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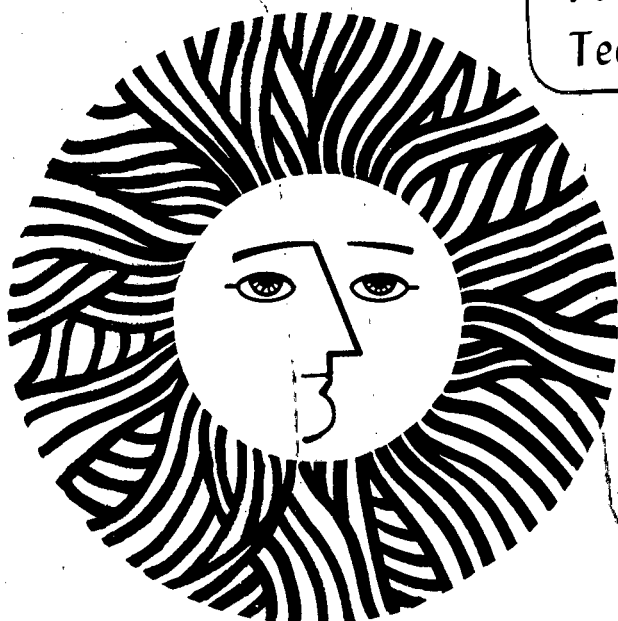
PROGRESS IN THE CHARACTERIZATION OF THE PRODUCTS
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Larry L. Schaleger and Hubert G. Davis

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"PROGRESS IN THE CHARACTERIZATION OF THE PRODUCTS
OF DIRECT LIQUEFACTION OF DOUGLAS FIR"

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ABSTRACT

Oils or tars produced by direct liquefaction of slurries of partially hydrolyzed Douglas fir in water have been quantitatively separated into nine distinct fractions by column chromatography using a modified SESC (sequential elution by solvents-chromatography) procedure. Molecular weight distributions of individual fractions and of whole oils have been obtained by high performance size exclusion chromatography (HPSEC). The predominant functional groups of each fraction have been identified by infrared spectroscopy. This information provides sensible chemical profiles of oil quality. Such profiles have been obtained for the organic products of some ten runs of LBL's continuous bench-scale liquefaction unit as well as for several oils produced at DOE's PDU at Albany, Oregon. Comparison among the various wood oils reveals differences not previously recognized. The significance of these observations will be discussed.

Aqueous effluent co-produced with wood-derived oil in the LBL process has also been examined. Reverse-phase and ion-exchange high performance liquid chromatography (HPLC) have been used to separate, identify and quantitate the major water-solubles--formic, acetic and glycolic acids.

Presented at the workshop/review meeting of the National Research Council, Saskatoon, Saskatchewan, February 16 and 17, 1982.

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

A continuous bench-scale liquefaction unit (CLU) has been operational at Lawrence Berkeley Laboratory (LBL) since early 1981. Some 14 runs have been conducted with slurries of prehydrolyzed Douglas fir in water as feed-stock. Carbon monoxide and/or hydrogen are used to provide reducing atmospheres at temperatures of 330-360°C and pressures of 3000-3400 psig. The products include a stream of off-gases, a black, semi-solid tar usually referred to as wood oil and an aqueous effluent approximately 5% by weight in water-soluble organics.

An aim of our program is to develop a better understanding of the relationships between operating parameters and product outcomes. While some progress has been made, biomass reactants and products are such complex chemical systems that attempts to develop correlations between reaction conditions and yields of product have not met with much success. This is partly because "wood oil" remains an ill-defined and highly variable material. Thus a focus of our analytical effort has been simply to develop a more precise chemical definition of the product. This paper describes recent progress we have made in characterizing wood-derived oils and water-soluble materials derived from Douglas fir by direct liquefaction.

Classification of Wood Oils by SESC Fractionation

Solvent extraction techniques have often been used to characterize synfuels, including those derived from biomass. The "oil" fraction of coal-derived fluids is typically defined, for example, as that portion which can be extracted into pentane. If this definition were applied to biomass liquefaction products, we would find virtually no "oil" in "wood oil." Thus wood oil is usually defined as the benzene, chloroform or acetone-soluble product. Unfortunately such solubility classifications tend to obliterate distinctions among chemical groups. For this reason we have turned to alternative ways to evaluate product composition and quality. An adaptation of a method based on column chromatography developed at Mobil Research⁽¹⁾ for the characterization of coal liquefaction products has proved most advantageous.

The method, called Sequential Elution by Solvents Chromatography (SESC), uses the series of solvents shown in Table 1 to elute nine distinct fractions from silica gel. In our adaptation of the method, fractions 1 and 2 are eluted together with 15% benzene-hexane, and pyridine is replaced by acetic acid.

Some 16 different oil samples have now been subjected to SESC fractionation. Chemical characterization of various fractions is in progress. Table 2 summarizes results to date.

Molecular weight distributions of fractions and of whole oil samples were obtained by high performance size exclusion chromatography (HPSEC), using columns packed with Bio-Beads (Biorad Laboratories), a satisfactory yet inexpensive substitute for commercially available gel permeation columns. Infrared spectra have been used to obtain preliminary structural information.

TABLE 1

SESC FRACTIONATION SOLVENTS FOR
COLUMN CHROMATOGRAPHY ON SILICA GEL

<u>Eluents</u>		
1. Hexane	}	OILS
2. 15% Benzene-Hexane		
3. Chloroform	}	ASPHALTENES
4. 4% Ether-Chloroform		
5. 3% Ethanol-Ether	}	PRE- ASPHALTENES
6. Methanol		
7. 3% Ethanol-Chloroform	}	
8. 3% Ethanol-Tetrahydrofuran		
9. Acetic Acid (Pyridine)		

TABLE 2

CHARACTERIZATION OF WOOD OIL SESC FRACTIONS

<u>Fraction</u>	<u>Wt %</u>	<u>Mn</u>	<u>Mw</u>	<u>% O</u>	<u>Predominant Cpd Type</u>
1,2	0-6	143	158	-	Aromatic hydrocarbons
3	1-10	172	210	11	Polar aromatics
4	5-30	173	211	16	Monophenols
5	35-55	210	286	21	Highly functionalized phenols
6	10-25	350	604	23	Condensed phenolics
7	1-3	181	195	46	Polyhydroxy compounds
8	5-20	687	892	-	Uncharacterized
9	0-10			-	Uncharacterized
Char (not eluted)	-			8-15	Uncharacterized
Whole oil	-			13-19	All of the above

The predominant absorption in the spectra of most fractions is that due to hydroxyl stretching, except that this band is absent in F12 and weak in F3. Other evident bands are those due to carbonyl stretching (F3-F6 and F8) and those characteristic of the aromatic ring.

Fractions 1-5 are liquid while fractions 6, 8 and 9 are solid. Fraction 7, always minor, is usually solid. Capillary gas chromatography indicates that the volatile components of wood are found in fractions 1-5 exclusively, as would be expected on the basis of their molecular weight distributions. Also, fractions 4-6 are largely soluble in 5% aqueous sodium hydroxide, suggesting that the phenolic contents of the oil is concentrated in these cuts. It appears that these fractions may represent stages in the conversion of lignin to monophenols, and that maximizing F4 at the expense of F5 and F6 might therefore be a feasible process goal.

SESC profiles of five wood-derived oils are shown in Fig. 1. TR-7 oil was produced by Rust Engineering at the DOE's Albany, Oregon, PDU by the one-pass, water-based LBL process using a slurry of prehydrolyzed, neutralized and refined Douglas fir wood as the feed at a concentration of about 20% solids. TR-12 oil, also produced at Albany, was the result of a recycle process using wood flour (7.5% solids) initially slurried with anthracene oil in the presence of aqueous sodium carbonate. The sample of TR-12 examined was judged by Rust to be over 99% wood-derived, that is, less than 1% anthracene oil was present.

The other three samples of wood oil profiled in Fig. 1 were produced with LBL's one pound per hour continuous bench-scale process using 18% slurries of prehydrolyzed wood provided by Rust Engineering Co. Conditions and yield data for these five runs are summarized in Table 3.

A few generalizations may be drawn from these data. CL-6 oil has the highest proportion of volatiles (F1-F5), is the least viscous and has the lowest average molecular weight of any of these oils. On the other hand, it was produced in the lowest yield (15%) and was accompanied by the greatest amount of char. These and other facts led us to believe that this oil was flashed or steam-distilled out of the one-gallon reactor, the heart of the LBL CLU, owing to a combination of too low an overall pressure and too high a gas feed rate. Thus CL-6, although not representative, does exemplify the capability of the SESC characterization technique.

Among the other runs, it is clear that the proportion of lights (F1-F4) is much higher in the two Albany oils than in the CLU runs. The proportions F1-F4 are 56% (TR-7), 39% (TR-12), 8% (CL-8) and 19% (CL-12B). The respective yields of F1-F4, based on dry wood, are 13%, 21%, 3% and 5%. At this time the most likely explanation for the comparatively low quality of CLU-produced wood oils is incomplete reaction. The residence times of CLU runs have been around 20 minutes, whereas those of Albany runs TR-7 and TR-12 were on the order of several hours.

SESC Profiles of selected wood oils

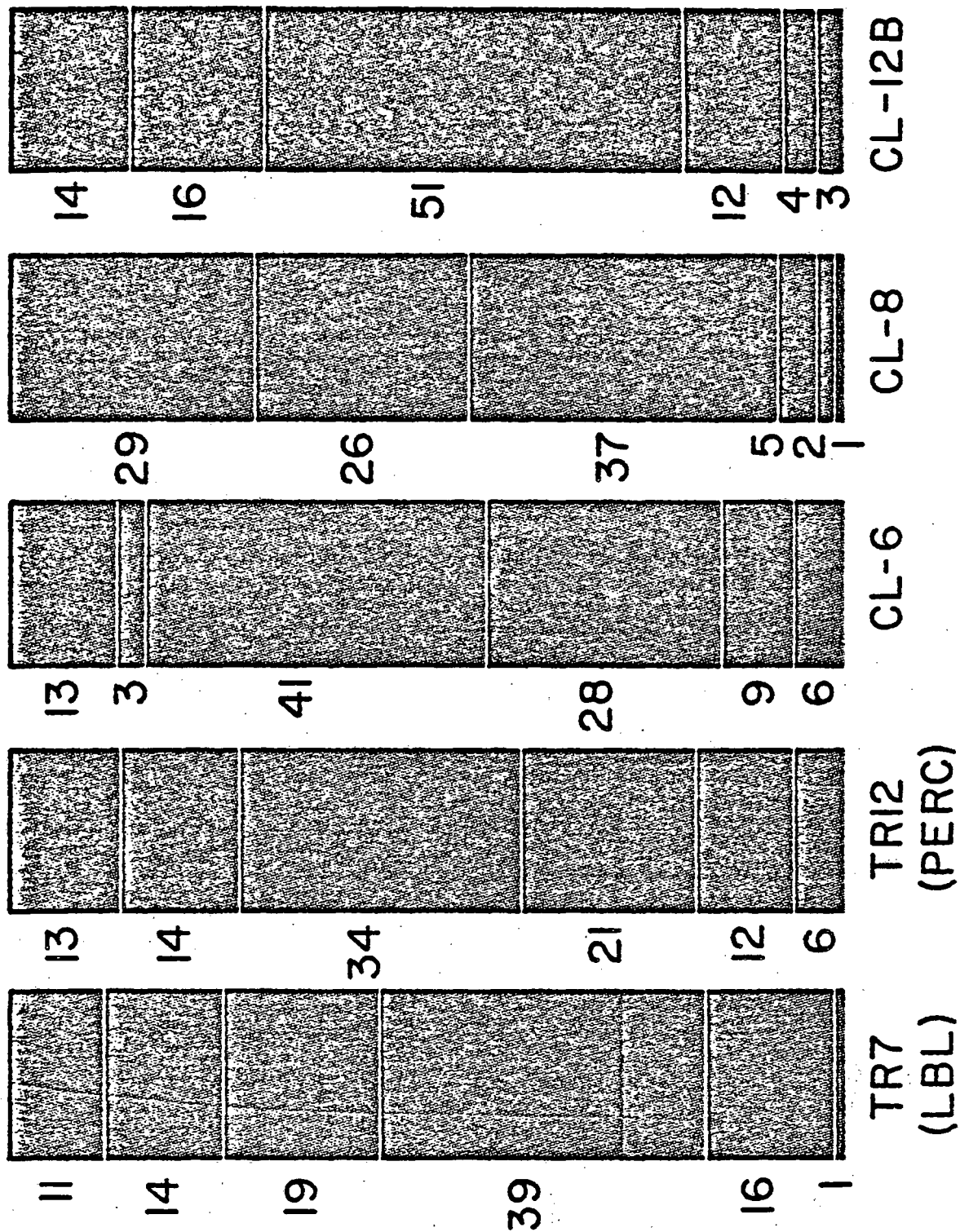


Fig. 1. SESC Profiles of Selected Wood Oils. Each segment represents that fraction of whole oil eluted by a particular solvent. From bottom to top, these SESC fractions (Table 1) are F1-2, F3, F4, F5, F6, and F7-8-9-Residue (combined).

TABLE 3

OPERATING PARAMETERS AND PRODUCT CHARACTERISTICS OF SELECTED WOOD OIL RUNS

<u>Run</u>	<u>T, °C</u>	<u>PSIG</u>	<u>Oil Yield, %</u>	<u>CO/H₂</u>	<u>Mol Wt</u>		<u>% O</u>
					<u>M_n^a</u>	<u>M_w^b</u>	
TR7	~340	3000	23	60/40	215	306	13
TR12	~360	3000	53	60/40	240	370	13
CL6	354	3000	15	50/50	176	232	13
CL8	330	3000	32	50/50	-	-	19
CL11B	360	3400	33	100/0	-	-	16
CL12B	360	3400	27	0/100	-	-	16

^a Number average molecular weight determined by HPSEC. ^b Weight average molecular weight determined by HPSEC.

CLU runs 11B and 12B were identical except for the use of pure carbon monoxide in the first case and pure hydrogen in the second. Although the SESC fractionation results for CL-11B are still incomplete, the available data fail to reveal significant differences in oil composition, yield or quality.

SESC fractionation appears to offer significant advantages over methods based on solvent extraction for assessing the character of biomass-derived oils. Its major disadvantages seem to be the amount of time (about 8 hours from start to finish) to do a single run and the cost of solvents. We are currently investigating a new methodology, flash chromatography, which promises to reduce significantly both time and solvent requirements.

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, constituting either a difficult recovery or costly disposal problem. A typical mass balance for an LBL run (Table 4) shows that 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 (2). We have now turned to reverse-phase HPLC and HPIEC to determine formic and glycolic acids.

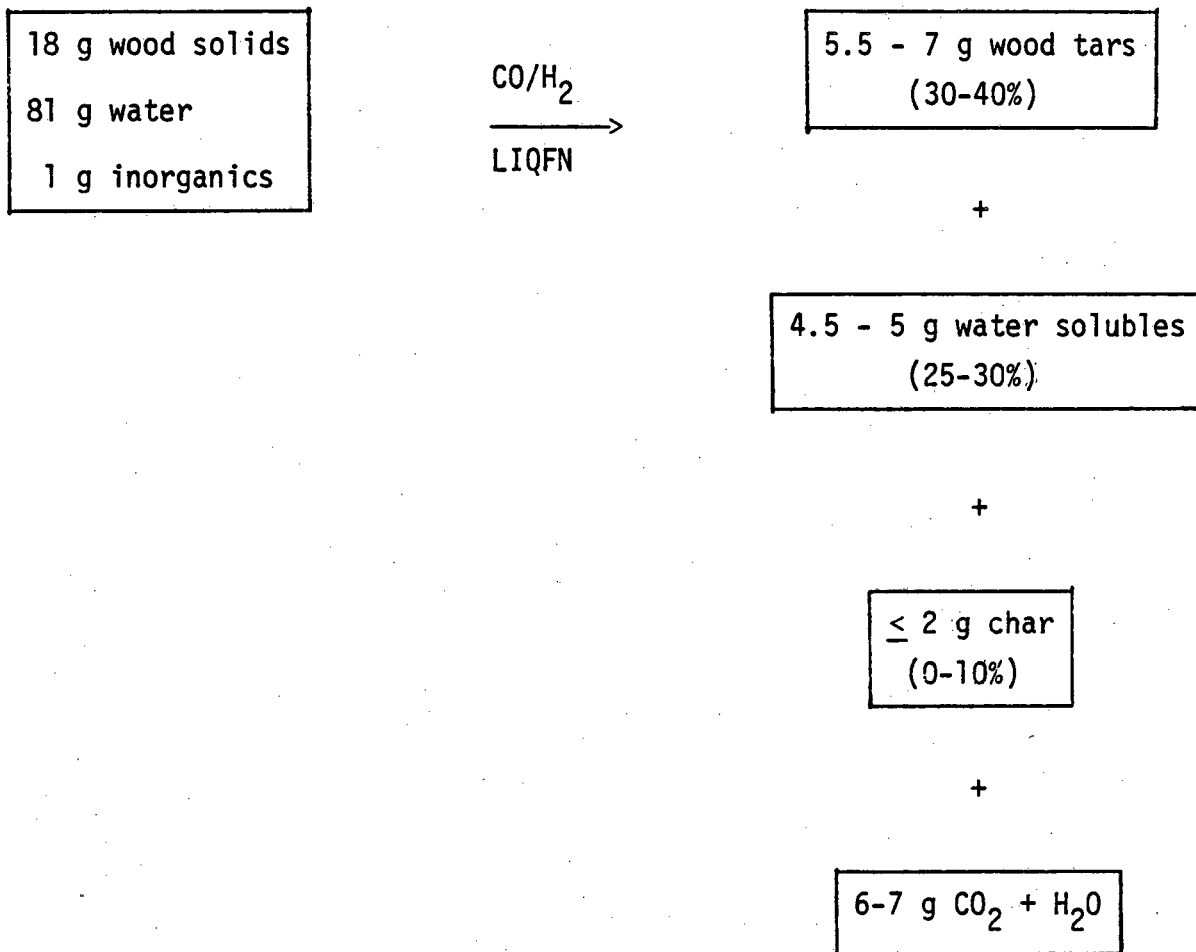
Fig. 2 shows a chromatogram of aqueous effluent from run CL-12. All other process waters display comparable HPLC traces. It was established that no aromatics, e.g., phenol, guaiacol, are eluted within the 25-min time frame of Fig 2. Of some 15 acid standards that were chromatographed under the same conditions, only three--acetic, formic and glycolic acids--had retention times corresponding to peaks of Fig 2. 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 compared in Fig 3. Glycolic acid is cleanly separated from formic and acetic. Levulinic acid appears between acetic and glycolic as a minor component of slurry water.

TABLE 4

MASS BALANCE FOR LIQUEFACTION OF DOUGLAS FIR BY THE LBL PROCESS



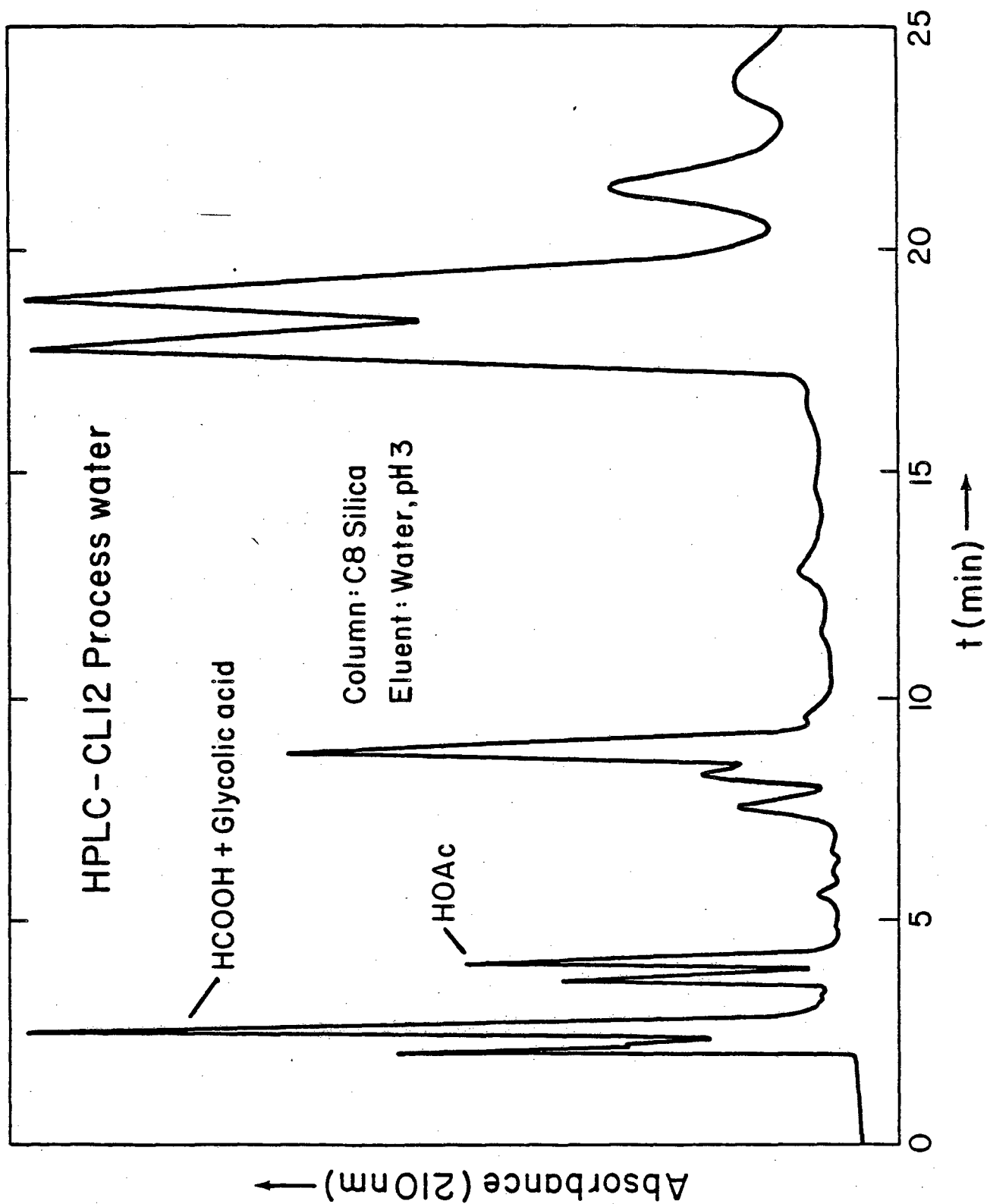


Fig. 2. Reverse phase HPLC chromatogram of aqueous effluent from run CL-12. The flow rate was 1.6 ml min^{-1} .

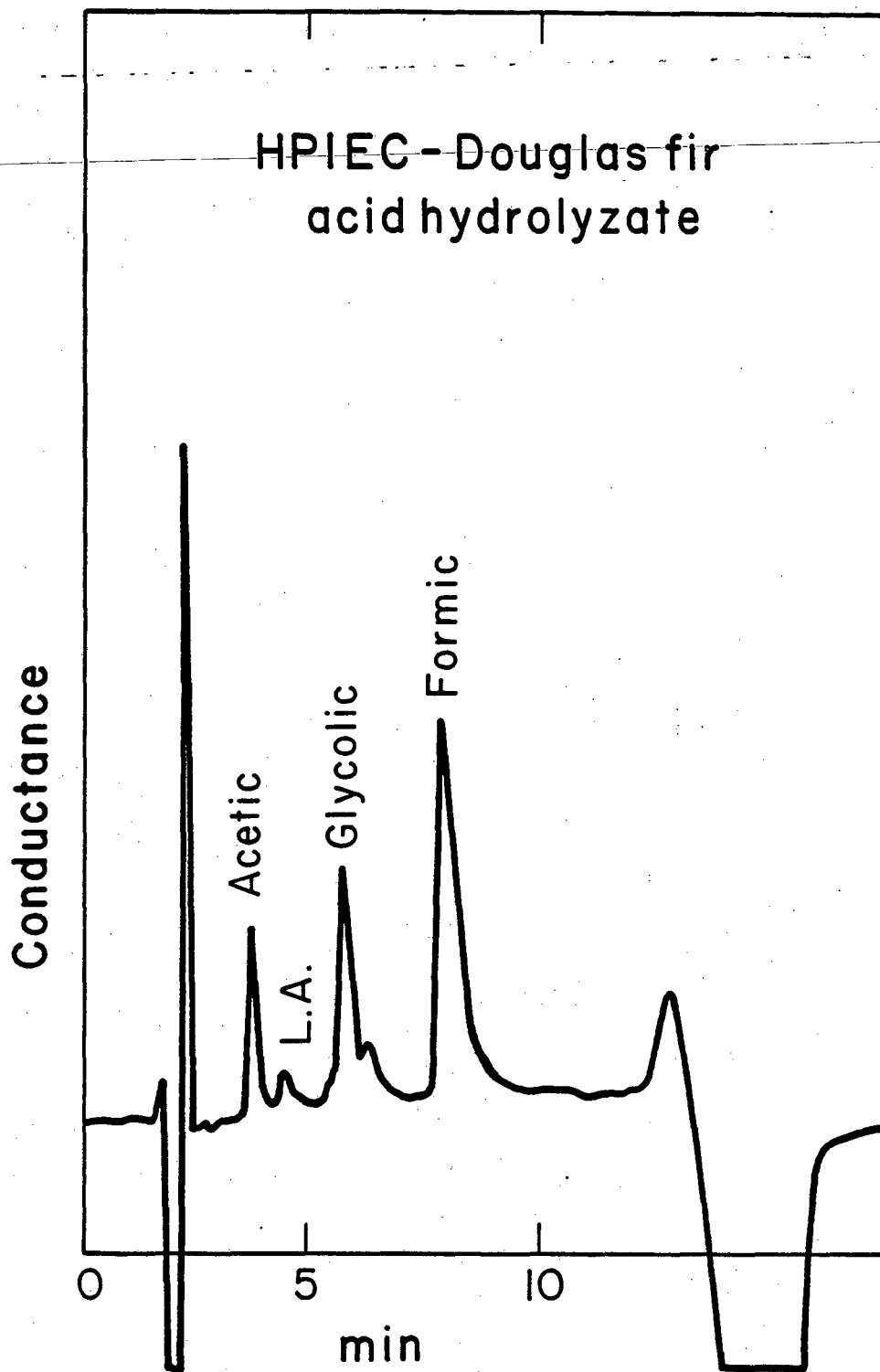


Fig. 3A. High performance anion exchange chromatogram of water from slurry feed. The flow rate of 0.001M phthalate buffer (pH 3) was 2.0 ml min⁻¹.

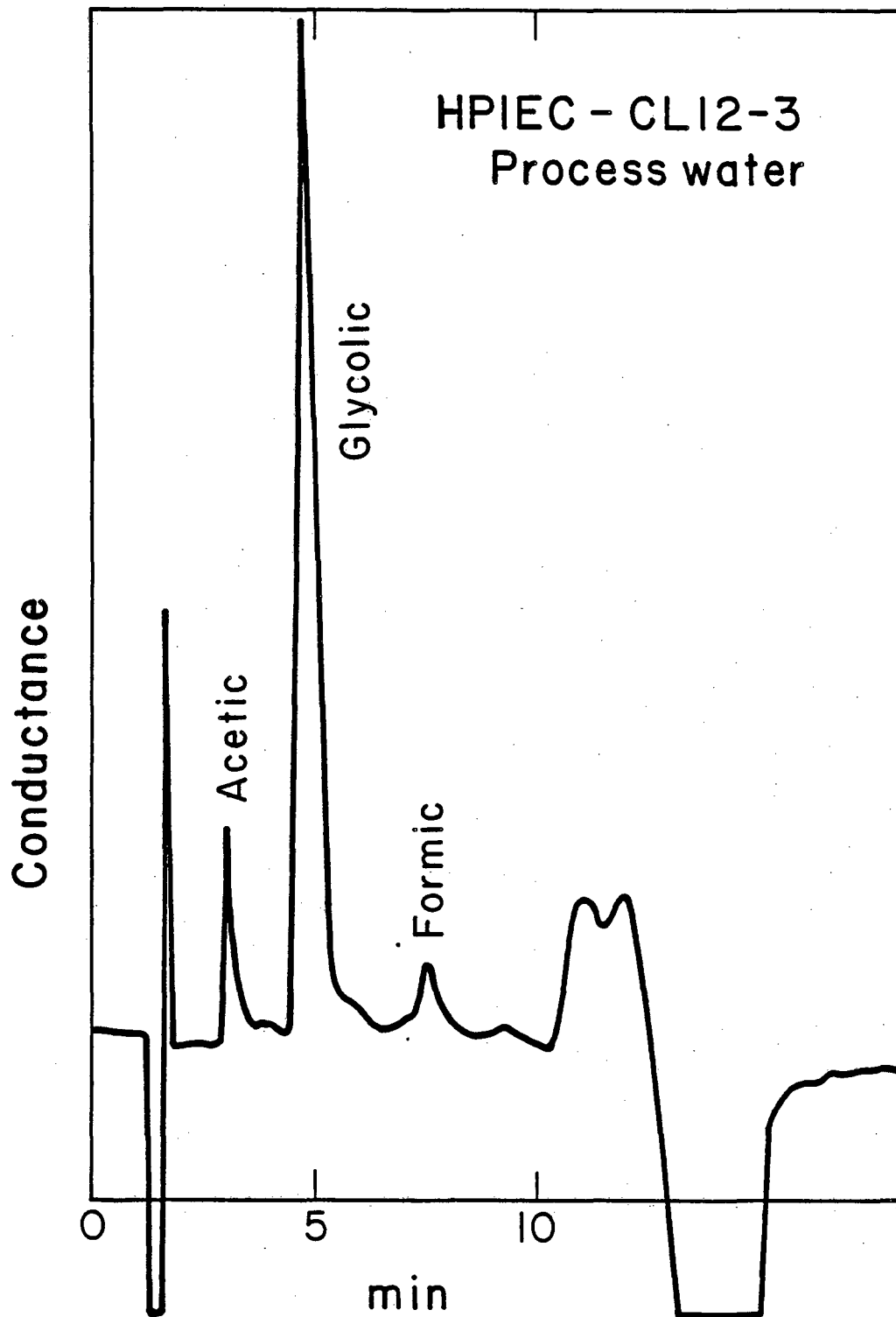


Fig. 3B. High performance anion exchange chromatogram of aqueous effluent from run CL-12. The conditions and sample size were identical to those of Fig 3A.

A great deal of chemistry is exemplified in Fig 3. 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 5 shows that glycolic acid undergoes a very large increase upon liquefaction. This increase occurs when either CO or H₂ is used. Thus glycolic acid is not the result of the carbonylation of formaldehyde but almost certainly originates from carbohydrate.

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.

References

- (1) M. Farcasiu, Fuel, 56, 9 (1977)
- (2) D. Kloden, unpublished results.

This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry, Biomass Energy Systems Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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TABLE 5

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.

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