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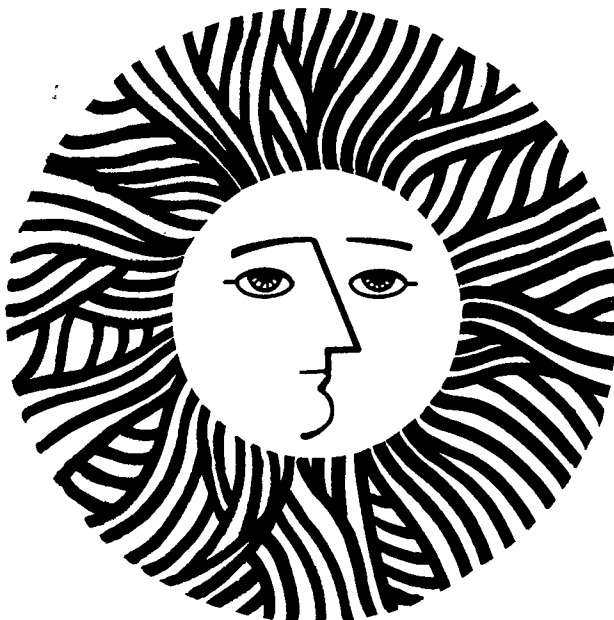
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RESEARCH AND DEVELOPMENT ACTIVITIES
ON DIRECT LIQUEFACTION TECHNOLOGY

QUARTERLY REPORT
January-March, 1982

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A. INTRODUCTION AND SUMMARY

During the second quarter we continued to operate the continuous liquefaction unit. The major emphasis was on problems of coking and of reduced oil yield during the early parts of individual runs. Only after at least 8 hours of initial running are oil yields in the range expected (about 35-40% by weight) obtained. The most important factor is shown to be hang-up on the walls of our receivers.

The previously developed methods of product characterization: HPSEC (size exclusion), HPIEC (ion-exchange), SESC (sequential solvent elution) and GCMS have been improved and applied to current CLU samples. Significant differences among samples prepared under different conditions such as a reduction of molecular weight on raising reactor temperature are reported.

The ten-gallon autoclave is being used to produce new wood slurry. By following the previously developed recipe, prehydrolysis at 180°C for 45 minutes in water containing 0.075 wt % sulfuric acid, we obtain highly friable wood chips from which excess water can be drained. The wet chips are converted to the usual slurry in a laboratory-scale Waring blender followed by homogenization in a colloid mill. Initial batches were made with 25% wood (dry basis) 75% water, but considerable water can be drained from the prehydrolyzed chips. First slurries made can be pumped readily with a Moyno pump. However, they contain some gritty particles and fibers and probably need to be improved before feeding through the small check valves of the CLU.

A test pumping loop is being set up to check pumpability of slurries before use in the CLU and to determine viscosities over a range of temperatures.

Alternative feedstocks are being screened for inclusion in the CLU program. Of those tested, sugar beet pulp and rye grass are probably suitable substrates. Since aspen, as a member of the fast-growing *Populus* genus, is of particular interest, we have obtained a supply from Minnesota.

Equipment for trickle-bed hydrogenation of oils has been designed and is being installed. This is necessary for continuous flow study of solvolysis by recycle wood oil. The equipment can be also used to test continuous hydrogenation of product oils.

B. OPERATION OF THE CONTINUOUS LIQUEFACTION UNIT (CLU)

Run Summary

The most recent CLU runs were aimed at finding the causes of coking in the reactor itself and the reasons why very little product oil is recovered during the first few hours of a run. For this purpose we made three runs of relatively short duration, CLU-15, -16 and -17. The causes of low initial recovery, and the consequence on yield calculations, became clear--especially from the results of the planned 3.5 hour run CLU-17. Runs CLU-15 and -16 showed that there can be very high coke build-up in the early stages of a run and that the type of stirring used can strongly influence the amount of coke formation.

In run CLU-16, more than half the reactor was filled--apparently early in the run--with coke, but this did not disrupt the operation. We infer that we may be better off with less reactor volume, especially less potentially dead space where oil poorly mixed with the aqueous phase can collect and coke. We have therefore made a steel removable insert for the reactor. This will roughly halve the liquid retention time. At the same time average local turbulence in the reactor should be much increased.

Comments on specific runs follow:

CLU-15. This was a planned short run with hydrogen as reducing gas. The feed rate of hydrogen was cut in half compared to the longer runs CLU-12 and -13. The chief effect was on run length. The feed sparge tube plugged off after only six hours of operation. This is considered to be an operational problem--a minimum flow through the sparger is needed to keep it clear--rather than an effect of hydrogen partial pressure. Much of the bottom of the reactor was already filled with coke in this short period.

CLU-16. In this 16-hour (planned) run, we used three downward flow impellers on the magdrive shaft. This gave us the worst coking situation observed to date. The entire lower half portion of the reactor was filled with coke and the total coke volume was at least half the initial effective liquid space. Yet liquefaction continued reasonably smoothly. Clearly, the kind of agitation used influences the amount and type of coking. This run induced us to plan future runs with reduced reactor retention time, since the bottom part of the reactor seemed to contribute little to either heat transfer or reaction.

CLU-17. This was a very short (3.5 hour) run conducted to observe the distribution of oil and coke during the very early part of a run. This run was particularly useful in helping us determine the reasons for very low product oil recoveries in the early hours of each run. The observations are written up in connection with the discussion of yields below. The heavy wood-oil product coats the walls of our large collection vessels (initially clean) and can be recovered from them only by patient and lengthy heating of the walls. Other product is held up in other portions of the reaction system. If great care is taken to recover oil for the collection vessel in identical fashion at each sampling a steady-state can be achieved. This will take about three hours of initial collection time into each of our two collection vessels. The previously unheated top flanges of the collection vessels will be heated in the future to reduce the build-up of oil near the top of the vessels.

Effect of Duration of Run on Yield Calculation

One of the more difficult operating problems to understand and cope with has been the lengthy initial period of very low yield. If we look at the data of runs 11 to 13, we see the following (Table I).

TABLE I

<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)	

Oil recoveries in Period 1 are invariably very low. Oil recovery in CL-12 period 2 was only somewhat low, but other than this all period 2 recoveries have also been very low. Period 3 and 4 recoveries have varied from very low (CL-13-4) to moderate to in one case (CL-11-4) impossibly high. Period 5 is less variable (moderate to high) and period 6 and 7 recoveries have been high. Run 10 was of short duration (11 hours) with an overall yield of 28%. All oil was collected and weighed together so that it cannot be attributed to specific periods. If, based on Table I, we guess that the recovery in periods 1 and 2 would have been 7 g/100g wood organics, we calculate about 40 g/100 g for periods 3 and 4.

There are several possible causes for the delayed recovery and the scatter, and perhaps all are involved in varying degrees. (1) There is a hold-up of our heavy viscous product on the walls of the initially clean receiver vessels and, to some degree, on the walls of tubing; (2) oil and aqueous phases present a difficult mixing problem, and the deviations from good mixing in the reactor cause the oil to have a longer than average residence time;

(3) coking is, therefore, more rapid in the early part of a run until reduction in volume of the reactor by coke reduces the overall retention time in the reactor; and (4) temporary blockage of the outlet valves of the recovery vessels by the product can cause part of the product to be retained and appear in the next recovery. An equivalent result would be obtained if a large amount of cool product were retained in some portion of the receiver, then fell off and was recovered during a later period. Item (4) must account for the two very high recoveries marked with exclamation points, CL-11-4 and CL-13-6. These both follow periods, CL-11-2 and CL-13-4, of very low recovery.

The results of the planned 3.5 hour run, CL-17, show the operation of item 1. Only one collection period was used. Despite care to allow the product to drip from the receiver at the end of the run, the apparent yield was low (~ 12%). On the next working day, after reheating and another lengthy wait, an additional 10% yield was recovered from the receiver. Further small amounts were found in lines and a knock-out pot. Of about 300 g predicted to have made during the short run, about 280 g could be accounted for as recovery from the receiving vessel, oil in lines and knock-out pot or coke and oil remaining in the reactor.

The general conclusion is that between about 800 and 1200 g of wood organics must be fed before a steady state of operation is reached. This corresponds to 300 to 450 g oil. Even this amount will not be sufficient unless the receivers are uniformly warmed to prevent very large build-ups of cooled oil, which may be released later to confuse the yield pattern. At our present slurry concentrations and feed rates we should run two preliminary "unsteady-state" periods, one into each receiver, of three hours each. Our balances and yield calculations should be based on the sample periods that follow, either taken separately or combined.

Except where we have made calculations ignoring the early hours of running, our previously reported yields are systematically low. We can estimate the overall yields by subtracting from the total wood organics fed the amount estimated above (800 g) as needed before steady-state recovery can be maintained. This gives for the oil yields in the series CL-10 through CL-13:

CL-10	39%
CL-11	41%
CL-12	32%
CL-13	38%
	<hr/>
Average	37.5%

Yield of Water Dissolved Organics

The high yield of water-soluble organics in the aqueous effluent is a serious problem of the LBL liquefaction process. The low concentration of these organics in the effluent water makes recovery or disposal difficult. Simple recycle of the aqueous phase through prehydrolysis and liquefaction is impractical because of the need to acidify for hydrolysis and reneutralize for liquefaction. We have therefore spent some time trying to think of possible water cycles which might be effective. The most obvious to try is simple displacement of the hydrolysate water by reactor effluent water in a plug-flow cylinder--a sort of large scale chromatographic column. A quick experiment showed, however, that diffusion of hydrolysate from the interior of the hydrolyzed wood chips is too slow for this displacement to be effective. Also the irregularly shaped chips pack poorly, leaving large open channels through which the displacement solution flows preferentially.

An alternate possibility involves a simple press, such as is used in dewatering many types of slurry. If prehydrolyzed chips can be pressed to 60 vol % aqueous (compare wet-carbonized peats, which can be pressed to less than 40% water), a reasonable cycle can be set up. One possibility with approximate flow of water and with solubles, is shown in the block diagram (Fig. 1).

The scheme proposed doesn't change the overall yield of water-solubles much (from 25 to 23% in this estimate). But it puts the water-dissolved organics out at about three times the concentration found without recycle. This makes recovery or disposal more economical. The sodium carbonate requirement should also be reduced by about 30%. The process, or an improved one, has possibilities. We have therefore suggested it to a mechanical engineering graduate student. He expects to build his M.S. thesis experimental work around slurry preparation and properties in general and possibilities for aqueous recycles in particular.

C. OTHER ENGINEERING LABORATORY ACTIVITIES

1. Prehydrolysis, with 10-gallon autoclave.

Shake-down tests of the autoclave began in mid-February. Currently we can operate consistently at 25% wood, dry basis, but the quality of the slurry product needs to be improved a little. Experiments with draining excess water and break-up of the friable prehydrolyzed chips indicate that concentrations of over 30% can be achieved, and we will attempt in the spring quarter to determine the upper limits.

2. Trickle-bed Hydrogenation Reactor.

A continuous hydrogenation unit has been designed and is currently under fabrication (cf fig. 2). Installation should be completed by June 1, 1982.

FIG. 1 DOUBLE RECYCLE SCHEME, FLOWS OF H₂O AND WATER SOLUBLES

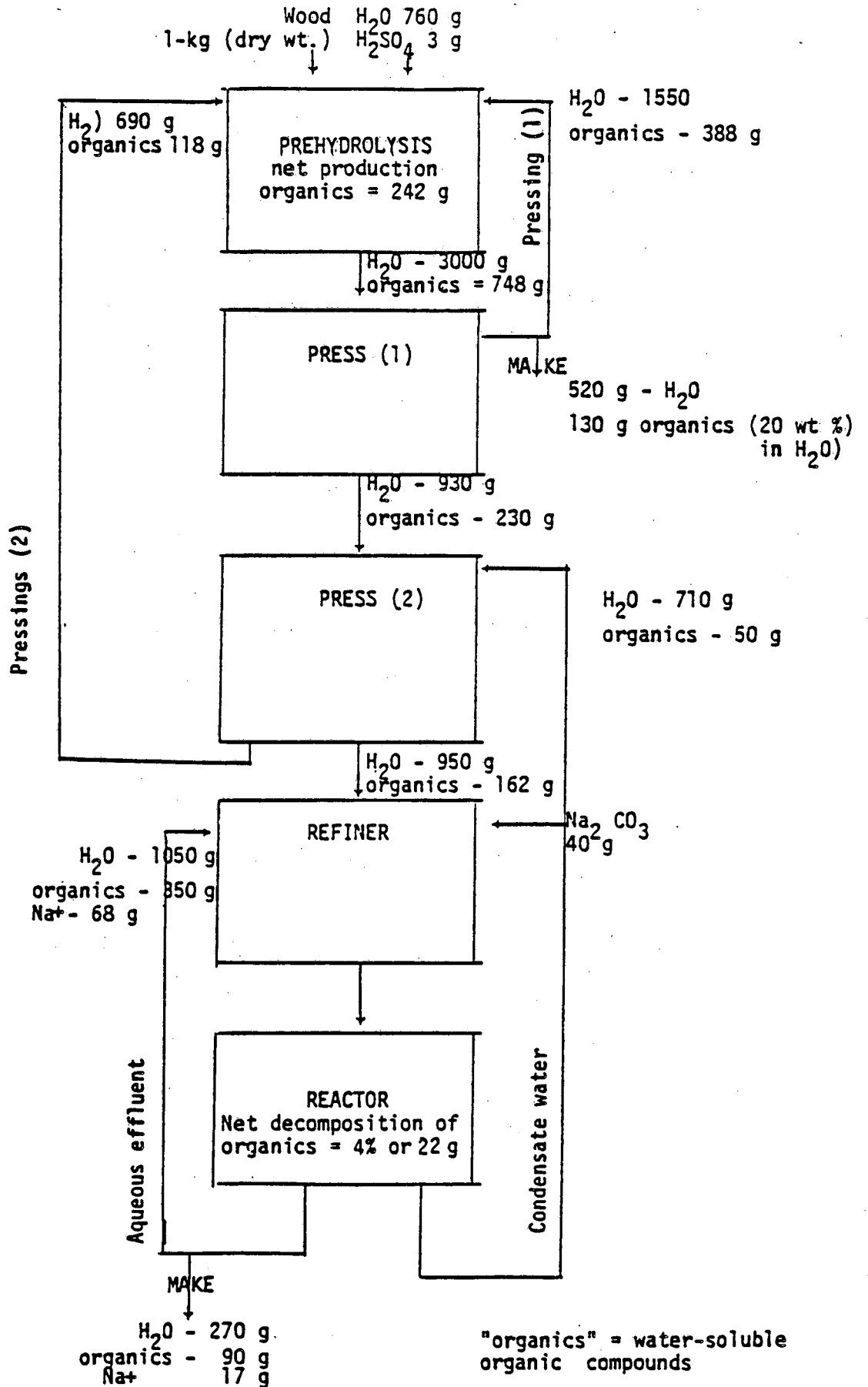
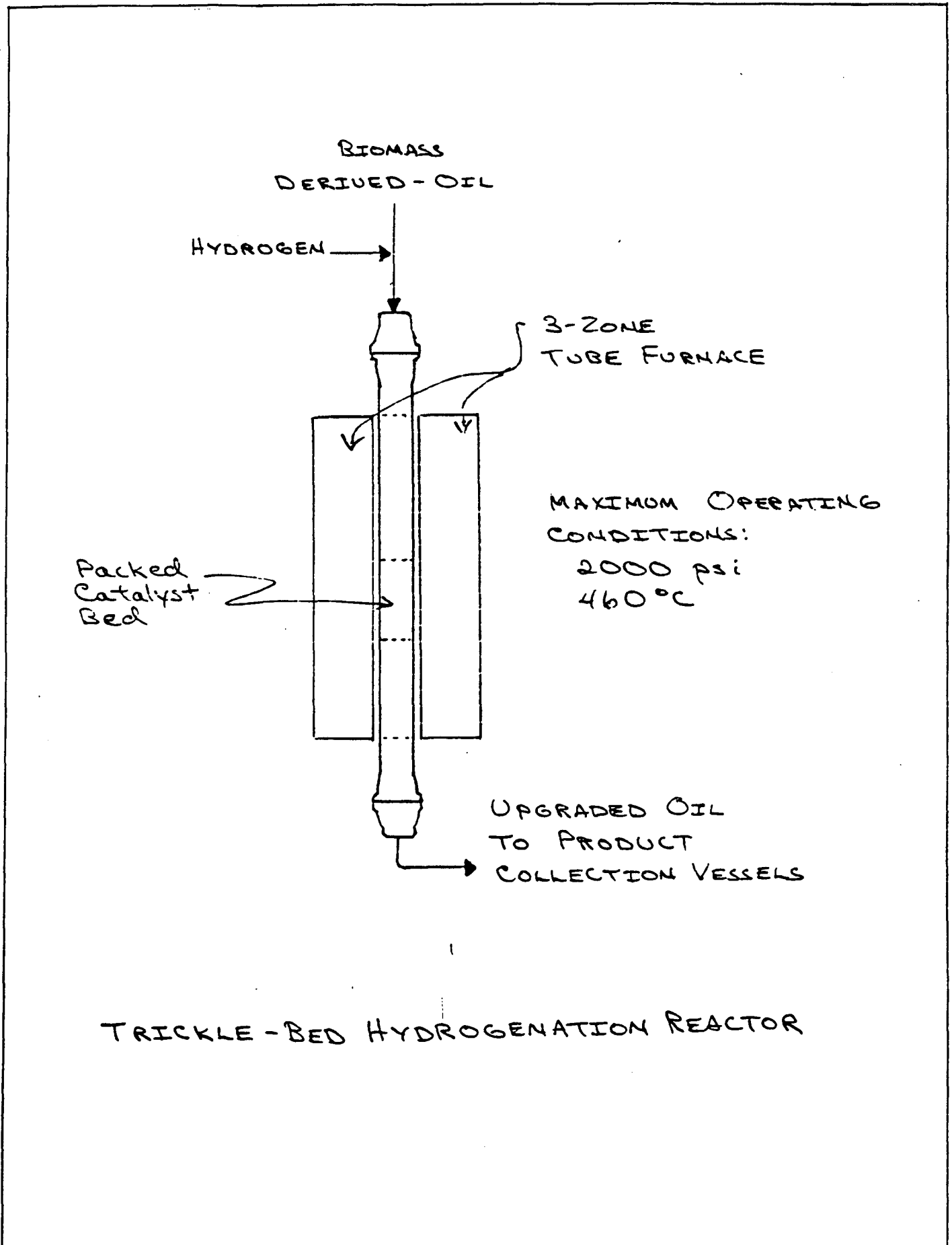


FIG. 2



The ability to hydrogenate biomass oils of various kinds is essential-if we are to develop a new process based on solvolysis as an initial step. The unit will also be available for secondary hydrogenation on a continuous basis of primary biomass oils to further reduce oxygen content. While scouting experiments can be done by way of batch tests in autoclaves or rocker bombs, the continuous unit is essential for any realistic follow-up. Catalysts to be tried include typical commercial hydrocracking catalysts used in beneficiation of petroleum residues, coal liquefaction products and shale oil, and other hydrogenation catalysts.

3. Pump-loop Apparatus

A gear-pump loop will be completed during April. This will be used for viscosity measurements of water-based and oil-based fluids over a range of temperatures. It will be available for checking out slurries made from our prehydrolyzed wood before using them in the CLU. Eventually the gear pump will become the primary low pressure feed pump for the CLU giving it further capabilities for handling oils or solvents.

4. Alternative Sources of Biomass

As part of a Master's thesis program Ray Gansley (with Prof. Ted Vermeulen) has been checking out an assortment of biomass forms for their liquefaction potential. As we are using batch autoclaves, the results are not highly quantitative and any conclusions reached require confirmation in a continuous unit. Based on their conversion to product other than insoluble residues and or the appearance of slurry made after prehydrolysis we rank the feeds used to date as follows (Table II).

TABLE II

FEED	ASH CONTENT	PREHYDROLYSIS	LIQUEFACTION
Sugar beet pulp	3.1	Successful	A
Rye grass	4.1	Incomplete	A
Rice straw	17.7	Incomplete	B
Jerusalem artichoke	-	Successful	In progress
Eco-II fuel *	22.5	Successful	B
North Carolina peat **	0.5	Not needed	B

* This is not biomass, but a processed municipal waste, containing cellulose, mineral matter, etc. ** Peat is, of course, not biomass, but fossil material from bog-land. It is in general less reactive than biomass.

Sugar beet pulp and rye grass were tried because we felt that they are characteristic types of agricultural wastes. The "A" in liquefaction indicates that they can be handled, within the rather broad limits of our tests, like Douglas fir wood. Rice straw can be converted to oil, but the insolubles yields are high--no doubt related to the high ash content. This is probably not the way to use rice straw. The high ash content of ECO-II fuel, plus perhaps a content of unreactive materials, results in a high insolubles yield. The peat sample did not process well in this screening. However, our previous work has shown that necessary conditions for its liquefaction are significantly different from those for biomass.

We are most interested in testing woods of the poplar (*Populus*) genus, since fast-growing hybrid poplars are prime candidates for energy plantations. We have received a quantity of aspen (*Populus Tremuloides*) from Minnesota and plan to test slurries of it in both batch screening and the CLU.

D. CHARACTERIZATION OF PRODUCTS OF LIQUEFACTION

Determination of Carboxylic Acids in Process Waters by HPIEC

The LBL and PERC process both seem capable of producing a 55-60% yield of condensed-phase organics from Douglas fir wood. In the LBL process, however, almost two-fifths of this product emerges in the form of an aqueous solution. Typically a 30% yield of wood oil is accompanied by a 25% yield of water-soluble organics at a concentration of 5.5% by weight in water.

We have shown that roughly half of these water solubles are carboxylic acids (or their sodium salts, depending upon the pH). Acetic acid was previously identified and quantified by gas chromatography. We have also identified about 30 minor acid components by GC-MS. We have now turned to reverse-phase HPLC and HPIEC to determine formic and glycolic (hydroxyacetic) acids.

Fig. 3 shows a chromatogram of aqueous effluent from run CL-12. All other process waters display comparable HPLC traces. It was established that no aromatics, e.g., phenol, guaiacol, are eluted within the 25-min time frame of Fig 3. Of some 15 acid standards that were chromatographed under the same conditions, only three -- acetic, formic and glycolic acids -- had retention times corresponding to peaks of Fig 3. Moreover the retention times of formic and glycolic acids were identical.

Formic and glycolic acids were resolved by high-performance ion exchange chromatography (HPIEC). A Wescan anion exchange column was used with an eluent of 0.001 M phthalate buffer at pH 3.0. Interpretation of chromatograms was simplified through the use of a Wescan Model 213 conductivity detector which selectively monitors ionic species.

The ion chromatograms of 1 μ l samples of prehydrolyzed wood slurry water and CL-12-3 process water are shown in Figs. 4 and 5. Glycolic acid is cleanly separated from formic and acetic. Levulinic acid appears between acetic and glycolic as a minor component of slurry water.

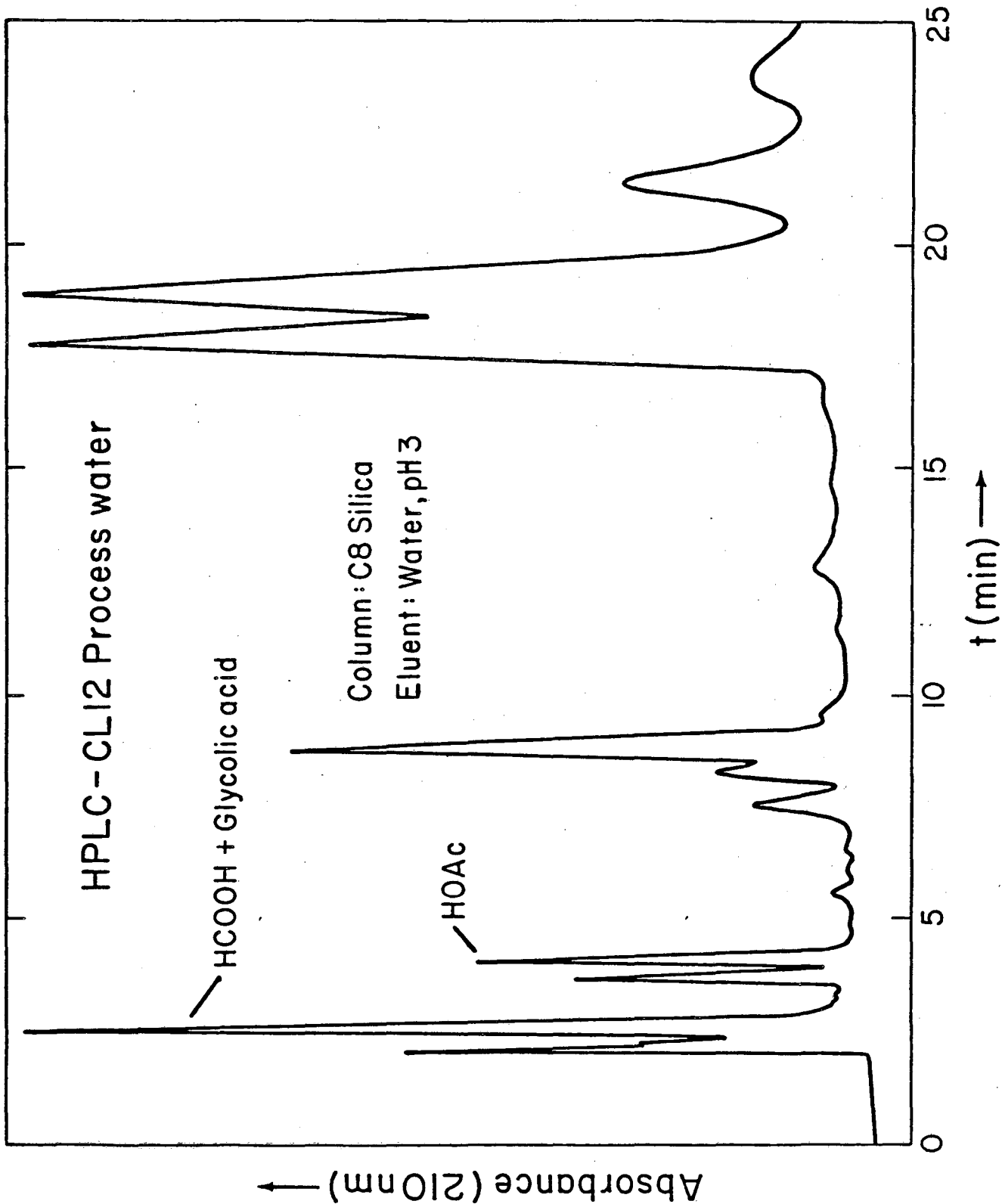


Fig. 3. Reverse phase HPLC chromatogram of aqueous effluent from run CL-12. The flow rate was 1.6 ml min⁻¹.

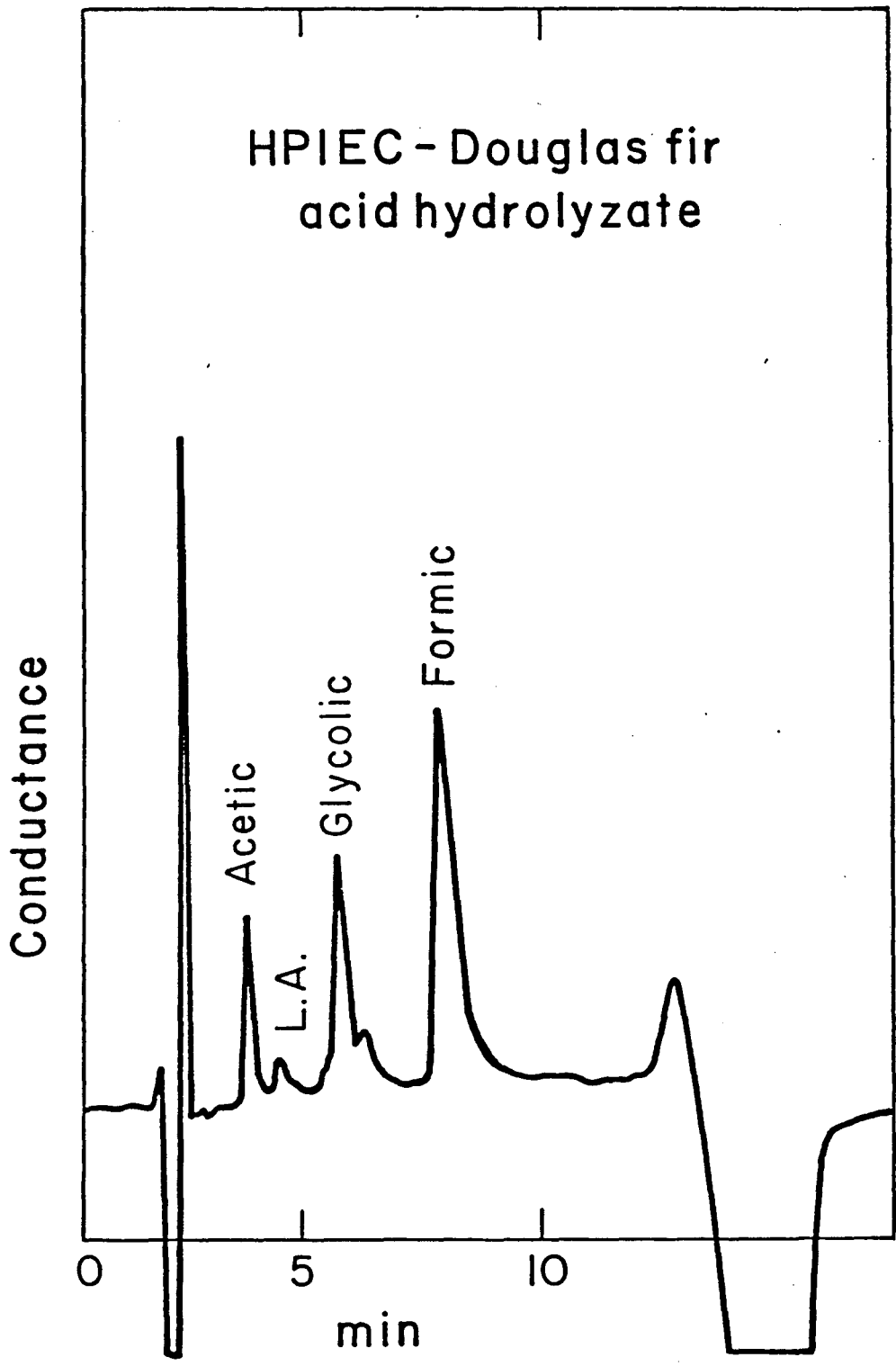


Fig. 4. High performance anion exchange chromatogram of water from slurry feed. The flow rate of 0.001M phthalate buffer (pH 3) was 2.0 ml min⁻¹.

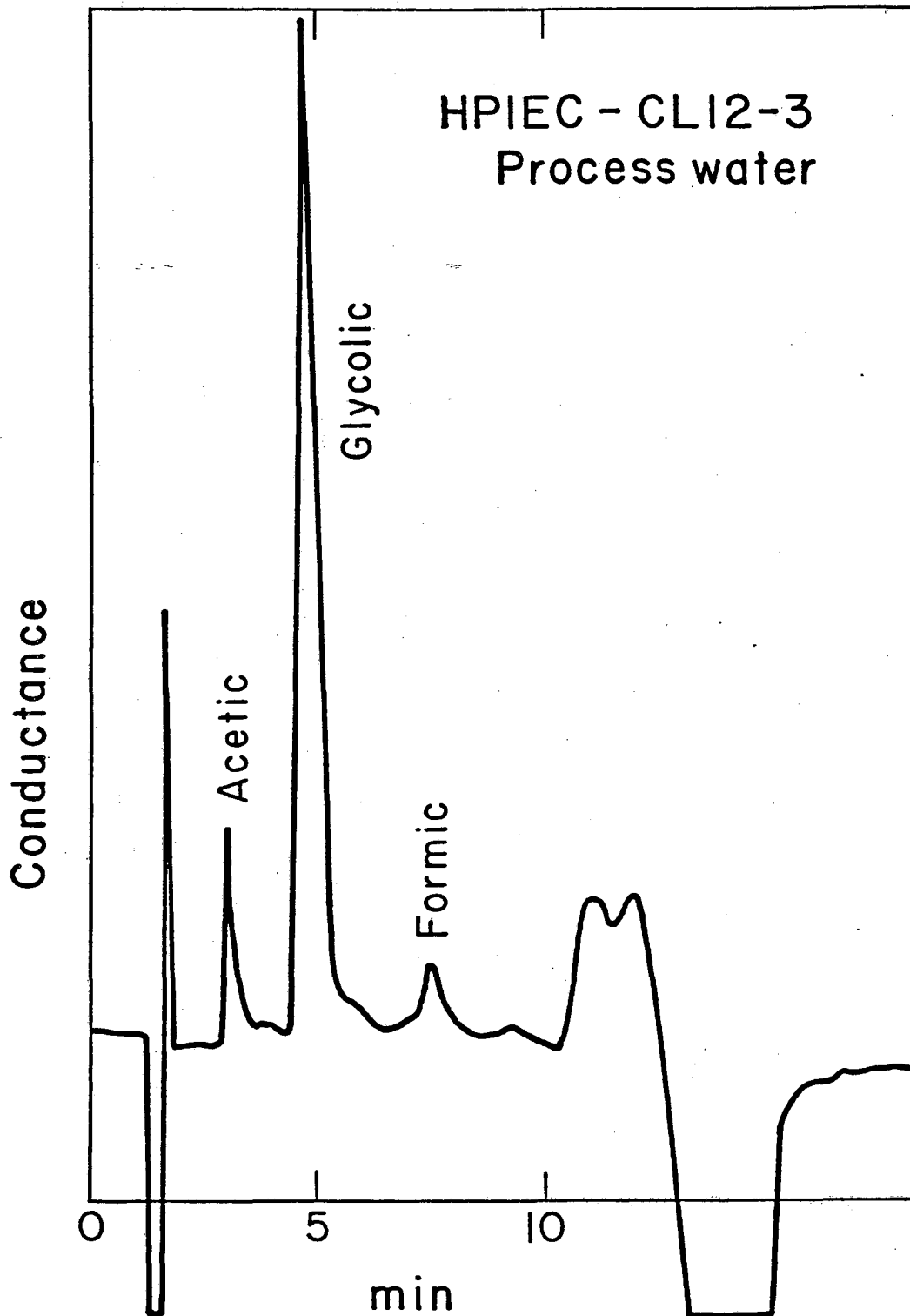


Fig. 5. High performance anion exchange chromatogram of aqueous effluent from run CL-12. The conditions and sample size were identical to those of Fig 3A.

A great deal of chemistry is exemplified in Fig 4. Liquefaction conditions with hydrogen as reducing gas, as in CL-12, result in the decomposition of levulinic and formic acids and the formation of acetic and glycolic acids. In the presence of carbon monoxide, the concentration of formic acid invariably increases due to the reaction between CO and hydroxide ion or water. Reference to Table III shows that glycolic acid undergoes a very large increase upon liquefaction. This increase occurs when either CO or H₂ is used. We have shown that the liquefaction of glucose and cellulose in batch autoclaves produces comparable amounts of glycolic acid.

The three acids account for approximately 90% of the acid content and about 30% of the total carbon of the aqueous effluent. Both Battelle PNL and LBL have shown that the remaining organics consist largely of cyclic ketones and monophenols. The possibility that these water-solubles represent intermediates in the process of oil formation has been quashed by batch experiments in which process water was resubjected to liquefaction conditions. Separation of an oil phase did not occur.

Glycolic acid has now been established as the single most abundant product of the LBL process, being formed in about 9% yield on a dry wood basis. PERC process water also contains glycolic acid, but it is much more concentrated. A sample of TR-12 water analyzed for 9.7% glycolic acid, 10.9% acetic acid and 2.7% formic acid. Glycolic acid is a non-volatile, comparatively inexpensive commercial product so the possibility of economic recovery is remote. If the mechanism of its formation were understood, it might be possible to suppress its formation in favor of more desirable products.

Molecular Weight Distributions of Wood Oils

Molecular weight distributions for CL 7-12 oils have been determined by high performance size exclusion chromatography (HPSEC) as previously described. The accuracy of the values shown in Table IV depends on several factors including the appropriateness of the standards used to generate the calibration curve and is probably no better than ± 30 amu's. However, the precision of these computer-generated numbers is extremely high. Thus the decrease in both number-average and weight-average molecular weights which occurs with a 20°C temperature increase as in runs 11 A/B and 12 A/B is undoubtedly significant. Therefore, we can say with some assurance that higher temperatures lead to lower molecular weight product. The similarity between the molecular weights of CL-11B and CL-12B oils further confirms our conclusion that, under the particular conditions of time, temperature, etc., in the LBL CLU, no significant differences due to the nature of the reducing gas, CO or H₂, can be observed.

SESC Fractionation

We have also reduced the time to carry out our version of the SESC sequential elution procedure, while at the same time increasing the reproducibility. Details will be reported later.

GC-GCMS

We have analyzed the recent CLU oil products with the GC program developed in our GC-MS studies. There are effects of process conditions. The general conclusion, however, is that the type separations -- SESC, various kinds of HPLC and extraction techniques -- are more useful for characterizing crude products. GC-MS is limited to identifying key components in the volatile product fractions.

TABLE III

EFFECT OF REACTION CONDITIONS ON CONCENTRATIONS
OF CARBOXYLIC ACIDS IN PROCESS WATERS FROM DIRECT
LIQUEFACTION OF DOUGLAS FIR

	<u>Glycolic</u> ^a	<u>Acetic</u> ^a	<u>Formic</u> ^a	<u>Levulinic</u> ^a	<u>Total</u> ^b
Slurry Water (180°, 45 min, pH 2)	<u>.04N</u>	<u>.10N</u>	<u>.11N</u>	<u>.02N</u>	<u>.26N</u>
CL11-4 (340°, 20 min, CO gas)	.25	.16	.05	tr	.50
CL11-5 (360°, 20 min, CO gas)	.21	.17	.04	tr	.45
CL12-3 (340°, 20 min, H ₂ gas)	.22	.12	.01	tr	.40
CL12-6 (360°, 20 min, H ₂ gas)	.18	.16	.01	tr	.37

^a Determined by HPIEC, ^b Measured by acid-titration.

TABLE IV

MOLECULAR WEIGHTS OF CLU OILS BY HPSEC

<u>Oil</u>	<u>Temp</u>	<u>\bar{M}_n^a</u>	<u>\bar{M}_w^b</u>
7	350	251	325
8	350	282	364
9	350	277	350
10	350	272	344
11A	340	323	400
11B	360	254	336
12A	340	271	349
12B	360	256	336

a Number-average mol. wt.

b Weight-average mol. wt.

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