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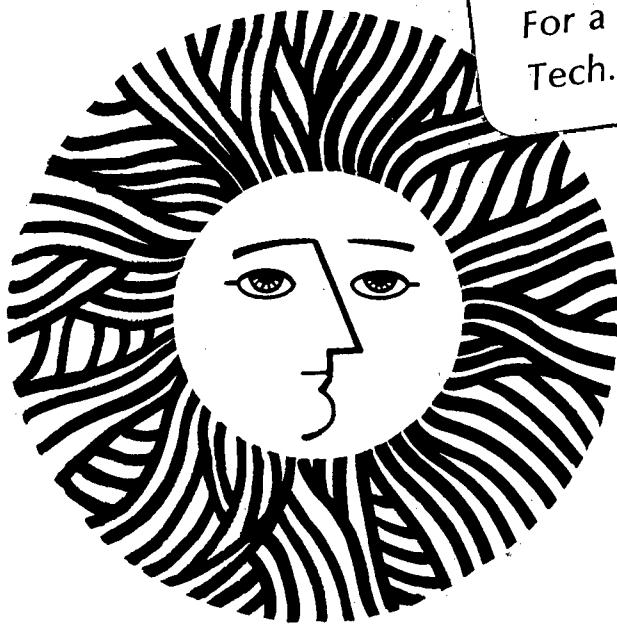
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Hubert Davis, Carlos Figueroa and Larry Schaleger

June 1982

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RESEARCH AND DEVELOPMENT ACTIVITIES
ON DIRECT LIQUEFACTION TECHNOLOGY

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ABSTRACT

We are now in a position to assess the status and future potential of the existing direct liquefaction processes. The oil-recycle (PERC) process has an excellent chance of achieving reliability but needs a major reduction in the amount of recycle. The single-pass water slurry (LBL) process leads to a less desirable product distribution. In both cases, the crude biomass oil product should ultimately be upgraded.

Two strong possibilities for better processes, based on using product biomass oil as a solvolytic agent are described. The solvolysis solution or quasi-solution of biomass in recycle oil is treated with reducing gas and steam as in the present processes or, alternately, hydrocracked. In either case, major gains can be foreseen. Product upgrading by hydrogenation would be a natural add-on to either system.

First promising steps towards developing the new process are described below, along with our activities in further understanding the old processes, and current improvements in characterizing the oil and water-soluble products. A statistical study of Rust Engineering's final PDU run, TR-12, was made and is discussed. This throws considerable light on the stoichiometry of the liquefaction process.

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 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.

INTRODUCTION

As we work our way into the second half of fiscal year 1982, it is clear that a major improvement in the liquefaction process is necessary. Both present approaches can be made to work, but despite our efforts (1, 2, 3), and those of Rust Engineering (4, 5) at the Albany, Oregon PDU, both remain flawed. The oil recycle process, besides requiring drying and fine grinding of wood feed, has only been made to operate well at very low wood concentrations. Recycle ratios of both product oil and aqueous effluent are inordinately high. The resulting high heat load and poor space yield are severe economic burdens. While the single-pass water slurry process bypasses the recycle problem, the water in the feed still creates a serious heat load. The oil yields, though higher than found in PDU runs, are lower than in the oil-recycle process, and the yields of water solubles are higher. With both processes, the primary oil product is usable only as a heavy fuel oil or a gasifier feed. Product improvement is certainly desirable and probably necessary.

The most promising pathway to a better process starts with our studies over a three year period of the phenomenon of solvolysis (6, 7, 8, 9). When wood chips are heated with certain solvents containing alcoholic or phenolic hydroxyl, at temperatures in the range of 180°-270°C, they are converted to a more or less homogeneous material soluble in powerful organic solvents like acetone and tetrahydrofuran (6). Liquefaction product oils, because of their phenolics content, are suitable solvents (9). Part of the solvent reacts chemically with the wood product and the solvent is not directly recoverable without additional chemical treatment. Solvolysis is an interesting phenomenon, but is useful only as the possible front end of a full process with solvent regeneration and product recovery in the downstream stages. Attractive features are that the wood chips do not have to be dried or ground and that other feedstocks can be handled.

The second intriguing point about solvolysis is that it must occur in the oil recycle process during heat-up. When the feed reaches reaction temperature, liquefaction must have already taken place. Further reaction is simply the reduction of oxygen content and of average molecular weight of the newly-formed liquid under the influence of temperature and pressures

of steam and reducing gas. If, in the PDU, the temperature at which the wood flour feed and recycle were blended had been higher — say 200°C instead of 100° — a low recycle ratio might have been possible.

A solvolysis — CO-steam process, therefore, looks very much like the PERC process as finally used by Rust Engineering, with a higher blender temperature and with a lower oil and water recycle. Drying — beyond perhaps partial air drying — and fine grinding would be eliminated.

It is at least equally reasonable to combine solvolysis with a catalytic hydrogenation step. In this case water is not recycled and a phase separation stage is added to remove the water formed during solvolysis, especially if undried biomass is fed. The reactor can be a trickle-bed catalytic converter containing a sulfided hydrocracking catalyst such as nickel-tungsten. Or it could be a slurry reactor of some type containing an expendable catalyst.

The object of the reactor is to convert the solvolysis product to a recyclable liquid, i.e., one with an oxygen content in the range of 11-16 wt %. Conversion of the net crude product to a low oxygen, distillable liquid, if this is needed, requires a further hydrogenation step.

The LBL group is currently setting up equipment to study the following under flow conditions:

- (1) Trickle-bed hydrogenation-hydrocracking of solvolysis product and/or crude wood oil.
- (2) Slurry hydrogenation of solvolysis product.
- (3) CO-steam treatment of solvolysis product.

We will also be able to do batch hydrogenation of either solvolysis product or wood oil with catalyst supported in a basket or slurried in the oil. Fig. 1 shows the trickle-bed set-up.

At present we are carrying out clean-up experiments on the water-slurry liquefaction, while preparing and initiating the solvolysis liquefaction program. "Clean-up" includes such items as trying additional feedstocks such as aspen and other forms of biomass and increasing slurry concentration. However, from our efforts to date we feel we know what the

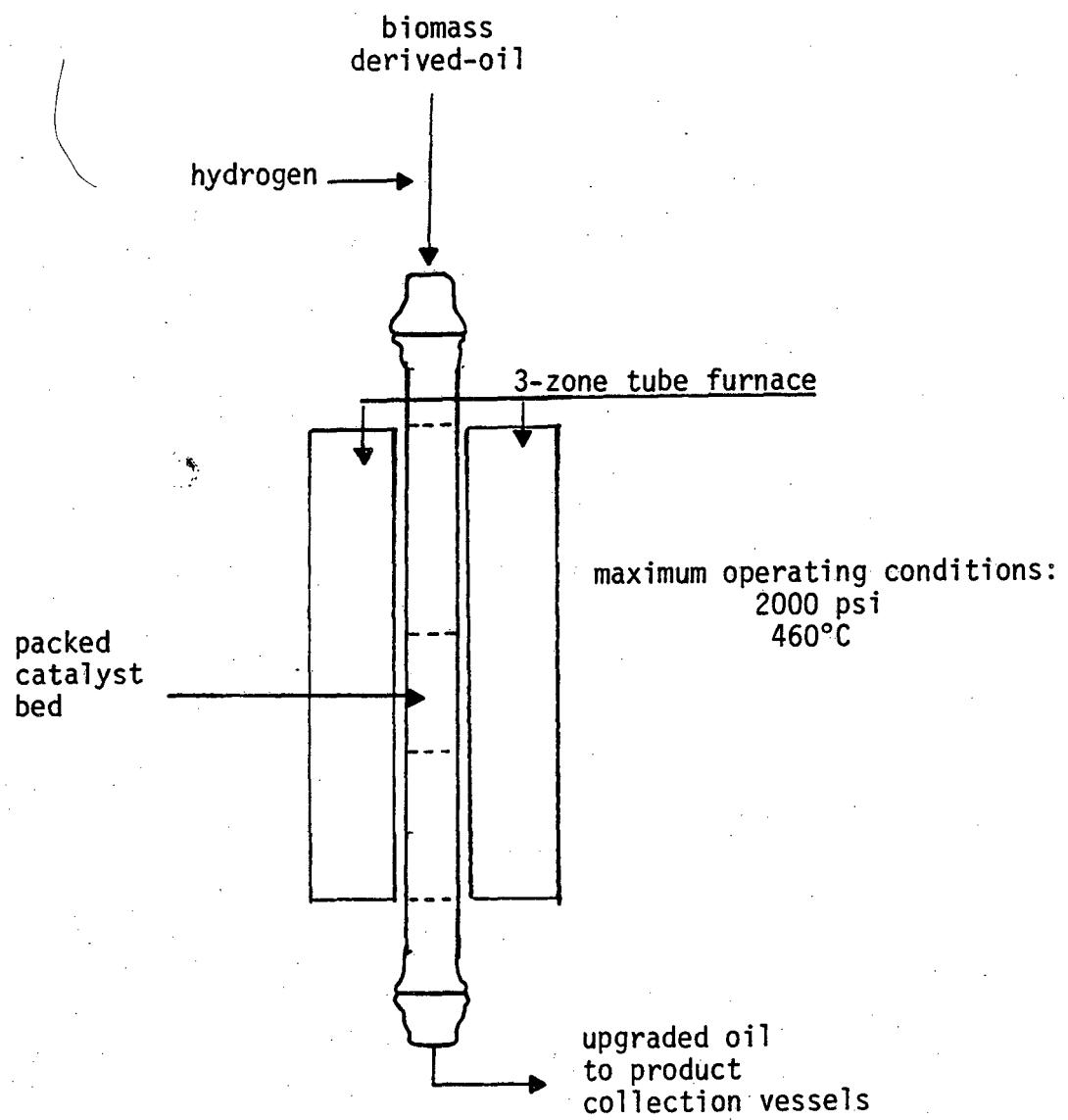


Fig. 1. Trickle-bed hydrogenation reactor

yields and their limits are (Table 1), and what the basic elements of a process must be. Fig. 2 is a block diagram of such a process.

OPERATION OF THE CONTINUOUS LIQUEFACTION UNIT (CLU)

The most successful CLU runs were the CL-8 through CL-13. Overall material balances were good and, as discussed below, accountability of the organics fed was good after an initial running-in period. Data are summarized in Table 2. From the Table we can make the following observations:

Temperature. At the typical residence time used of about 20 minutes, there is a small effect of reduction of oxygen content and a somewhat more impressive reduction in molecular weight on raising the temperature in the range 330-360°C. Temperatures above about 360°, as we approach the critical temperature of water, are hard to control. 360° or slightly lower is therefore the recommended operating temperature.

Atmosphere. There is little to choose among hydrogen, carbon monoxide and the synthesis gas mixture. Perhaps oil yields are a little lower and char yields a little higher when hydrogen is used, but the differences are small.

pH. There is at best a small benefit of increasing pH above 7. Certainly pH is not a major variable, although buffering capacity may be.

Char Yield. Char is formed at the reactor wall in the hottest parts of the reactor. It seems to be primarily an operational problem. Possibly it was a little worse with hydrogen as the reducing gas.

Soluble Organics. The yield of these materials is reduced by raising temperature, but all yields are much higher than we would like. Some form of water recycle is required to reduce the yields.

Calculations of atom balances about these runs⁽¹⁰⁾ indicate that little or no reducing gas is consumed. This suggests that, at these conditions, the water slurry process is a controlled pyrolysis in an atmosphere of steam and added gas. This conclusion is compatible with the observed lack of sensitivity to the nature of the gas. A comparison

TABLE 1

WHAT WE KNOW ABOUT THE WATER-SLURRY PROCESS

	PRESENT POSITION
1. OIL YIELD	~ 40 WT %
2. WATER SOLUBLES YIELD	~ 25 WT %
3. SLURRY FEED	20 WT % ORGANICS
4. ATMOSPHERE	H ₂ , CO, H ₂ /CO
5. TEMPERATURE @ 20 MIN RESIDENCE	~ 360° C
6. WT % O IN OIL	15 - 16

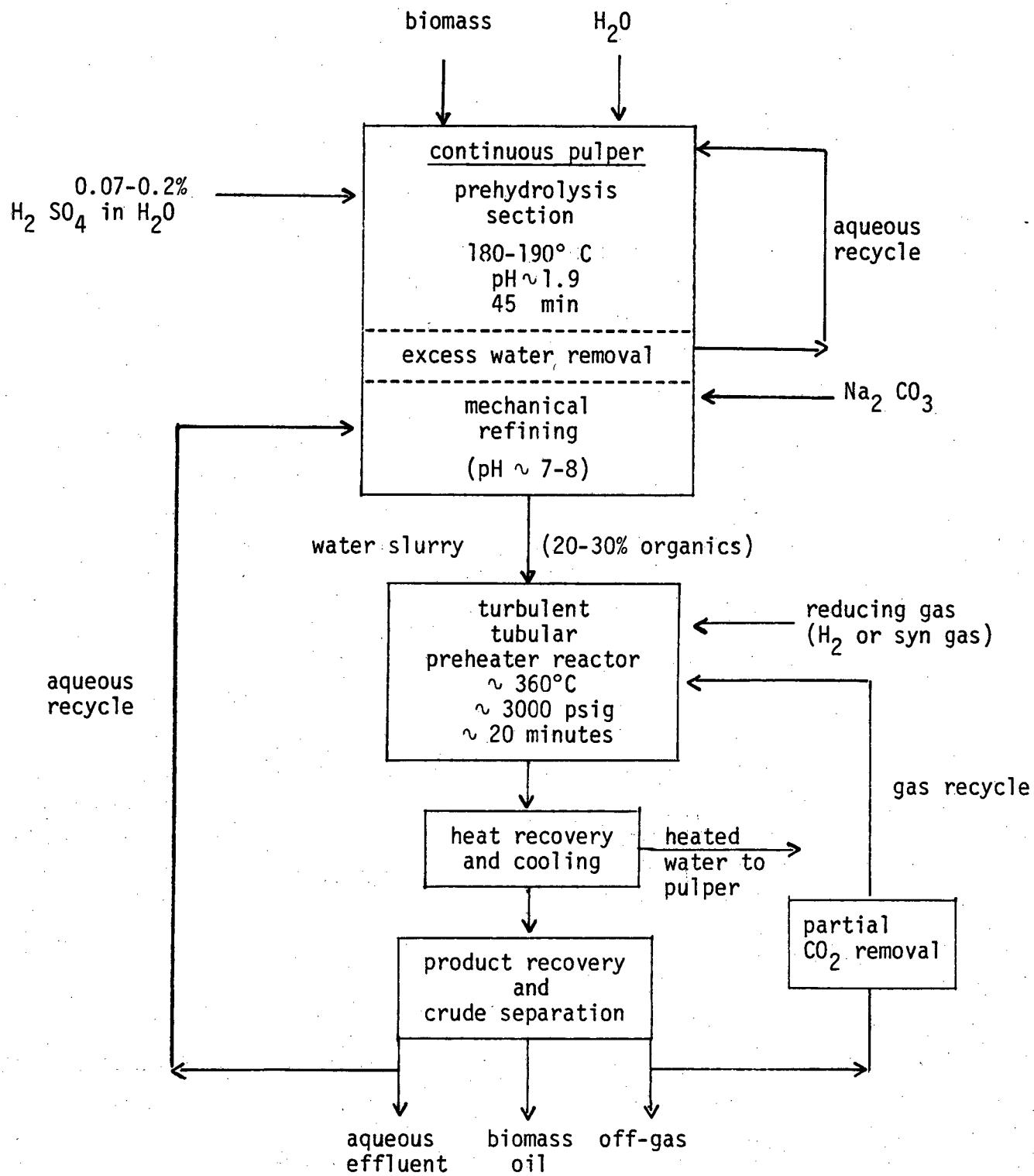


Fig. 2. SINGLE PASS WATER SLURRY LIQUEFACTION PROCESS

TABLE 2
PRODUCT YIELD AND ANALYTICAL DATA

RUN NUMBER, CL-	<u>8</u>	<u>10</u>	<u>11</u>		<u>12</u>		<u>13</u>
			A	B	A	B	
TEMPERATURE °C	330	350	340	360	340	360	340
ATMOSPHERE	H ₂ /CO	CO	CO		H ₂		H ₂
OIL YIELD (WT %)							
OVERALL	28	27	33		27		33
STEADY STATE	32-40	39	41		32		38
%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
M _N	282	272	323	254	271	246	295
M _W	364	344	400	336	349	336	389
CHAR YIELD (WT %)	<1	2	4		5		7
SOLUBLE ORGANICS (WT %)	29	22	26		24		25
INITIAL pH	7.5	8.9	7.7		8.0		8.9
FINAL pH	4.1	5.1	4.3	4.5	4.2	4.5	5.0

with the oil recycle process, where substantial quantities of CO are consumed is made below. The effective residence time in the straight-through process is of the order of 10% of that in the oil-recycle process. We would therefore expect a CO consumption of the order of 0.1 mol/100g wood vs. ~ 0.5 in the recycle process. Of course, in both cases larger quantities of CO (if it is fed) are consumed in forming hydrogen by the water gas shift reaction.

Runs CL-14 through 20.

These runs were primarily efforts to improve the oil yields and reduce the coke yields deduced from the data of Table 2. They were designed to test a number of working hypotheses. With one exception the results were negative. (See Table 3.)

It has always been observed, even in our most successful runs, that product oil recoveries were very low during the first few hours of running. While some of this was attributed to hold-up of the viscous product on the walls of the pressurized receivers and in valves and tubing, this did not seem to be enough. We looked for an explanation in a possible phase separation in the stirred reactor. This was thought to cause the liquid product to be held excessively long at high temperature. Only water phase would pass overhead out of the reactor until a sufficient level of oil was reached. Result: almost no oil recovered for the first two to six hours and an early build-up of coke.

Run CL-17.

This run was purposely allowed to proceed for only three and a half hours to test this hypothesis. Instead it showed that quite large amounts of oil are held up in the receiver, besides some in the lines. After an unusually lengthy effort to recover this oil hold-up, the oil product per 100 g organics fed was found to be 26 g. This can be compared with apparent yields in the first two collection periods of earlier runs in the range of 1-5%⁽³⁾. Also the char yield, at 5%, was not excessively high.

Run CL-18.

This run was made with a false bottom insert reducing the overall volume of the reactor, i.e., mimicking an early build-up of coke. The result was very bad. Temperatures could not be controlled and there was

TABLE 3
CLU - SUMMARY OF RUNS WITH BACK-MIXED REACTOR

Run No. CL-	Date	Run Duration (hours)	Reactor temp. (° C)	Reaction Pressure (atm)	Slurry feed rate (Kg/hr)	Reducing gas feed rate (stpm)	Feed gas type	Oil yield, wt %	Off-gas concen. %	Char yield	Overall mass recovery	Reason for run termination	Observations
14	12/14/81	9.6	340	232	1.15	1.0	H ₂	22/32*	65% H ₂ , 32% CO ₂ , 3% CO	11	99	Isolation valve failure	
15	2/23/82	4.7	340	232	1.04	0.5	H ₂	--	75% H ₂ , 25% CO ₂	11	83	Isolation valve failure. Reactor plug.	Erratic pressure on inlet line to reactor.
16	3/3/82	18.2	340	232	1.17	1.0	H ₂	21/28*	14% CO ₂ , 86% H ₂	9	94	Vent lines plugged with oil.	Erratic inlet pressure to reactor.
17	3/31/82	3.8	340	232	1.14	1.0	CO	26	52% CO ₂ , 29% H ₂ , 19% CO	5.4	70	Voluntary	Oil/gas leak in outlet line from reactor.
18	4/20/82	3.5	340	232	1.19	1.0	H ₂	--	--	19	~85	Erratic reactor temperature. Furnace problem	False bottom in reactor to mimic coke buildup. Very poor temperature control from start and rapid coke buildup.
19	5/11/82	2.0	340	232	0.7	1.0	H ₂	11	11	--	--	Isolation valve failure	Run aborted. No data.
20	5/25/82	9.0	340	232	1.49	1.0	H ₂	**	***	**	**	Low reactor outlet temperature due to char build-up.	New slurry, hydrolysis at 210°. Char particles in slurry. Result--rapid fill of reactor with coke.
21	6/8/82	11.0	350	232	1.27	1.0	H ₂	**	***	**	**	Voluntary	New feedstock: hydrolyzed aspen wood chips. Apparently successful run.

* Steady state (first 6 hours eliminated for yield calculation)

** Currently being evaluated; initial estimate for run 21 (aspen) is over 50%.

*** Gas analyzer not operating

excessive coking. This result helped to demolish the hypothesis that rapid early coking somehow improved the operation by reducing the oil residence time.

Finally, further convinced that the only important cause of initial low oil recoveries was system hold up, we looked at the yields by sampling periods in several of our runs⁽³⁾. Results are shown in Table 4. In all cases apparent yields are low in period 1 and low or medium in period 2. Even in periods 3 and 4 there are some low or medium oil recoveries. Occasionally, oil breaks loose and gives impossibly high recoveries (CL-11-4 and -13-6). Based on the analysis of Table 1 and other runs, we conclude that we have required on the average of about six hours to reach an approximately steady collection rate. Eliminating this early part of the runs we get for the steady parts of the runs:

CL-10	39%
CL-11	41%
CL-12	32%
CL-13	38%
average	<u>37.5 + 2.0%</u> (standard error).

This is a yield compatible with the yields of gas, water-solubles and coke observed. Under ideal circumstances, with coke minimized, the yields of oil should be about 40%. The yield, at least from Douglas fir, is unlikely to be higher unless we reduce the yields of water solubles.

Of the remaining CLU runs shown in Table 3, runs 15, 18 and 19 were aborted because of equipment failure. Runs 14 and 16 had higher than usual coke yields. In both cases we believe this to be related to some erratic temperature and pressure behavior. In the steady-state period — after the initial six hours of operation—oil plus coke yields were about 40% as we expect. Run 20 was made with the first pumpable slurry made after a pre-hydrolysis in the 10-gallon autoclave. To obtain pumpability we went to overly-severe hydrolysis conditions which led to evident charring of some of the wood. As a result the reactor filled with coke in the first four hours. Surprisingly, we were able to complete the planned nine hour run. On collecting product, however, we found it was largely partially

TABLE 4

<u>Period</u>	<u>Receiver</u>	<u>g oil/100 g organics fed (kg slurry in parentheses)</u>	<u>CL-11</u>	<u>CL-12</u>	<u>CL-13</u>
1	1		1.1 (1.4)	1.0 (1.6)	0.0 (1.4)
2	2		1.3 (4.6)	23.8 (5.0)	5.4 (4.0)
3	1		34.7 (5.1)	24.5 (4.7)	37.4 (3.8)
4	2		60.9 (5.5)	14.7 (4.7)	5.3 (4.1)
5	1		44.0 (3.7)	24.1 (4.7)	33.4 (4.6)
6	2		39.5 (5.6)	47.9 (4.0)	116! (2.5)
7	1		35.8 (2.2)	40.5 (3.2)	

reacted slurry solids which had bypassed the coke-filled reactor.

Operating conditions of run CL-21, the first CLU run with aspen slurry, are also given in Table 3. CL-21 was completed as this is being written so few analytical data are available. Operation was reasonably smooth, oil yield is high (perhaps over 50%).

Slurry Preparation

Several batches of slurry have been made in our 10-gallon autoclave at temperatures from 180°-210°C with Douglas fir wood chips. We find that, at the lower temperatures, mixing and temperature uniformity are not such as to give us friable wood chips. A pumpable slurry could not be made. At 210°C, we prepared a large batch of pumpable slurry for run CL-20. However, the degree of hydrolysis was excessive and there was excessive formation of organic acids and other water-solubles and volatiles. Also, the final slurry contained visible small grains of charred wood. As a result, CL-20 was an extremely poor run. Although it was terminated voluntarily, the reactor was found to be filled with soft char. In the second half of the run temperature could not be accurately measured or controlled.

For subsequent runs it was decided to use aspen wood chips as feed. Top temperature is limited to 190°C and heating rate is minimized. The conditions were set after a 1-gallon autoclave run which gave apparently acceptable slurry. As this is written, two batches of aspen slurry have been made. The first was made at 190°C with twice the concentration of sulfuric acid used with Douglas fir, 0.15 as opposed to 0.07 wt %, with 20% dry wood and 80% water. The result was a rather thin slurry (used in run CL-21). A repeat prehydrolysis run with 23% dry wood gave a very dry slurry. Some further experimentation is necessary.

A difficulty in this work is that our small substitute for a refiner, a colloid mill, does not do as good a job of breaking residual fibers as the larger disk refiners. We may have to over-hydrolyze to get a slurry pumpable by the small-size Bran-Lubbe pump used in the CLU.

Hydrogenation of Oil and Solvolysis Product

The trickle-bed reactor (Fig. 1) cannot be tested until the clam-shell heater ordered is received. Meanwhile, we have sulfided a batch of commercial nickel tungsten supported catalyst and are trying some batch experiments. No analytical data are yet available. Pressure changes indicate some consumption of hydrogen when TR-7 oil itself or a solvolysis product is treated.

Initial experiments with Douglas fir wood chips and TR-7 wood oil⁽⁹⁾ showed that a homogeneous product was achieved at 225°C with 3/1 oil/dry wood ratio and some added sulfuric acid.

The first of a series of experiments to determine minimum ratio of oil to dry wood and the minimum temperature has been run. In an initial run in the one-gallon autoclave at 240°C and a ratio of TR-7 oil to wood (dry basis) of 1.8, aspen wood chips had totally disintegrated and the product appeared to be homogeneous. No sulfuric acid was used. Solubility tests and SESC fractionation are proceeding.

CHARACTERIZATION OF PRODUCTS

The Quality and Nature of Wood Oil

Among the several methods of evaluating the quality of wood oil that have been developed in our laboratories, the two most useful have proved to be molecular weight determination by gel permeation chromatography (GPC) and column chromatography by the SESC technique (sequential elution by solvents-chromatography). We have described the methods in detail in quarterly reports and have given results for a series of oil products from CLU and Albany PDU runs. Here we would like to call attention only to the question of how well the results of the Albany PDU have been duplicated by the LBL CLU. Also some general remarks about the chemical nature of wood oil will be made.

In Table 5, oils from CL-11B and CL-12B are compared with TR-7 and TR-12 products. Although the temperatures of these runs were similar, the residence times were much greater in the case of the PDU runs. Nevertheless the similarities among the oils are more striking than their

TABLE 5
COMPARISON OF CLU AND PDU PRODUCT OILS

	<u>CL-11B</u>	<u>CL-12B</u>	<u>TR-7</u>	<u>TR-12</u>
T, °C	360	360	~340	371/ ^c 330 ^d
\overline{M}_n^a	254	246	215	240
\overline{M}_w^b	336	336	306	370
% oxygen	16	16	13	13
<u>SESC Fractions, %</u>				
Nonpolar	20	18	17	18
Monomeric phenols	20	25	39	21
Phenolic dimers	41	39	19	34
Phenolic oligomers	12	12	14	14

^a Number average molecular weight by GPC. ^b Weight average molecular weight by GPC. ^c Outlet temperature tubular preheater-reactor, short residence time.
^d Outlet temperature standpipe preheater-reactor, long residence time.

differences. The main point is 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.

The predominance of phenolic products is another interesting point that emerges from Table 5. That 70% of the wood oil product is phenolic is not particularly new. The news is that, except for TR-7, only one-third of the phenolic fraction is monomeric. Although work at PNL and LBL has established the identity of a number of monophenols by GC-MS, virtually no structural information is available on the phenolic dimers. Of interest in this regard is the nature of linkage between monomers which, if known, might provide a valuable clue to the question of which upgrading option to pursue. Clearly the maximization of monomeric phenols at the expense of higher phenolics represents a desirable processing goal.

Carboxylic Acids of the Aqueous Phase

Wood liquefaction results in the formation of a number of carboxylic 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 0.2N to 0.4-0.6N. Although many carboxylic acids have previously been identified by GC-MS^(9, 11), none save acetic proved to be major components. The other major acids have now been shown by high performance ion exchange chromatography (HPIEC) to be glycolic (hydroxyacetic) and formic.

Figs. 3 and 4 show chromatograms of slurry water and aqueous effluent, respectively. The production of glycolic acid under liquefaction conditions is particularly notable. It is formed in yields as high as 10% and is the single most abundant product of wood liquefaction. Concentrations of the three major acids in the aqueous effluents of a series of CLU runs are given in Table 6. Glycolic, acetic and formic acids typically comprise 90% of the total titratable acid content.

HPIEC - Douglas fir acid hydrolyzate

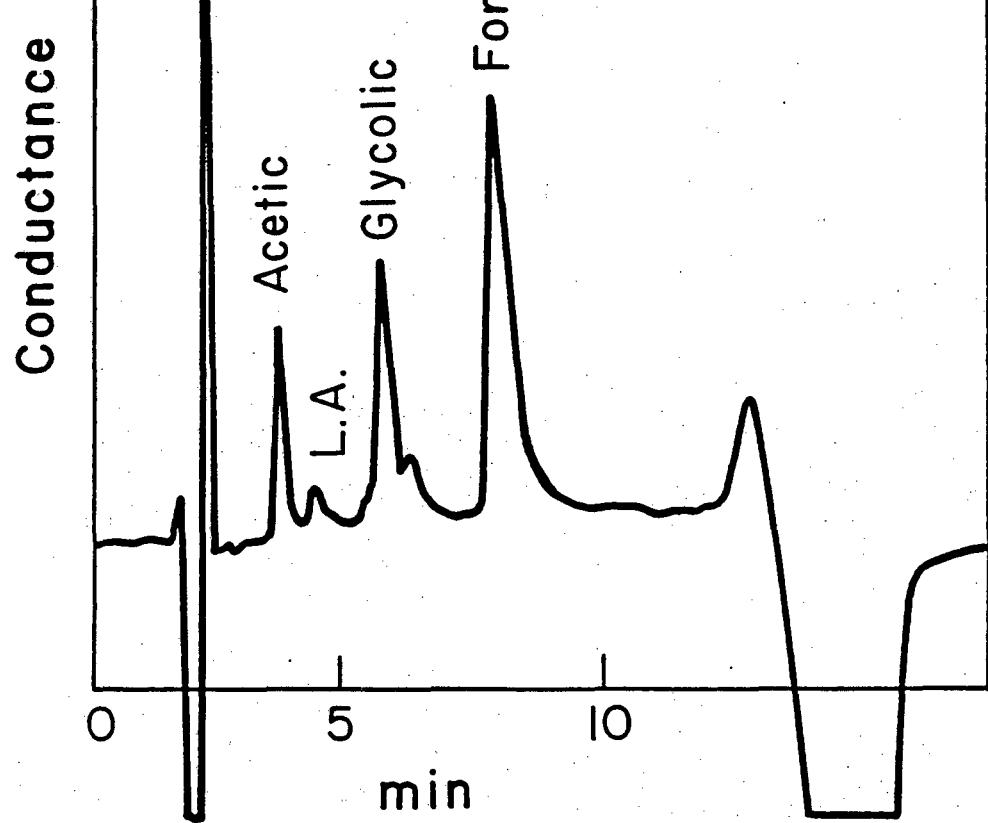


Fig. 3. High performance anion exchange chromatogram of water from slurry feed. The flow rate of 0.001M phthalate buffer (pH 3) was 2.0 ml min^{-1} .

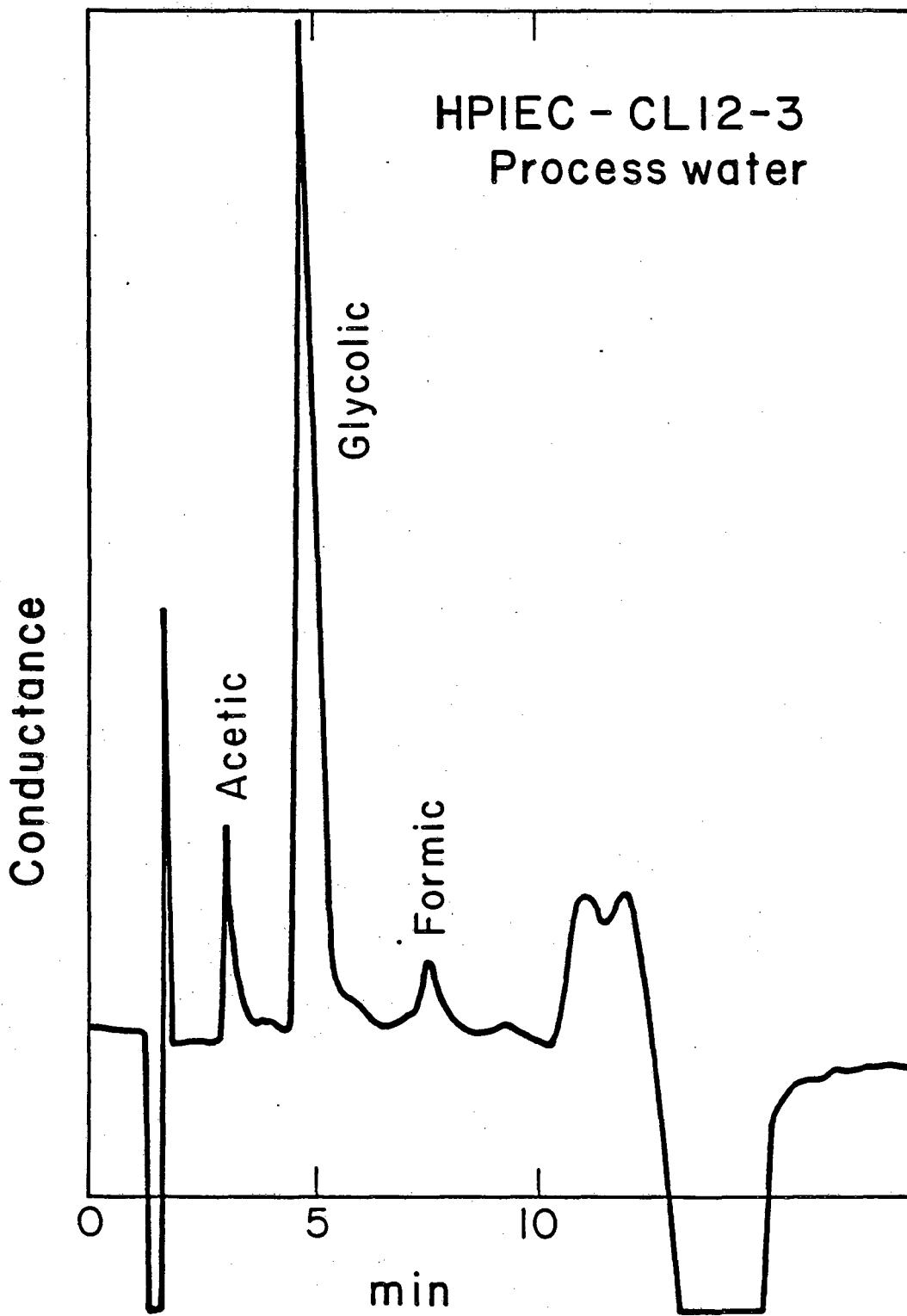


Fig. 4. High performance anion exchange chromatogram of aqueous effluent from run CL-12. The conditions and sample size were identical to those of Fig 3A.

Aromatic Constituents of the Aqueous Phase

We have previously reported the use of reverse phase HPLC to separate polar aliphatics contained in the aqueous effluent. With water as the solvent, only carboxylic acids are eluted from a C8-silica column. However, with water-methanol mixtures, polar aromatic constituents are also eluted. Fig. 5 shows a typical chromatogram. The methanol content, initially 25%, was increased at the rate of 1% per minute. UV detection at 254 nm was used.

A series of 20 standards was also run under these conditions to see what could be learned about the structures of the peaks of Fig. 5. These results indicate that compounds eluting in three minutes or less are aromatic carboxylic acids. The range from 3-8 minutes finds compounds with one benzene ring, two hydroxyl groups and not more than one methyl group. Fig. 5 shows that four well-defined peaks fall in this range. Phenol, guaiacol and cresols elute at 8.0, 8.7 and 12.7 min, respectively, while more highly alkylated phenols are more strongly retained, e.g., 2-n-propylphenol, 30.4 min.

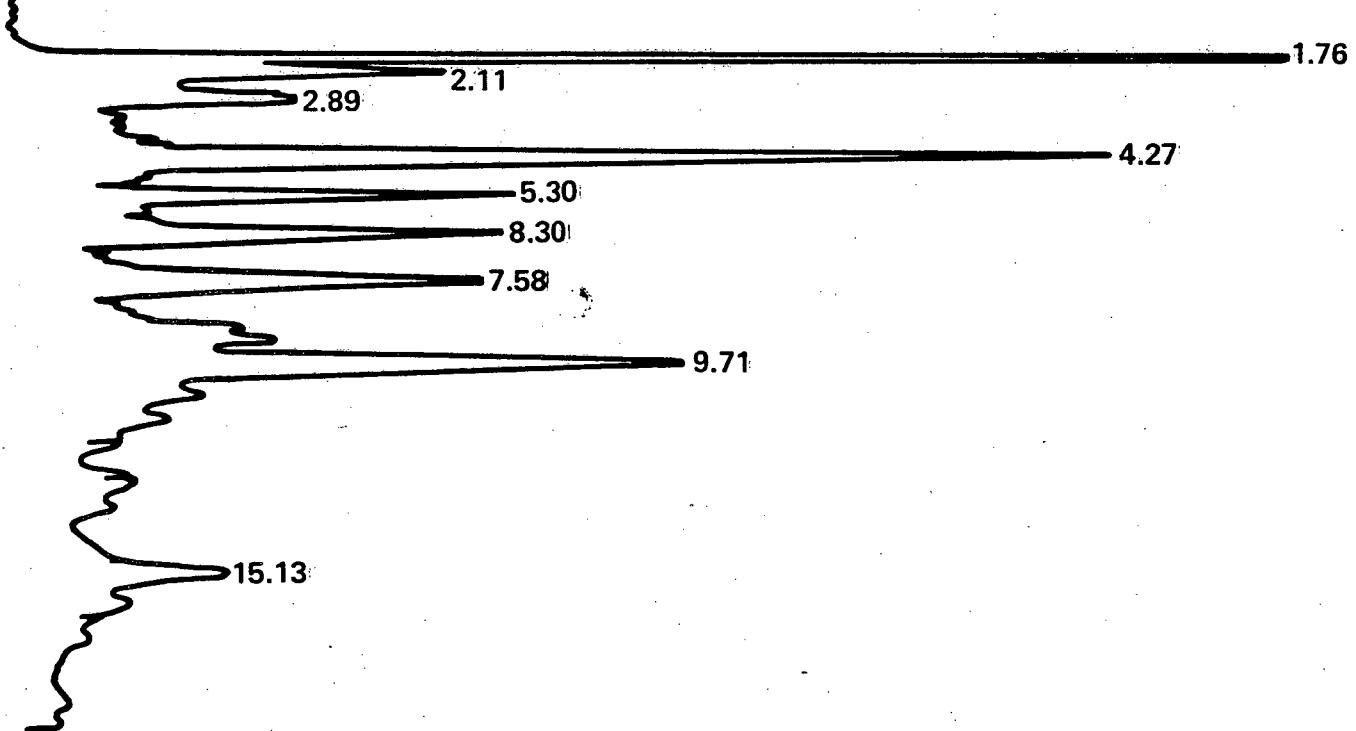
Although further work will be needed to identify specific compounds, it appears that the aromatic fraction of the aqueous effluent from the LBL process breaks down roughly as follows:

aromatic carboxylic acids	25%
dihydroxybenzene derivatives	50%
monophenols	25%.

These probably represent a 5-10 yield of product based on dry wood feed.

Recovery of Water-Soluble Products

About 25% of the biomass feed is converted to water-solubles in the LBL process. Enough is known now about the chemical nature of this fraction to make an assessment of the feasibility of recovery. Since recovery by distillation would require the evaporation of large amounts of water, the only operation with any chance of economic feasibility is solvent extraction. Unfortunately, it appears that less than half of the water solubles would be readily extractable — acetic acids, phenols and cyclic ketones. Glycolic acid is a chemical of commerce. It is used in the processing of



XBL 826-1481

Fig. 5. HPLC separation of aromatic constituents of aqueous effluent from CL-11. Column, 250 x 4.6 mm, Merck RP-8 10 μm . Mobile phase, methanol-water, linear gradient 25-45% in 20 min. Flow rate, 2.0 ml min^{-1} . Detection, UV 254 nm.

textiles, leather and metals, in electroplating, as a copper brightener, and as a general acid for pH control. However, it is not a candidate for recovery for two reasons. First, it has a much higher affinity for water than acetic acid and therefore is not amenable to extraction by ether or other low-boiling solvents. Second, it decomposes upon attempted distillation and therefore cannot be separated from a high-boiling solvent such as trioctylphosphine oxide (TOPO), which would probably be a suitably strong extractant.

Thus at this time recovery of the water-soluble product of wood liquefaction does not seem to hold much promise. Glycolic acid is formed from carbohydrate in the aqueous phase by acid-base catalysis. It is likely to be formed in large amounts even if the ratio of water to feed could be substantially reduced. If the carbohydrate fraction of biomass is to be effectively utilized in the production of liquid fuel by direct liquefaction, major process changes will have to be considered. The conclusion from this section of the report is therefore the same as from the first section: a major change is needed.

ANALYSIS OF PDU RUN TR-12 AND COMPARISON OF STOICHIOMETRY OF OIL RECYCLE AND WATER SLURRY PROCESSES.

From an operational point of view, Test Run 12 was the most successful run made at the Albany PDU. Rust Engineering has covered this in a technical report⁽⁴⁾, at the October 1981 Contractors' Meeting⁽¹²⁾ and in a paper presented in January, 1982⁽⁵⁾. The major objectives achieved included production of some 30 drums of wood oil, excellent overall material balances and demonstration of operability of key pieces of equipment, notably a gas-fired preheater-reactor. Liquefaction occurred in two reactors in series — the turbulent, direct-fired tubular preheater (reactor 1) and a low-velocity standpipe reactor improvised from a previously used scraped-wall preheater (reactor 2).

During the run, outlet temperatures of both the tubular preheater and the standpipe reactor were varied. Determination of temperature effects was not, however, a primary objective and no analysis of these

effects was made. Data given in the reports are not sufficient for such an analysis. However, Percy Thigpen of Rust Engineering has kindly given us further data (primarily elemental analyses of oil produced and analyses of effluent gas corresponding to various temperatures)⁽¹³⁾. Although the variation of operating conditions was not set up to obtain maximum information (there was no factorial design), statistical analysis does give some insight into the temperature effects.

The independent variables tested were T_1 , (outlet temperature °C of reactor 1), T_2 (outlet temperature °C of reactor 2), F_{in} (synthesis gas fed in pound mols per hundred pounds of fresh wood feed), F_{out} (dry product gas flow in mols/100 lbs wood), R_{flow} (molar ratio of outlet to inlet gas flows) and T_1^2 and T_2^2). Dependent variables included wt % C, H, and O in product oil, Mol % H_2 , CO and CO_2 in effluent gas, F_{out} , R_{flow} and the calculated variables described below.

It was quickly found that the data were not accurate enough to pick up quadratic terms, so that T_1^2 and T_2^2 could be eliminated. There was no significant dependence of anything except one of the calculated variables, on F_{in} . There was no significant dependence of R_{flow} on any variable used* so that of the three variables, F_{in} , F_{out} , and R, only F_{in} had to be kept as an independent variable. This left T_1 and T_2 as the significant variables. Separation of the effects of the two temperatures, except to show that both were of roughly equal importance, was not possible. Therefore, we also defined a composite temperature, calling it "Severity," S:

$$S = \frac{T_1 - \bar{T}_1 + T_2 - \bar{T}_2}{2} + 355^\circ C.$$

The statistical significances of the relations between the dependent variables and either S alone or T_1 and T_2 separately were virtually identical.

* Note that the feed gas was of constant composition throughout at 60.8 Mol % CO and 39.2 Mol % H_2 . R is a function of this composition.

The calculated dependent variables are estimates of the shift reaction, the CO consumed in reducing feed organics, and the CO₂ formed by pyrolytic decomposition of feed organics:

$$V_{sr} = \frac{(\text{Mols H}_2)_{\text{out}}}{100 \text{ lbs}} - \frac{(\text{Mols H}_2)_{\text{in}}}{100 \text{ lbs}} = \text{Mols shift/100 lbs wood.}$$

$$V_{CO, \text{ox}} = \frac{\text{Mols (CO + H}_2)_{\text{in}}}{100 \text{ lbs}} - \frac{\text{Mols (CO + H}_2)_{\text{out}}}{100 \text{ lbs}}$$

$$= \text{Mols CO oxidized by organics per 100 lbs wood.}$$

$$V_{CO_2, \text{PYRO}} = \frac{(\text{Mols CO}_2)_{\text{out}}}{100 \text{ lbs}} - V_{sr} - V_{CO, \text{ox}}$$

$$= \text{Mols CO}_2 \text{ formed by net pyrolytic decomposition per 100 lbs wood.}$$

We can now discuss the dependence of each of the dependent variables on T₁, T₂, S and F_{in}; the actual coefficients of dependence and the statistical parameters are given in Table 7.

Oil Elemental Analysis

% C - increases with T₁ and T₂ but is equally well-represented as a function of S. % H - barely significant increase with T₁ or with S. % O - decrease with T₁ and T₂ or with S.

Gas Molar Analysis

% H₂ - no dependence at t > 1.0

Mol % H₂ = 49.8 ± 0.5 (standard error of mean)

% CO decreases with T₁ and T₂ or S

% CO₂ increases with T₁ and T₂ or S

Gas Flows

Outlet flow is not significantly dependent on any variable except inlet flow. The ratio of outlet to inlet flows is not significantly dependent on any variable tried:

$$R_{\text{flow}} = 1.540 \pm 0.04 \text{ (standard error of mean).}$$

TABLE 7
STATISTICAL ANALYSIS OF TEST RUN 12 (PDU)

Dependent Variable	Independent Variable	Constant Term	Coefficient Ind. Var. 1	t	Coefficient Ind. Var. 2	t	Corr. Coeff.	R ²	Residual Standard error
% C, oil	T ₁ , T ₂	23.68	0.0825	10.4	0.0741	4.76	0.98	0.29	
	S	19.85	0.1598	20.6	-	-	0.98	0.27	
% H, oil	T ₁ , T ₂	6.68	0.0045	3.30	not sig.	-	0.55	0.07	
	S	6.14	0.0060	2.90	-	-	0.48	0.07	
% O, oil	T ₁ , T ₂	69.91	-0.0903	11.2	-0.0724	4.57	0.98	0.29	
	S	78.29	-0.1695	20.9	-	-	0.98	0.29	
Mol % H ₂ Out	none sig.	49.8+ .5*	-	-	-	-	-	-	
Mol % CO Out	T ₁ , T ₂	71.9	-0.1127	3.15	-0.0833	1.29	0.91	0.98	
	S	78.29	-0.2055	7.02	-	-	0.91	0.89	
Mol % CO ₂ Out	T ₁ , T ₂	-38.35	0.0738	1.99	0.1790	2.67	0.92	1.02	
	S	-32.88	0.2188	6.42	-	-	0.89	1.04	
R _{flow}	none sig.	1.54+ .04*	-	-	-	-	-	-	
V _{sr}	F _{in}	-0.221	0.444	3.38	-	-	0.70	0.14	
V _{CO, ox}	T ₁ , T ₂	0.53	not sig.	-	0.0167	3.30	0.69	0.12	
	S	-3.67	0.0118	2.70	-	-	0.59	0.13	
V _{CO₂, PYRO}	none sig.	0.66+ .03*	-	-	-	-	-	-	

1. R_(flow) = Ratio Volume Dry Gas Out/Dry Gas in

V_{sr} = Calculated Shift Reaction variable, Mols CO Shifted/100 lbs wood

V_{CO, ox} = Calculated CO oxidation variable, Mols CO oxidized/100 lbs wood

V_{CO₂, PYRO} = Calculated Pyrolysis CO₂ variable, Mols CO₂ by Pyrolysis/100 lbs wood

2. T₁ = Outlet Temp °C, Reactor 1

T₂ = Outlet Temp °C, Reactor 2

S = (T₁ + T₂) / 2 + 355°C

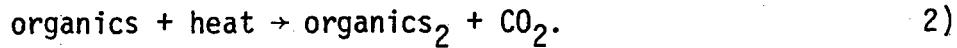
F_{in} = Dry gas feed, Mols/100 lbs wood

* Standard error of mean.

Two reactions cause R to be greater than 1.0: The shift reaction,



since H_2O is not counted as a gas, and



The constancy of R implies that both reactions are independent of T_1 and T_2 in the ranges studied. This is verified by the analysis which follows.

Calculated Variables

V_{sr} (shift reaction per 100 lbs wood). This is not significantly dependent on temperature. Inlet flow per 100 lbs wood was significantly above the average flow only during one period. During this period, as might be expected, there was more shift reaction per 100 lbs wood. I.e., the more CO we feed, the more gets shifted.

$V_{\text{CO}_2, \text{PYRO}}$. (Mols pyrolytic CO_2 per 100 lbs wood.) This variable is somewhat surprisingly independent of temperature in the range studied within the reproducibility of the data. The mean, $0.66 \pm .03$ Mols/100 lbs includes CO_2 formed from added Na_2CO_3 , about 0.04 to 0.06 mol.

$V_{\text{CO}, \text{ox}}$ (Mols CO oxidized to CO_2 by organics per 100 lbs wood.) This quantity increased with temperature. The statistics program picked T_2 as the preferred independent variable, but S works about equally well. The correlation is not as good as we would like. The sign of the slope and to a degree the magnitude of the coefficient are justified by the excellent negative correlation of the oxygen content of the liquid product with temperature (see below).

The dependence of the oil product elemental analysis on S is shown in Fig. 6 and the dependence of the outlet gas analysis is given in Fig. 7. Fig. 8 shows the dependence of the net syn gas consumption, by way of reaction 2, on temperature. In Fig. 7 it will be seen that one set of points is far out of line with the remainder. This point was eliminated from the statistical analysis. In every case the straight lines drawn are from the regression analysis.

FIG. 6. ELEMENTAL ANALYSIS OF OIL VS. SEVERITY

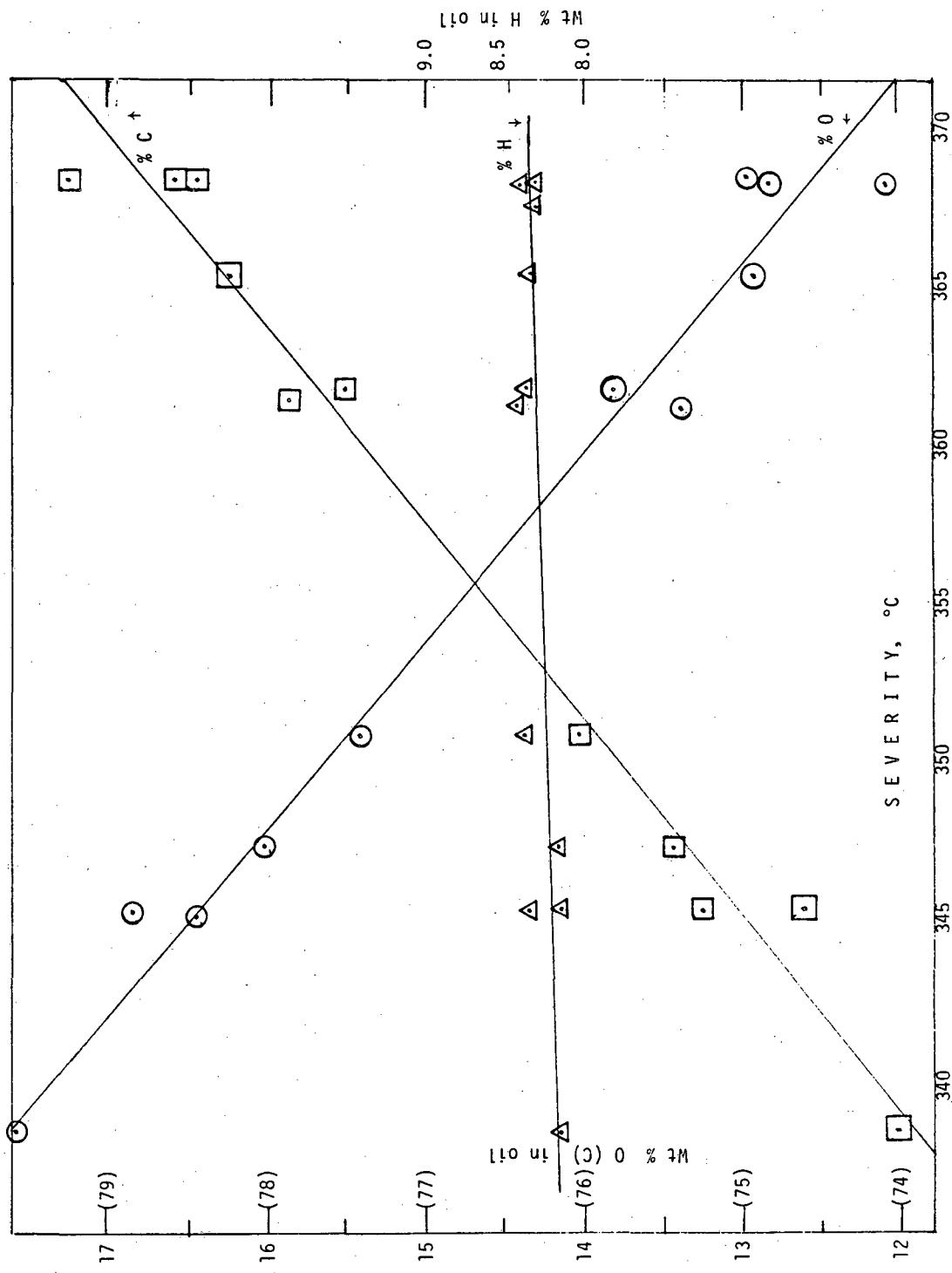


FIG. 7. MOLAR ANALYSIS OF MAKE GAS, PDU RUN TR-12

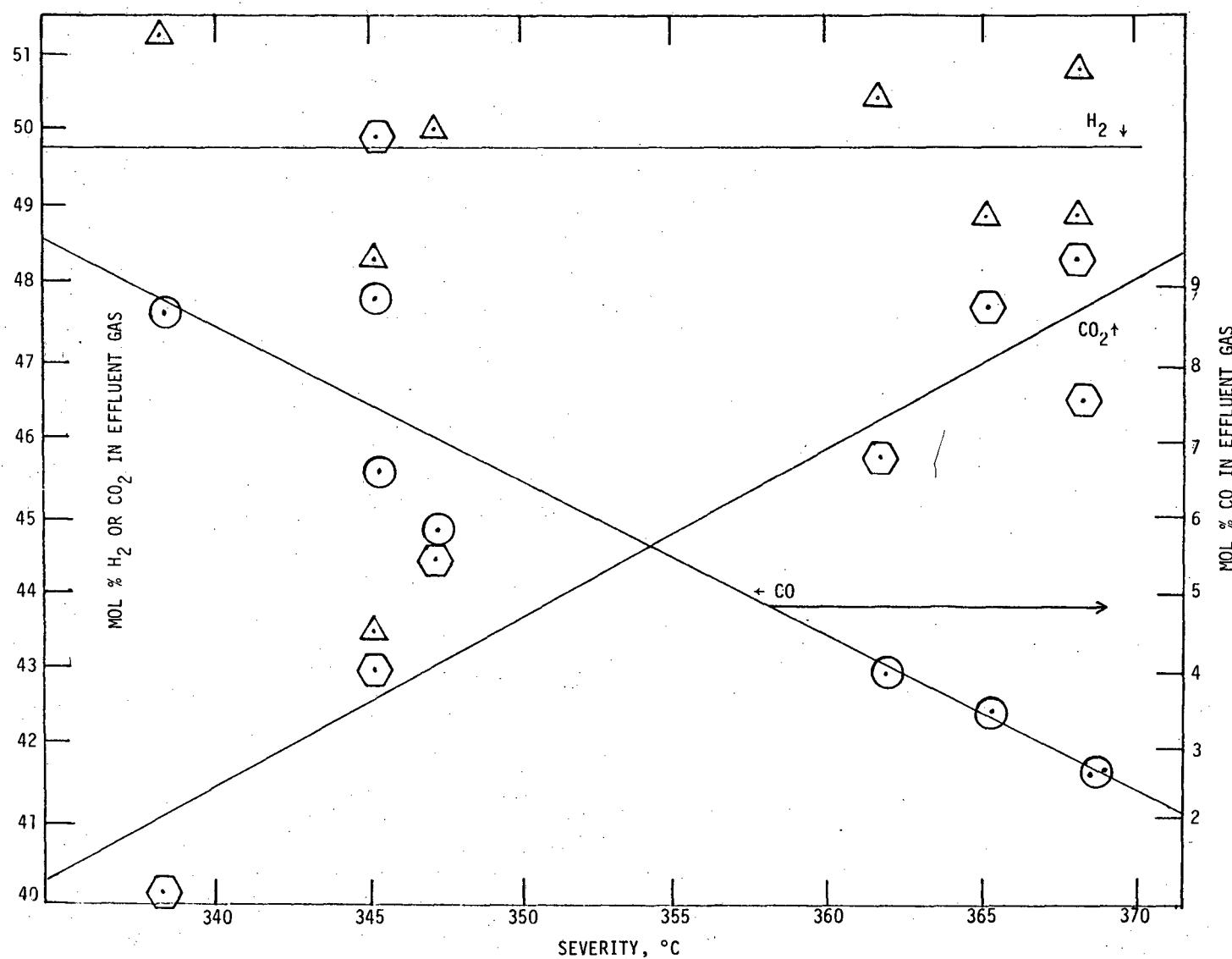
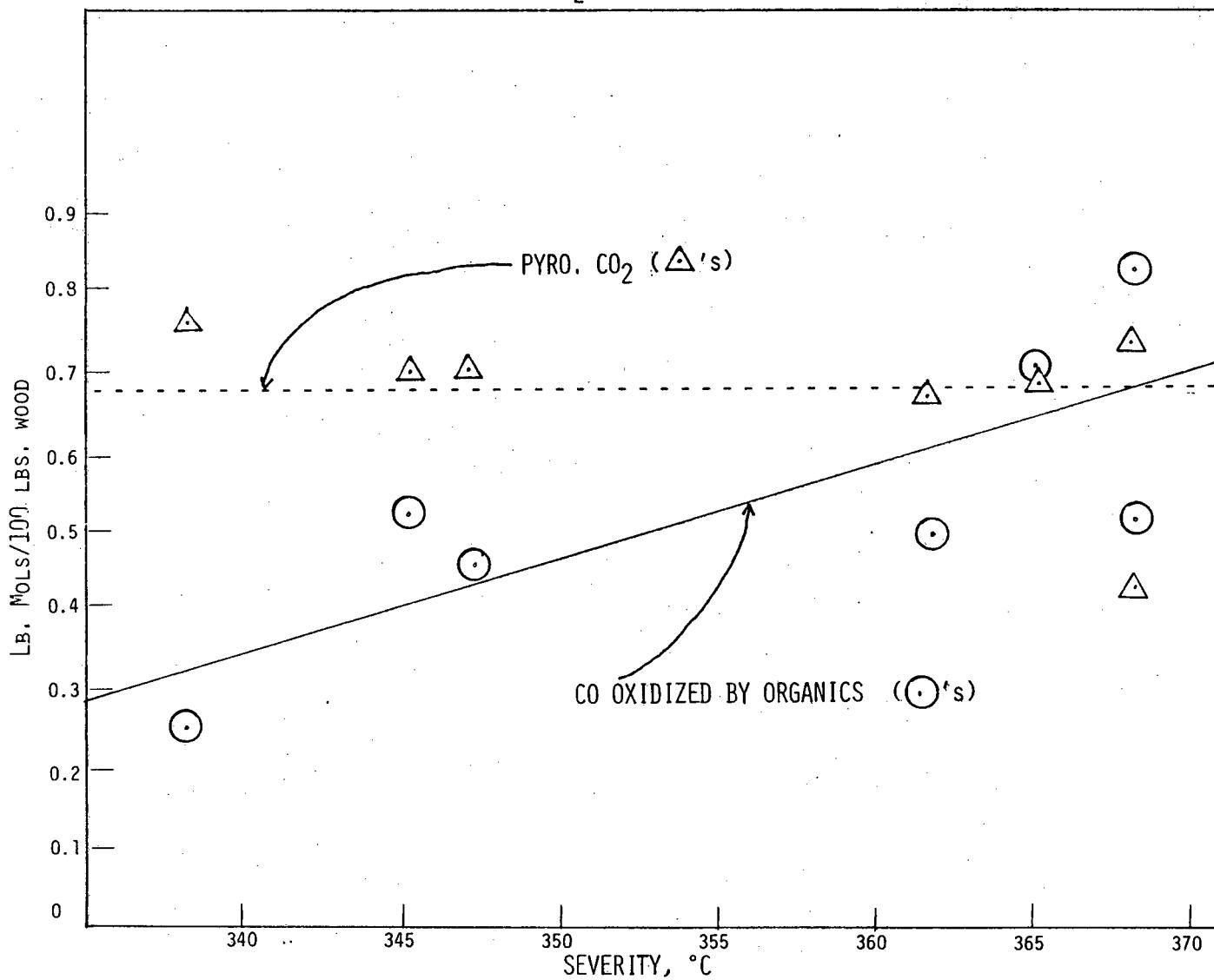


FIGURE 8, SOURCES OF CO₂ DURING LIQUEFACTION (PDU TR-12)



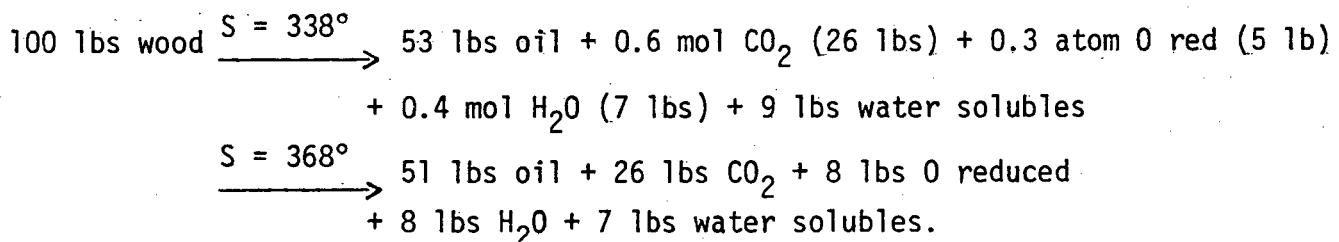
The change of elemental analysis of the oil, combined with the observations from the gas analyses and yields can be interpreted as follows. As severity increases percentage oxygen content falls by about 5 units between the minimum severity of 335° and the maximum of 368°. Carbon and hydrogen rise to keep the total at 100%. However, the rise in % H is proportionately less than that in carbon, implying that some H is eliminated as water. According to the statistical analysis % H increases over the interval by 0.18 units against a calculated 0.48 unit rise for no loss as water. 0.3 unit was lost as H_2O , corresponding to $8 \cdot 0.3 = 2.4$ units loss of O as H_2O and a residual 2.7 units of O lost by reduction.

With an average 53 wt % oil yield the change in atoms O reduced/100 lbs wood is given by

$$\frac{0.53 \cdot 2.7}{16} = 0.09 \text{ mol}/100 \text{ lbs wood.}$$

This is significantly less than the change in CO oxidized calculated from the gas data (0.35 mol/100 lbs wood increase over the same severity interval). Apparently CO reacts with water-soluble organics as well as with oil components. In the process some of the water-solubles may well be converted to oil solubles.

The above can be summed up briefly as follows:



The CO_2 by pyrolysis has been adjusted down to allow for the CO_2 formed from added sodium carbonate, and a 100% weight balance has been forced on the other products.

Comparison with CLU-Runs

The most striking similarity between the PDU oil-recycle runs and the CLU water-slurry runs is in the estimate of pyrolytic CO_2 formed. Within experimental and calculational uncertainties, both estimates are the same

at 0.6 mol/100 lbs of wood. The water gas shift reaction is catalyzed in both systems, but the precise amount of CO shifted is a function of the individual systems. CO appears to function quite definitely as a reducing agent in the oil recycle runs. This function is absent or minor in the CLU runs⁽¹⁰⁾. The suggestion we make above, that part of the action of CO is on the water-solubles may help explain this observation. Current estimates of the amount of water-soluble organics formed in the recycle (PDU) and single-pass (CLU) cases are 8 and 25 wt % respectively. Reaction of recycled water-solubles with CO, with formation of compounds containing less oxygen (and less water-soluble), could be a mechanism accounting for this difference in yields.

The severity scale was defined to give numbers in the range of actual CLU operating temperatures and PDU T_1 temperatures. The change in product oil oxygen content per degree change in PDU severity is roughly three times the change in CLU oil product oxygen per degree change in reactor temperature. This reflects the longer effective reaction times in the recycle process.

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