acetic Acid	Uncharacterized

TABLE 4  
 SESC OIL FRACTION, % (INCREASING POLARITY)

Run No.	F1	F2	F3	F4	F5	F6	F7	F8	F9	Residue	$\Sigma$ F1-F4
TR-7* (LBL Process)	-	1	16	39	19	14	-	7	-	4	56
TR-10* (LBL Process)	-	1	6	17	35	19	-	6	-	16	24
TR-12* (PERC Process)	-	6	12	21	34	14	-	2	-	11	39
CL-4	-	3	2	13	47	13	-	11	-	11	18
CL-5	-	1	5	21	46	10	-	16	-	1	27
CL-6	-	6	9	28	41	3	-	13	-	0	43
CL-7	-	1	2	19	50	15	2	5	-	6	22
CL-8	-	1	2	5	37	26	2	10	-	17	8
CL-11A	-	1	1	6	53	19	1	19	-	0	8
CL-12B	-	3	4	12	51	16	3	1	11	0	19

\* Samples from PDU



## DISCUSSION

### Yields

The highest oil yield shown in Table 1 is 35 weight percent of the wood organics fed. There is reason, however, to believe that the estimates we have been able to make so far are consistently low. The most significant mechanical losses during early operation arose from foaming of the liquids during pressure let-down. From about run CL-7 on, we believe this loss has been minimized. As discussed above, the solvent work-up procedure used has guaranteed a loss of some of the more volatile organic products -- probably of the order of about 3% of the wood organics fed. There are also minor losses resulting from coating of lines and fogging, but there is no evidence that these add up to as much as 1%.

Coking is a chemical loss. Apart from an effect of reaction temperature -- viz., the low char yield in run CL-8 at 330°C -- the amount of char left in the reactor appears to be largely random. We believe it to depend primarily on the reactor wall temperature required to drive the necessary heat into the reacting slurry, and therefore also on the amount of char which has built up in the reactor. Individual CLU runs like CL-8 and CL-10 show that it is possible to run with little or no char formation. This is also indicated by the most successful PDU run TR-12.<sup>(7)</sup> What appears as char because of reactor problems should appear as oil in the absence of problems.

When an oil product with 16% to 17% oxygen is formed (CLU temperatures about 350°C) the carbon dioxide yield is about 22% (0.5 Mol/100 g wood) and the water yield is estimated from a crude atom balance to be about 9% (0.5 Mol). The water soluble organics yield is about 25%. Thus, by difference the oil (+ char) yield is about 44%. Smooth operation is expected to result in yields in the following ranges:

Oil (plus char, if any)	35 - 45 wt %
Water solubles	20 - 30 wt %
CO <sub>2</sub>	18 - 26 wt %
H <sub>2</sub> O	8 - 10 wt %

### Comparison with PERC yields

To compare with PERC process yields, it is necessary to compare the above CLU results with PDU data. At the relatively long residence time of PDU TR-8, Rust Engineering <sup>(8)</sup> reports oil yields, at the 8% oxygen level, of slightly above 40 wt %. We concluded from an attempted atom balance <sup>(2)</sup> that the actual yield was about 44% -- perhaps 46% if the insolubles or char formed could be prevented in the smoothest operation. More recently in TR-12, with shorter residence time and a range of operating temperatures, Rust Engineering reports <sup>(7)</sup> an average oil yield of about 53 wt %. In this case, the oxygen contents ranged from about 17% at the lowest temperatures to about 12% at the highest. Atom balances verify that the average yield should be about 53%.

Because of the very high recycle of both oil and aqueous effluent, the higher ratio of oil to water, or both, yields of water soluble organics have been relatively low in the PDU PERC runs. We estimate their range at about 6 to 8%. Since this compares to yields of the order of 25% in our runs, it constitutes a major difference. Also, presumably for the same operational reasons of high recycle and high oil/water ratio, there is strong evidence that CO reduces a significant part of the wood oxygen in the PERC runs (at least at the higher operational severities).

With the yields of water-solubles running 15% or more higher, it is inevitable that the LBL oil yields should run considerably lower than those found with PERC, as is found. Improvement of this situation by recycle of effluent water -- e.g. to the prehydrolysis step -- is not economical with the present process. Recycle would involve re-acidification for prehydrolysis, followed by realkalization for liquefaction, the cycle consuming excessive amounts of both sulfuric acid and sodium carbonate. Improvement requires either modification of the process steps or the achievement of a higher degree of reduction in single-pass operation, perhaps by incorporation of a small amount of active catalyst with the feed.

With the differences in gross product distribution observed, it is remarkable that there are more similarities than differences in the oil products. This is shown both by the range of elemental analyses obtained in CLU and PDU runs and by the SESC fractionation shown in Table 4.

In SESC fractionation of wood-oil, fractions 1 to 4 are both less polar than the higher-numbered fractions and also of lower molecular weight (see Table 5). The sum of the weight %'s in F1 to F4 is therefore a measure of both reduced polarity and of formation of lower molecular weight liquids.

The loss of high volatiles in our oil product work-up -- mostly F1 to F3 -- probably biases the CLU runs vs. the PDU runs somewhat. CL-8, for example, has somewhat better flow properties, visually, than TR-10, despite the apparently substantial difference in F1-F4. These two samples, from the lowest severity run in the CLU and the low severity PDU run had the highest amounts of inelutable residue, and this may be a better measure of insufficient reaction. The other CLU samples reported showed SESC residues equal to or lower than that of PERC product TR-12, but show larger amounts in the polar, high molecular weight F6 to F9 region. As with the question of matching oil yields, the problem seems to be to obtain sufficient reduction of molecular weight and of oxygen content in a single-pass process to obtain a product oil of a desired quality.

## CONCLUSIONS

The LBL bench-scale direct liquefaction process is operational in a CSTR mode. While operated to date with water slurries of lightly prehydrolyzed Douglas fir wood, it should be able to handle a wide variety of biomass forms and peat.

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

Since a high proportion of carbon monoxide reacts to form hydrogen and carbon dioxide by the water gas shift reaction, use of hydrogen as the reactant gas is an economic plus.

In the single-pass water-slurry process as operated so far, yields of water-soluble organics are of the order of 25%.

Coke formation is somewhat dependent on reaction temperature, but in general has seemed to depend on irrelevant variables such as smoothness of run. Coke is believed to form at hot reactor surfaces where heat is being added to the system.

Yields of recovered oil in early runs have been 20 to 35 wt % of wood organics fed. Preliminary atom balances indicate that with improved product recovery and reduction in coke formation yields of over 40% should be achievable.

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