

UC 61a



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED  
LAWRENCE

BERKELEY LABORATORY

## ENERGY & ENVIRONMENT DIVISION

APR 5 1982

LIBRARY AND  
DOCUMENTS SECTION

Presented at the Third Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, TN, May 13-15, 1981; and to be published in the Proceedings

CHEMISTRY AND STOICHIOMETRY OF WOOD LIQUEFACTION

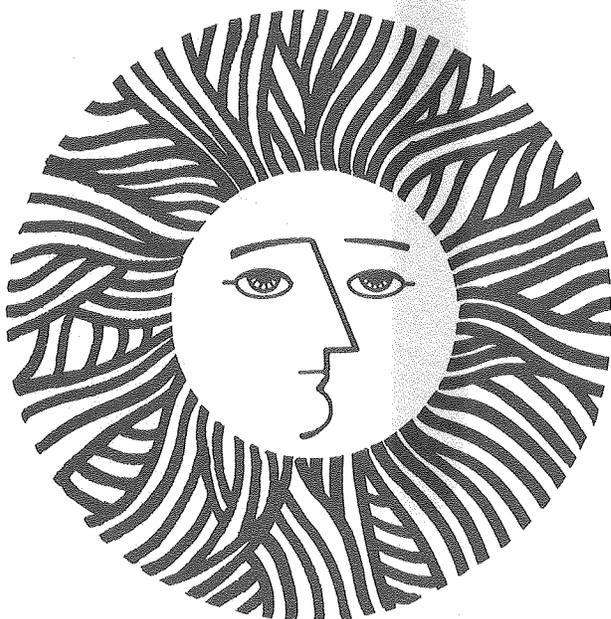
H.G. Davis, D.J. Kloden, and L.L. Schaleger

June 1981

### TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.*

*For a personal retention copy, call  
Tech. Info. Division, Ext. 6782*



LBL-12202  
e.g.

## **DISCLAIMER**

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

CHEMISTRY AND STOICHIOMETRY OF WOOD LIQUEFACTION

H.G. Davis, D.J. Kloden, and L.L. Schaleger

Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

Presented at the Third Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, TN, May 13-15, 1981

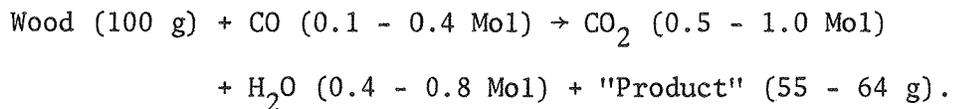
This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry, Biomass Energy Systems Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098; and funded through Battelle Pacific Northwest Laboratory, Lead Laboratory under Contract No. DE-AC06-76LO-1830.



## CHEMISTRY AND STOICHIOMETRY OF WOOD LIQUEFACTION

### SUMMARY

The approximate stoichiometry of liquefaction, from data of two PDU runs and a laboratory run is



"Product" includes wood oil, water soluble organics and residues. Water is formed by decomposition, carbon dioxide by decomposition and reduction of wood oxygen by CO.

Aqueous products include many carboxylic acids plus a roughly equal percentage of non-acids. The wood oil is divided into a neutral fraction and three phenolic fractions of varying molecular weight. Some specific compounds found in water and oil phases are listed.



## CHEMISTRY AND STOICHIOMETRY OF WOOD LIQUEFACTION

### A. INTRODUCTION

Efforts to generate a feasible process for liquefaction of biomass under an atmosphere of steam and carbon monoxide were initiated at the Pittsburgh Research Station of the Bureau of Mines in the 60's.<sup>(1)</sup> Between 1974 and 1976, a process development unit was designed and built in Albany, Oregon. Feedstock for this unit is Douglas fir wood chips. Operation proved to be difficult and there were clearly flaws in both the process concept and the mechanical design. However, from about mid-1979 to the present, with Rust Engineering (Division of Wheelabrator Cleanfuel) managing the plant for the Department of Energy, the PDU has had increasingly successful operation. Laboratory support--both R & D and analytical--has been supplied by the Lawrence Berkeley Laboratory and by Battelle Pacific Northwest Laboratory (PNL). Important background information on the processes used, including flow sheets, is given in a paper from PNL, also presented at this Symposium.<sup>(2)</sup>

Two types of continuous processes have been developed. An oil recycle process, which resulted from adaptation of the original U.S. Bureau of Mines concepts, has been called the PERC process (for Pittsburgh Energy Research Center). This process has some obvious economic disadvantages. It involves the expensive steps of drying and of grinding the wood to flour. It involves a quite high recycle of product oil and process water. In the PDU operations, this has been of the order of eight or nine parts recycle to one of fresh wood. An initial stock of slurring oil is necessary and because of the high recycle ratio, the coal tar anthracene oil which has been used is washed out of the system only slowly and this tends to confuse analyses.

The LBL process has been practiced without recycle. Partially hydrolyzed wood chips are "refined" to form an aqueous slurry which is then pumped directly to the reaction system. The LBL process avoids drying and grinding and permits a higher concentration of feed.

Sodium carbonate to the extent of 3 to 6% of the weight of dry wood is in general used as a "catalyst." Organic acids are generated in both pre-hydrolysis and liquefaction steps, and a major function of the carbonate is to neutralize these acids.

There has been considerable discussion in the past as to the roles of carbon monoxide, water and sodium carbonate in liquefaction. The goal of this paper is to throw light on these, and, where possible, to begin to quantify the stoichiometry. The chemistry involved is complicated by the diverse behavior of the components of wood. Nevertheless, a preliminary attempt to discuss the stoichiometry in the light of this chemistry will be made.

#### B. GENERAL PROCESS DESCRIPTION

The sequence of reactions begins with a partial hydrolysis. This is an explicit separate step -- prehydrolysis -- in the LBL process, but probably occurs in the early stages of reaction in any case. The LBL sequence is described here.

A partial hydrolysis at 180° of wood chips in very dilute sulfuric acid, followed by 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 (see Typical Composition, Table I). The water phase contains reducing sugars, acetic and other acids, and other organics.

The chemistry and stoichiometry of the prehydrolysis steps are discussed in more detail later in this paper.

The water slurry (or in the PERC process a slurry in recycled product) is pumped into a reactor, tubular or back-mixed. There it is heated to about 350°C under an atmosphere of carbon monoxide, hydrogen and steam at about 200 BAR and maintained at temperature for a residence time of the order of 1 to 60 minutes. The original wood components lose carbon dioxide and water and are partly reduced by carbon monoxide. They are thereby converted into a heavy oil, soluble in such organic solvents as acetone, chloroform, tetrahydrofuran and pyridine, and a water soluble fraction. The water gas shift reaction occurs



so that 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 ketones and alcohols. 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.

The elemental analysis of the wood-oil product derived from the above sequence includes anywhere from 7 or 8% to 20% or more O, depending upon the severity of liquefaction; i.e., upon the temperature and reaction time. The oil is highly polar and contains little actual hydrocarbon.

#### C. STOICHIOMETRY

Reliable complete material balances have proved difficult to obtain. In part, this is because water formed by decomposition, while substantial, is small compared to the amounts used as slurry vehicle. In batch autoclave work, small size of sample, leaks, and problems of correcting for gas imperfection complicate the material balance. As a result, it has even been questioned whether carbon monoxide was essential to the reaction at all.

We have used data<sup>(3)</sup> from the first long run (TR-8) in the Albany PDU with a reasonable material balance, to estimate overall stoichiometry. Run TR-8 was in the PERC mode. Single-pass residence time was rather long, over one hour in the 120 gallon continuous stirred autoclave of the PDU. Also there was a high recycle of product oil, so that the average total residence time was of the order of 10-20 hours at about 340°C. As a

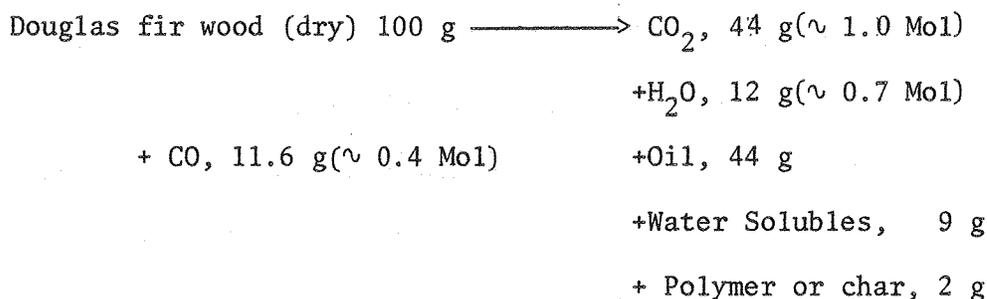
result the product oil has about 8% O. Initial slurring vehicle was coal-tar anthracene oil. Only in the latter part of run TR-8 was this reduced below 5-10% of the product. However, the elemental analysis of 100% wood-oil can be derived from the data.

The results are summarized in Table II. The data used were recorded in two "windows," periods during which special efforts at steady-state operation were made. In both periods, volume of gas out is considerably above volume in. This is because both shift reaction and the pyrolytic reactions yielding  $\text{CO}_2$  give a net expansion. Carbon monoxide out is less than carbon monoxide in during both periods and hydrogen is produced. The amount of water gas shift can be estimated from the net hydrogen production, and CO and  $\text{CO}_2$  yields can be corrected for this reaction. After correction, there remains a net loss of CO and a net gain of  $\text{CO}_2$ , but there is some disagreement between data for the two periods.

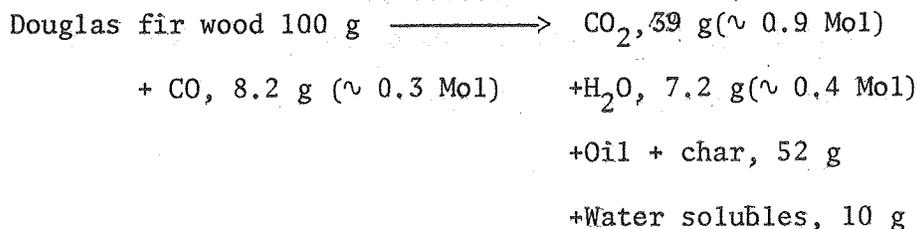
At the time of TR-8, there was little information on the water-soluble product. Later work has shown that carboxylic acids (as anion) are formed in an amount roughly equivalent to the amount of sodium carbonate added (about 4% of the wood). Also, water soluble neutrals about equal in weight to the acids are formed, largely as vapor during pressure let-down. They are then dissolved in a condensate water phase.

From the above information we can put together an "experimental" balance for the two windows as shown in Table III. The amount of water can be estimated from a rough H-atom balance, but no effort has been made to force a balance on either carbon or oxygen.

In fact, however, all three elements must be in balance. It turns out that we can force balances among all three major elements without doing serious injustice to the experimental observations. Such a forced balance is shown in Table IV. The stoichiometry can then be summarized as follows:



It is probable that oil products with oxygen contents below 10% cannot be obtained without the considerable usage of carbon monoxide shown above. At lower liquefaction severities, however, oils with much higher oxygen, (e.g. 11 to 20%) are obtained. In recent successful PDU run TR-12<sup>(4)</sup> for example, the yield of oil was ~ 53% and the preliminary estimate of elemental analysis was C 77%, H 8.3%, O 14%. Total organic carbon in the aqueous effluent recovered with the oil was 14.3% and in the condensate water 3.5%, whence a total yield of water soluble organics of 10% can be estimated. Again, an atom balance can be forced and the stoichiometry appears to be:



A very rough balance can be also given for a batch autoclave run. The run chosen seems to have been leak-free, but the char or polymer yield was excessive, as has been typical of this type of experiment. The data and a forced balance are shown in Table V. This gives approximately

Douglas fir wood, 100 g	—————>	CO <sub>2</sub> , 25 g (∞ 0.6 Mol)
		+H <sub>2</sub> O, 14 g (∞ 0.8 Mol)
+CO, 4 g		+Oil, 35 g
(∞ 0.1 Mol)		+Water solubles, 12 g
		+Char or polymer, 17 g

The high water yield indicates that dehydration reactions were overly important.

The above discussion avoids reference to the complex chemistry of liquefaction, although at least some feel for this is being developed. It is clear that the pyrolytic reactions which lead to carbon dioxide and water formation are by no means completely suppressed, but proceed even in the presence of high pressures of steam, CO and H<sub>2</sub>. If the more important oxygen-removing reactions involve CO<sub>2</sub> formation (whether by decomposition or by reduction with CO), we can obtain an oil with an H/C ratio higher than that of wood and with an acceptable molecular weight distribution. If dehydration becomes too important, we can obtain insoluble polymers or char, as in the autoclave run used for illustration.

#### D. CHEMICAL AND PHYSICAL CHARACTERIZATION OF WOOD OIL

Douglas fir liquefaction product is a heavy oil or bitumen which would be classified in conventional petroleum nomenclature as a No. 6 bunker fuel. However, being high in phenolic materials and very low in hydrocarbons, it bears scant chemical resemblance to petroleum crude oil.

Some of the properties of oils produced at Albany are listed in Table VI. The oxygen content of the product varies between 8 and 25%, depending on the severity of operating conditions. The atom ratio, H/C, is typically 1.2. About 70% of the oil is normally distillable under high vacuum.

Gel permeation chromatography of four Albany oils (Fig. 1) suggests that their number average molecular weights are on the order of 300-500. TR-7 and TR-10 were produced in the LBL mode while TR-8C and TR-12 were made in the PERC mode. The chromatogram for TR-8C oil indicates an anomalously high concentration of light material; this probably represents a small amount of strongly absorbing residual anthracene oil. TR-10 oil, which is a solid at room temperature, is evidently of higher average molecular weight than the others.

Because of multiple oxygen functionality and fairly wide molecular weight range, these oils are chemically complex. Although a completely satisfactory group separation scheme has not yet been developed, some progress is being made. A fractionation scheme for removing high molecular weight phenolics is shown in Fig. 2.

When a large excess of ether is added to a solution of whole oil in alkaline methanol, a precipitate of sodium polyphenolates is formed. This precipitate is dissolved in water and acidified to yield two fractions of free polyphenols, one insoluble in ether (designated HMP-1) and one soluble (HMP-2).

The addition of water to the alkaline solution of lower molecular weight materials results in the formation of two phases, an upper ethereal phase containing neutrals (fraction E) and a lower aqueous phase containing phenolates of lower molecular weight. A backwash of the aqueous phase with ether yields fraction F, and acidification and ether extraction of the aqueous layer gives fraction G containing free phenols. Amounts of the fractions obtained from PDU samples, together with some elemental analyses are given in Table VII.

Gel permeation chromatograms of the fractions from TR-7 are compared with a chromatogram of whole oil in Fig. 3. Separation of the high molecular weight phenolic fraction of TR-7, shown in Fig. 3, appears to have been good. This simple and fast procedure makes it possible to divide the oil into a non-acidic fraction and phenolic fractions of different molecular weights without getting involved in sticky resinous materials which always appear when organic solutions of the oils are extracted by alkaline water solutions.

The more volatile components of wood oil can be separated and identified by capillary gas chromatography-mass spectroscopy (GC-MS). A list of representative components of the major compound types is given in Table VIII. (See ref. 2 for a longer list.) A capillary gas chromatogram of whole wood oil reveals the presence of hundreds of individual compounds, none of which is present to the extent of even 1%. Hydrocarbons are present in trace amounts only. The light end is dominated by saturated and unsaturated cyclic ketones while at longer retention times, the major constituents are alkylated methoxyphenols and phenols. It may be inferred on the basis of boiling point data that gas chromatography is capable of probing no more than one-third of whole wood oil. This range can be extended by making use of

chemical volatilization techniques such as methylation, acetylation and trimethylsilylation; such work is in progress.

#### E. COMPOSITION OF THE AQUEOUS PHASE

Whether liquefaction is run in the LBL mode (water slurry feed) or in the PERC mode (wet oil slurry plus aqueous catalyst) there is a large amount of aqueous effluent. In the LBL mode a prehydrolysis step results in the solubilization of approximately 30% of the input solids. Thus a substantial part of the overall liquefaction process must take place within the aqueous phase. In fact, the aqueous streams of both the PERC and LBL modes contain fairly large amounts of organics which pose a difficult recovery or a serious disposal problem. For these reasons we have undertaken an investigation of several aspects of the chemistry of the aqueous phase including a study of the stoichiometry of prehydrolysis, a detailed examination of the acid-base chemistry of aqueous process effluent, and a preliminary study to speciate and quantify major constituents of the water phase.

#### PREHYDROLYSIS

Douglas fir wood has cellulose, hemicellulose and lignin contents of about 41, 26 and 28%, respectively. The remaining 5% includes uronic acid moieties, extractives, acetyl groups and ash. Acid hydrolysis of wood chips of 1¼" nominal length at about pH 2.0 and 180°C for 45-min results mainly in the hydrolysis of the hemicellulose fraction.

Hydrolysis accompanied by vigorous agitation also effects near total breakdown of the fibrous character of the lignocellulosic residue. The resulting solids consist of small particles, half of which are less than 5 mm. in diameter, and friable, partially hydrolyzed chips. These larger pieces are readily comminuted by passage through a disc refiner or colloid mill to give a slurry with a consistency like that of a milk shake. Slurries containing 20-30% total solids show little tendency towards settling; they can be pumped into and through a liquefaction reactor.

As was discussed in Section B, hemicellulose is almost completely hydrolyzed under these conditions, but cellulose is only slightly hydrolyzed. The aqueous phase contains reducing sugars, acetic and levulinic acids, sugar degradation products such as furfural, and other organics. Neither formic nor propionic nor more than trace amounts of any other volatile acid could be detected by gas chromatography, (acids like glycolic would not be detected).

Table IX shows an approximate material balance for prehydrolysis. About 91% of the input solids could be accounted for. Most of the remainder comes from loss of volatiles and dehydration of sensitive carbohydrate residues during drying.

## ACID-BASE TITRATIONS

In the Albany PDU operation the aqueous effluent exits as two streams. These are an aqueous condensate recovered by cooling vapors obtained after the main pressure let-down valve and a liquid aqueous effluent collected with the wood-oil product. The condensate contains water-soluble, volatile light organics, both acidic and non-acidic. The liquid effluent contains similar materials which are, on average, less volatile and of higher molecular weight. Since the liquid aqueous effluent is recycled along with oil product in the PERC runs, samples of the PDU stream are likely to be quite high in organics. Since these are largely sodium salts of acetic and other acids, the specific gravity is high. Rust Engineering personnel report a range of about 1.15 to 1.25.

A number of aqueous effluents have been titrated with aqueous sodium hydroxide to determine free acid and with hydrochloric acid to determine carboxylates. The general conclusion is that the acid plus anion content is substantial (of the order of 0.2 to 0.5 gram equivalent per kilogram for single-pass total aqueous effluent). Also, the yield of acid plus anion is a significant part of the total material balance, 4 to 10% or more of the dry wood feed.

Samples of the two effluent streams from PDU run TR-12<sup>(4)</sup> (PERC mode) were titrated to pH around 8-9 with 1N NaOH, then back-titrated with 1N HCL to determine total acid plus anion. As the overhead condensate contained no anion, the acid and base titers were nearly identical. As the liquid aqueous effluent was recovered with pH >7 it contained very little free acid. Fig. 4 shows the results of potentiometric titrations of the anions with HCl.

Since the recycle ratio was high and most of the acids are retained in the slightly alkaline bottom water, the anion concentration has built up to a high level. Total organic carbon was determined as 14.3%, and the sodium carboxylate content was about 35%. Non-acid organics, extracted with chloroform and recovered by evaporation, were 1.3%, but much of this fraction is lost by failure to extract or by volatilization during evaporation. From the organic carbon and the elemental analysis of the acidic components, we estimate the total neutrals content at about 3 wt %.

The curves for HCl titrations of both bottom and condensate waters are shown in Fig. 4. Since the concentration of acids in the condensate was low, we titrated a large sample and the amount of titrant was multiplied by 5 before plotting. Both curves have been corrected for the excess 1N HCl required to reach the low values of pH near the endpoint.

The half-titration point of the upper curve (condensate water) is at about pH 4.65, roughly equal to the  $pK_a$  of acetic acid, 4.75. Thus the small amount of organic acid which goes overhead with product vapor is, as would be expected, simple, volatile carboxylic acids.

The lower curve has a half-titration point at about 4.15 and a very broad straight region between about 4.9 and 3.5. This type of curve is typical of all those we have obtained with total or bottom water products either from PDU or laboratory samples. It indicates that a significant proportion of the acids present are much stronger than acetic acid,

succinic acid or their homologues. Such acids could be alpha-substituted acids (e.g., glycolic acid,  $pK_a = 3.8$ , citric, first ionization 3.1, etc.), but up to now we have not positively identified any such components.

Table X shows elemental analyses of some materials recovered from aqueous effluents. The water soluble materials, whether acidic or neutral, have oxygen contents comparable to that of the original wood.

Also shown in Table X are total organic carbon analyses and acid plus anion contents determined on several product waters. From the total organic carbon, the estimated percent acid plus anion and information about the equivalent weight and carbon analysis of the acid/anion fraction, a very rough estimate of the non-acidic content of the waters can be made. This is generally more than we have been able to recover by extraction and evaporation -- not surprising since many of the compounds are highly hydrophilic or highly volatile or both.

The equivalent weight of product carboxylic acids has been estimated in several ways. (1) A sodium carboxylate solution (e.g., the bottom water from PDU run TR-12) is titrated to determine the equivalents present and is evaporated and weighed. Waters from several runs gave values from  $\sim 79$  to  $\sim 85$ . The highly concentrated TR-12 water was run twice, giving 78 and 85, with probable errors tending to raise the result rather than lower it. (2) The dried sodium carboxylate from TR-12 water was analyzed for sodium. Assuming one Na per carboxyl, the calculated equivalent weight is 79. Extracted acids from run TR-10

were titrated with NaOH solution. The result obtained, 93, is expected to be high because of loss of volatiles in evaporation and light or dicarboxylic acids in the extraction. A value of 80 should be reliable to perhaps  $\pm 5$  for the overall aqueous carboxylic acid product.

#### MAJOR COMPONENTS OF THE AQUEOUS PHASE

Analysis by capillary GC-MS of ether, methylene chloride or chloroform extracts of aqueous process waters from TR-7 reveals the presence of many of the same neutrals and phenols found in product oil (Table VIII). This is not surprising in view of the fact that these oxygenated species all exhibit partial water solubility. However, a large part of the water-soluble organic fraction consists of carboxylic acids, a number of which have been identified as their methyl esters by GC-MS. A list of some of the major acids which we have thus far been able to identify is given in Table XI.

Many of these acids are also detectable by direct gas chromatographic analysis of aqueous samples. Fig. 5 compares the gas chromatograms of two samples of aqueous phase from a batch autoclave run, one obtained at pH 2 and the other at pH 10. At high pH the stronger acids exist as sodium salts and are not volatilized, thus revealing the neutrals and weaker acids.

#### F. THOUGHTS ON MECHANISMS

Although a clearer picture of the nature of wood liquefaction is coming into view, there remains a shortage of basic mechanistic information. The identification of increasing numbers of individual components of the wood oil mixture provides ample opportunity for speculation about

mechanistic pathways. However, the absence of kinetic data and the likelihood that our ideas about the solution chemistry that occurs at ambient temperatures and atmospheric pressure might not carry over to the conditions of liquefaction render such speculation premature. Nevertheless, a few comments about mechanism seem worth mentioning at this time.

Several basic questions have been posed by earlier investigators: What is the role of carbon monoxide and of hydrogen? What is the function of sodium carbonate? To these we would add: How is the formation of excess carbon dioxide accounted for? How is the generation of carboxylic acids in a reducing atmosphere explained?

The necessity of carbon monoxide seems well established.<sup>(13)</sup> Equally clear now is that hydrogen contributes little or nothing to the process. Appell and co-workers<sup>(13)</sup> found that either carbon monoxide in aqueous alkaline media or aqueous sodium formate is effective in reducing acetophenone to a mixture of alcohol and hydrocarbon. They suggested that formate ion is the actual reducing agent. The role of sodium carbonate would therefore be to provide hydroxide ion and to maintain a buffer capacity for neutralization of acids produced by other pathways.

Although the formate mechanism has certain attractive features, it remains a matter of speculation as to whether it plays an important role in wood liquefaction. Sodium carbonate's importance may lie in its promotion of the water gas shift reaction or in reasons as yet unknown.

The reduction-depolymerization of the lignin portion is very incomplete as indicated by the isolation of a large polyphenolic fraction by the solvent fractionation technique described earlier. It is well-known that lignin is solubilized and partially depolymerized in alkaline solution as in the soda pulping process.<sup>(6)</sup> Sodium carbonate may, therefore play a role here.

The formation of comparatively large quantities of acids such as propionic, succinic and glutaric is not readily explained at this time. These are probably mainly derived from wood carbohydrate and certainly a large number of base-catalyzed, acid-forming disproportionation reactions and rearrangements of carbohydrates are known. The possibility that carbon dioxide formation is due in large part to the decarboxylation of such acids must also be raised.

If the  $\text{CO}_2$  formed by decomposition all comes through carboxylic acid intermediates, then, from the stoichiometry reported in Section C 0.4 to 0.6 g mol of carboxyl must have been formed per 100 g dry feed. If we accept an equivalent weight of the order of 80, we conclude that the total formation of carboxylic acid intermediates would have to be remarkably high range of 30 to 60% of the wood. This is of the same order as the total polysaccharide content (60-70 wt %)

Many of the products observed in wood liquefaction are also formed in wood pyrolysis, 14-18, suggesting that thermal degradation is also an important mode of reaction under conditions of liquefaction.

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. DE-AC03-76SF00098.

This work was funded 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.

TABLE I

## COMPOSITION OF TYPICAL DRY DOUGLAS FIR WOOD

A. ELEMENTAL (ASH-FREE), WT%	B. TYPE	WT%
C 51.0	Cellulose	41
H 5.8	Hemicellulose	26
O 43.0	Lignin	28
N 0.1	Other	5
S 0.1		
Ash (0.3-0.9)		

TABLE II

SUMMARY OF DATA REPORTED<sup>(3)</sup> BY ALBANY PDU FOR PERC PROCESS RUN TR-8

GAS FEED, Kg Mols			GAS OUT (dry), Kg, Mols			CHANGE, Kg Mols		
H <sub>2</sub>	2.75	3.74	H <sub>2</sub>	5.35	4.91	H <sub>2</sub>	+2.60	+1.17
CO	<u>4.18</u>	<u>5.37</u>	CO	0.23	1.82	CO	-3.95	-3.55
TOTAL	6.93	9.11	CO <sub>2</sub>	6.73	4.80	CO <sub>2</sub>	+6.73	+4.80
			CH <sub>4</sub>	<u>.09</u>	<u>0.06</u>	CH <sub>4</sub>	<u>+0.09</u>	<u>+0.06</u>
			TOTAL	12.40	11.59	TOTAL	+5.47	+2.48

	(1)	(2)
Wood in, Kg (dry)	304	318
Na <sub>2</sub> CO <sub>3</sub> in, Kg	11.4	15.5
Wood oil* out, (Kg, net product)	130 (42.8%)	139 (43.7%)
Char or Polymer out, Kg	5.5 (1.8%)	9.1 (2.9%)
Estimated Organics in Water, Kg	23 (7.6%)	31.4 (9.9%)

(1) "WINDOW" (13 hour steady state period) TR-8B

(2) "WINDOW" (12.5 hour steady state period) TR-8C

---

\* Elemental Analysis Oil, wt% - C 84.2; H 8.3; O 7.3. This is based on extrapolation of results for oils containing anthracene oil to 100% wood oil.

TABLE III

YIELDS IN DOUGLAS FIR WOOD LIQUEFACTION FROM ALBANY PDU DATA RUN TR-8<sup>(3)</sup>

	Oil, wt%	Water Solubles, wt%	Solids, wt%	CO <sub>2</sub> -1, wt% *	CO <sub>2</sub> -2, wt%**	TOTAL wt%
WINDOW TR8-B	42.8	7.6	1.8	39.2	7.4	98.8
WINDOW TR8-C	43.7	9.9	2.9	15.8	11.7	84.0
AVERAGE	43.2	8.8	2.4	27.5 (0.62 Mol CO <sub>2</sub> formed by decomposition)	9.6 (0.60 Mol CO reacted)	91.5
FORCED*** BALANCE	44.3	9.9	2.4	25.7	6.6	88.9

\* CO<sub>2</sub> by decomposition

\*\* CO<sub>2</sub> by oxidation of CO - only single O-atom counted

\*\*\* See Table IV, Yields adjusted to give C, H, and O balances.

TABLE IV

## ATOM BALANCES-PDU RUN TR-8

g/100g feed in		g/100g feed out						
	WINDOW TR8-B	Oil	Water Solubles	Char	CO <sub>2</sub> -1	CO <sub>2</sub> -2	H <sub>2</sub> O *	TOTAL
C	51	36.0	3.8	1.5	10.7	-	-	52.0
H	5.8	3.55	0.55	0.11	-	-	(1.6)	5.8
O	43	3.1	3.3	0.2	28.5	7.4	12.8	55.3
	TOTALS	42.6	7.6	1.8	39.2	7.4	14.4	113.1
	WINDOW TR8-C							
C	51	36.8	4.9	2.6	4.3	-	-	48.6
H	5.8	3.63	0.7	0.18	-	-	(1.3)	5.8
O	43	3.2	4.3	0.2	11.5	11.7	10.4	41.3
	TOTALS	43.6	9.9	2.9	15.8	11.7	11.7	95.7
	AVERAGE							
C	51	36.4	4.4	2.1	7.5	-	-	50.4
H	5.8	3.59	0.63	0.16	-	-	(1.4)	5.8
O	43	3.15	3.8	0.16	20.0	9.6	11.2	47.9
	TOTALS	43.1	8.8	2.4	27.5	9.6	12.6	104.1
	FORCED BALANCE							
C	51	37.4	4.5	2.1	7.0	-	-	51.0
H	5.8	3.7	0.64	0.16	-	-	1.3	5.8
O	43	3.2	3.9	0.16	18.7	6.6	10.4	43.0
	TOTALS	44.3	9.0	2.4	25.7	6.6	11.7	99.8

\* H<sub>2</sub>O yields calculated to give H-atom balance

TABLE V  
 ATTEMPTED BALANCES FOR AN AUTOCLAVE RUN<sup>(5)</sup>  
 (330°C, 60 minutes, cold pressure 35 BAR, 60 Mol % CO, 40 Mol % H<sub>2</sub>)

A. Observed Yields, wt % of Dry Organic Feed

	Oil (acetone solubles)	Residue (acetone or char Insolubles)	Water Solubles	CO <sub>2</sub> -1	CO <sub>2</sub> -2	TOTAL
	32	17	11	13	2	75

B. Observed Atom Balance

IN, g/100g feed	OUT, g/100g feed						TOTAL
	Oil	Residue	Water Soluble	CO <sub>2</sub> -1	CO <sub>2</sub> -2	H <sub>2</sub> O	
C - 51	24.4	13.0	5.5	3.5	-	-	46.4
H - 5.8	2.24	0.90	0.77	-	-	( 1.89)	( 5.8)
O - 43	5.3	3.1	4.7	9.5	2.0	(15.1)	39.

C. A Forced Balance

	IN			OUT			TOTAL
	Oil	Residue	Water Soluble	CO <sub>2</sub> -1	CO <sub>2</sub> -2	H <sub>2</sub> O	
C - 51	26.6	13.0	6.0	5.4	-	-	51.0
H - 5.8	2.52	0.90	0.84	-	-	( 1.54)	5.80
O - 43	5.8	3.1	5.2	14.6	2.0	(12.3)	43.0
TOTALS	99.8	34.9	17.0	20.0	2.0	13.8	99.7

TABLE VI

BULK PROPERTIES OF DOUGLAS FIR WOOD OILS<sup>a</sup>

	<u>TR-7</u>	<u>TR-8</u>	<u>TR-10</u>
Viscosity, cp at 100°C	22-140	50-110	2700
HHV, But/lb (dry basis)	14,400- 15,300	16,300	13,300
Density, 22°C	1.09	1.11	1.2
Solids, %	0.6-2.0	5-11	1-2.5
Elemental analysis (maf basis)			
C, %	78-80	84	75
H, %	7.8	8	7
O, %	12-14	18	17
Distillation			
% distilled at 10 torr	68	69	54.5
B.P. upper limit	265°C	310°C	450°C

---

<sup>a</sup> Data provided by Rust Engineering Co.

TABLE VII

## A. FRACTIONS FROM WOOD DERIVED OILS (10g SAMPLES)

FRACTIONS	RUN		
	TR-7	TR-8 *	TR-10
High MW Phenols (HMP)	3.8	1.4	6.8
Non-Acidic Material (E)	3.3	4.8	1.5
Low MW Phenols (F)	0.2	1.2	0.1
Low MW Phenols (G)	1.9	1.3	0.8
Loss in Workup	0.8	1.3	0.8

## B. ELEMENTAL ANALYSIS OF PRODUCT FRACTIONS (PRELIMINARY VALUES, WT %)

FRACTION	RUN	C	H	N+S	O (DIFF.)
Low MW Phenols (G)	TR-7	72.7	7.4	(0.2)	19.7
High MW Phenols (HMP-1)	TR-7	71.8	5.4	(0.2)	22.6
Non-Acidic Material (E)	TR-7	80.8	8.2	(0.2)	10.8
Milled Lignin from Douglas Fir (6)		63.4	6.1		30.5

\* Sample of TR-8 separated contained much anthracene oil.

TABLE VIII

SELECTED VOLATILE COMPONENTS OF DOUGLAS FIR LIQUEFACTION PRODUCTS<sup>a</sup>

	<u>Source</u>
A. Hydrocarbons	
Ethylbenzene	Distillate <sup>b</sup>
1-Ethylcyclohexene	Oil <sup>c</sup>
B. Ketones	
Cyclohexanone	Oil <sup>d</sup> , aqueous <sup>e</sup>
2-Methylcyclopentenone	Oil <sup>d</sup> , aqueous <sup>e</sup>
2-Pentanone	Aqueous <sup>c</sup>
C. Furans	
Dimethylfuran	Distillate <sup>b</sup>
2,3-Dihydro-4-methylfuran	Oil <sup>c</sup>
D. Esters	
Butyl acetate	Aqueous <sup>c</sup>
Butyrolactone	Aqueous <sup>c</sup>
E. Phenols	
Guaiacol	Oil <sup>d</sup> , distillate <sup>b</sup> , aqueous <sup>e</sup>
4-n-Propylguaiacol	Oil <sup>d</sup> , distillate <sup>b</sup>
p-Cresol	Distillate <sup>b</sup>
F. Dihydric Phenols	
1,4-Benzenediol	Aqueous <sup>c</sup>
3-Methyl-1,2-benzenediol	Aqueous <sup>c</sup>
G. Aldehydes	
Methylpentenal	Distillate <sup>b</sup>
H. Alcohols	
2,4-Dimethyl-3-heptanol	Aqueous <sup>c</sup>

a. All identifications were made by capillary GC-MS; most are unconfirmed.

b. Reference 2, 7

c. Present work.

d. Reference 8

e. Reference 9

TABLE IX

## MATERIAL BALANCE FOR PREHYDROLYSIS OF DOUGLAS FIR WOOD CHIPS

## Input

Wood chips (dry basis)	1.0 kg
0.05% Aqueous sulfuric acid	3.5

## Output

Insoluble solids	0.72
Non-volatile soluble solids (Reducing sugars, 0.11)	0.19
Acetic acid	0.013

## Material Balance

Carbon	96%
Hydrogen	92%
Oxygen	84%

TABLE X

LIQUEFACTION OF DOUGLAS FIR WOOD  
ANALYSES OF SOLUBLE ORGANICS IN AQUEOUS STREAMS

SAMPLE	Total Organics Carbon, wt %	Acids + Anions* (12)		Estimated neutrals* wt %
		wt%	wt% carbon	
1. Batch, 0 min, 330°C	4.70	4.6	2.2	5.0
2. Batch, 60 min, 330°C	2.92	3.3	1.6	2.6
3. Batch, 0 min, 360°C	2.72	2.7	1.3	2.8
4. Batch, 0 min, 340°C water recycled	-	5.6	2.6	-
5. Continuous, 20 min 350°C, laboratory	1.60	1.54	0.74	1.7
6. Water from wood used in continuous slurry run	3.57	1.29	0.62	6.0
7. PDU-TR-10 Bottom water, LBL run no recycle	1.96	2.80†	1.34†	1.2
8. PDU-TR-12 Bottom water, PERC run, recycle	14.3	27.0†	12.7	3.2
9. PDU-TR-12 Condensed overlead water	3.56	.43	0.21	6.7

References - Samples 1-6 (5, 11)  
Sample 7 (12)  
Samples 8-9 (4, 11)

\* From titration with equivalent wt = 80, % C in acids = 48, in neutrals = 50

† Sample 7 - Extracted acids (1.9% of sample) had C - 53.5, H - 6.8, O - 39.7%  
Sample 8 - Total acid from sodium salt C - 47.2, H - 6.9, O - 45.9%  
Sample 7 - Extracted neutrals (0.8% of sample) C - 56.6, H - 6.65, O - 36.7%

TABLE XI

SOME ACIDIC COMPONENTS OF THE WATER SOLUBLE PRODUCT<sup>a</sup>

A. Monocarboxylic Acids

Acetic  
Propionic  
Butyric  
Isobutyric  
Palmitic

B. Dicarboxylic Acids

Succinic  
Glutaric  
Methylsuccinic  
Adipic  
2-Methylglutaric

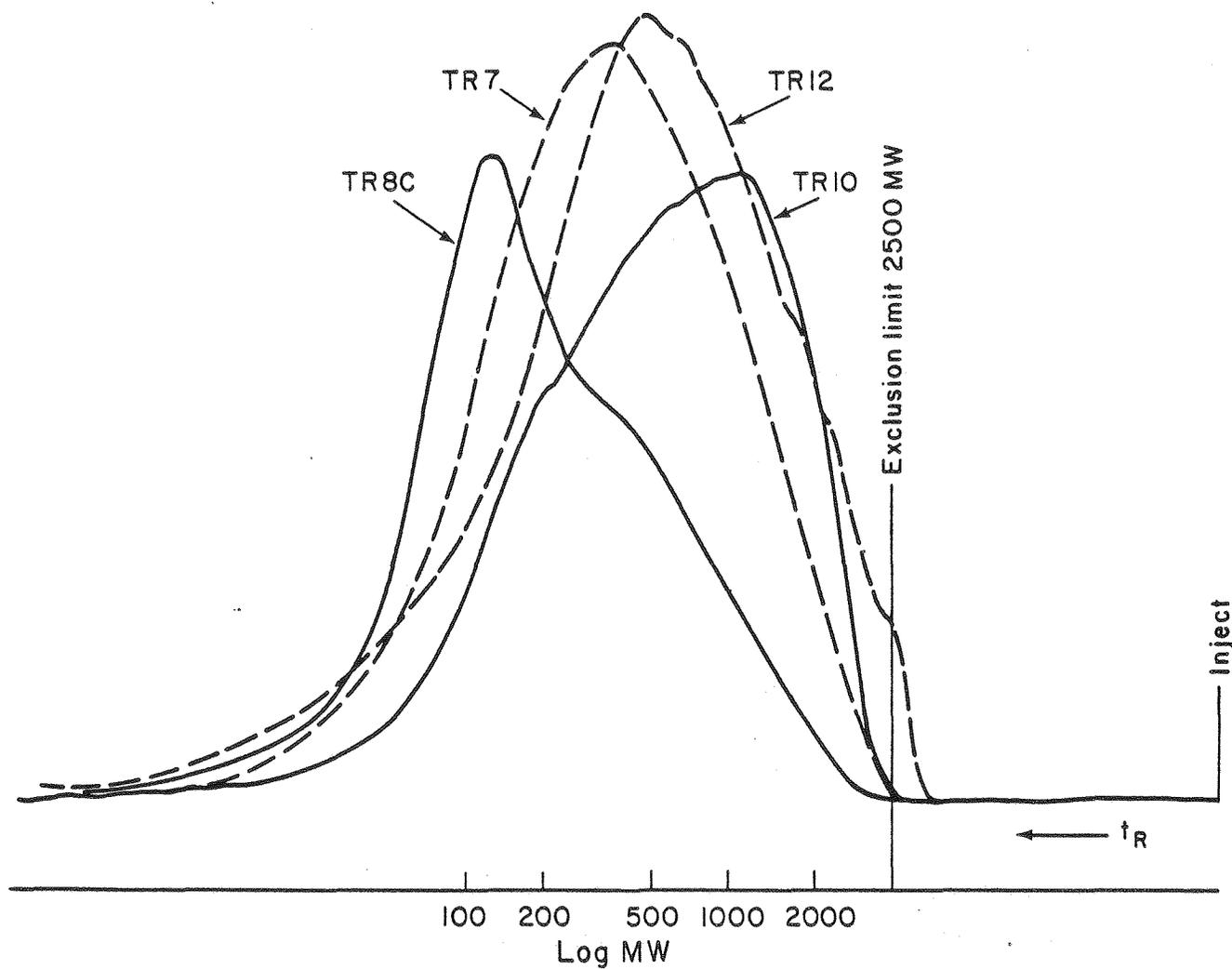
C. Oxo - or Hydroxy-Acids

Levulinic  
2,3-Dihydroxybenzoic  
4-Oxohexanoic

---

a. Identifications were made by capillary GC-MS of the methyl esters. (10)

Fig. 1. Gel permeation chromatograms of various Albany-produced wood oils using uv detection at 254 nm. The molecular weight scale is very approximate and not to be taken literally. Columns: two 30 cm x 7.8 mm i.d. columns connected in series, one packed with BioBeads S-X2 and the other with BioBeads S-X8 (Biorad Laboratories). Conditions: flow rate, 1.2 ml/min; solvent, THF.



XBL 815-812

Fig. 2. Separation scheme for product oils.

FRACTIONATION SCHEME FOR WOOD DERIVED OILS

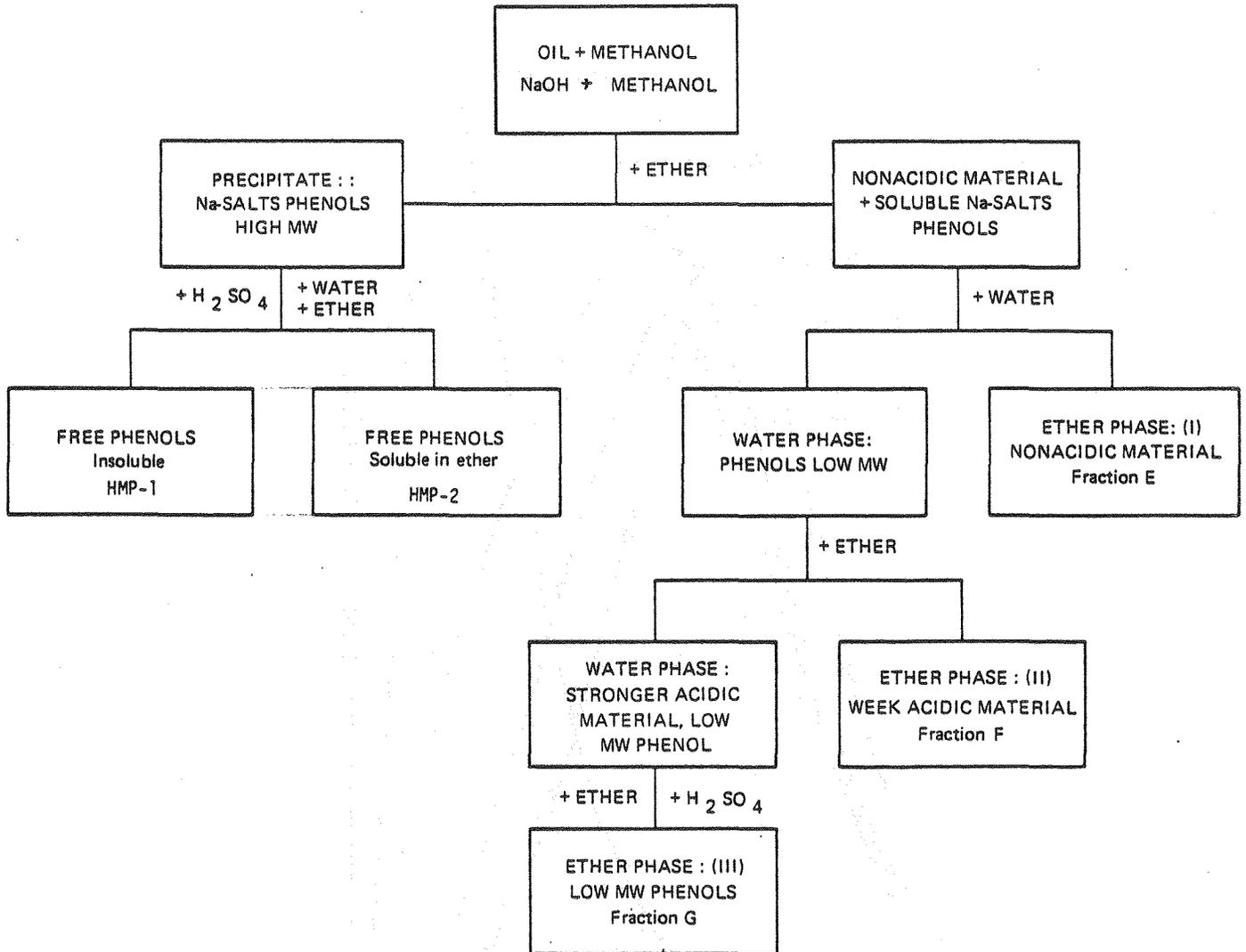
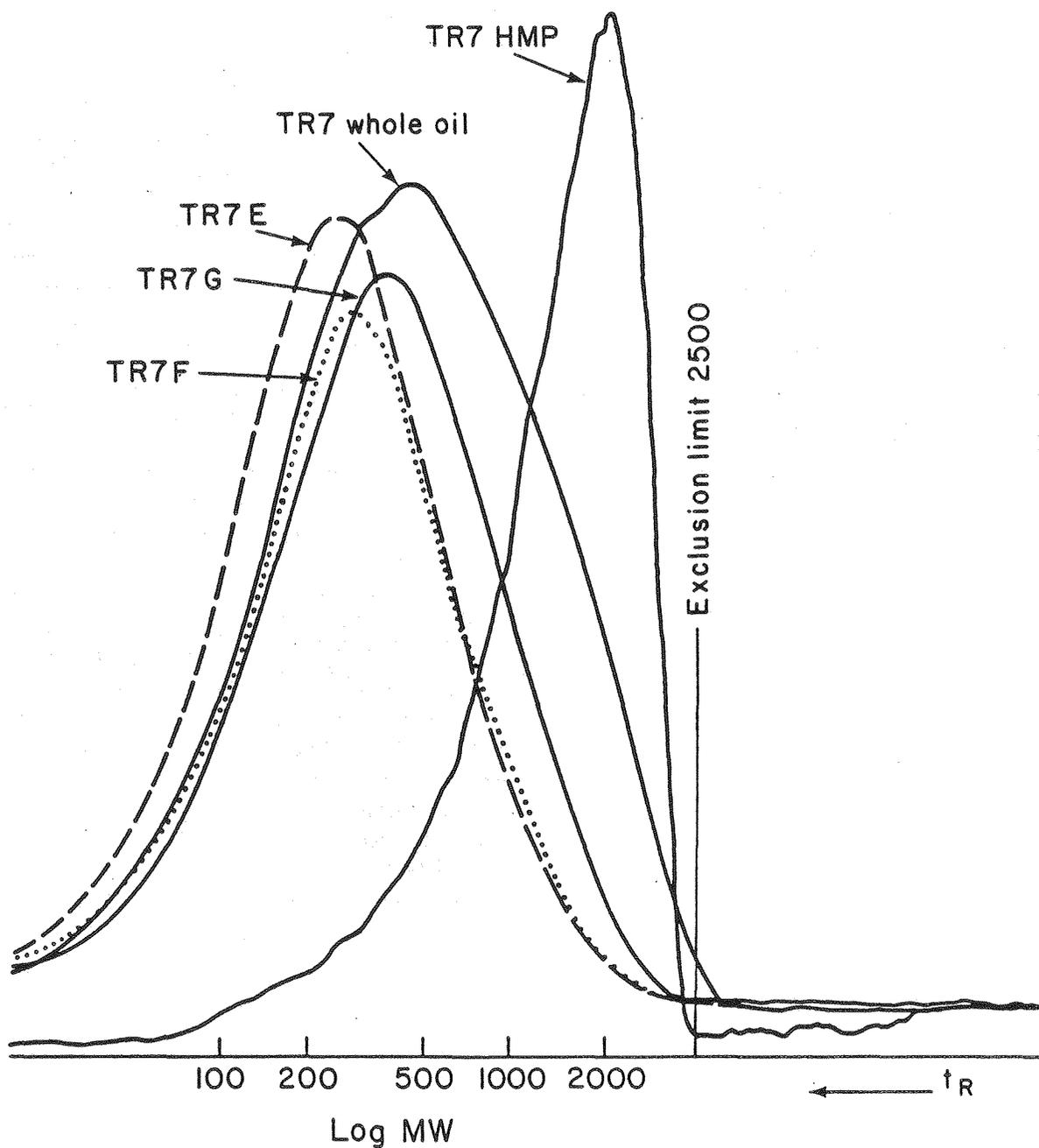


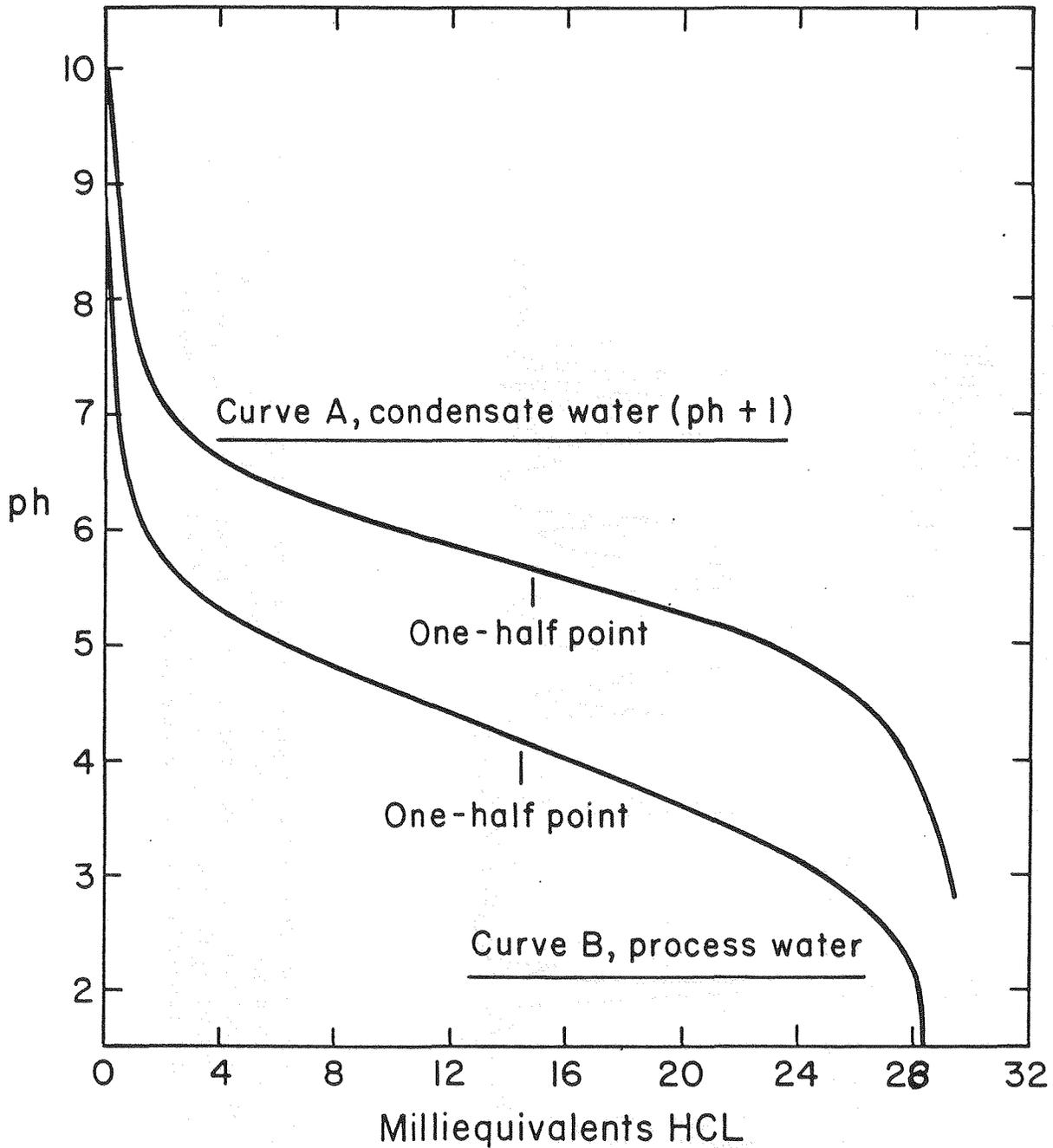
Fig. 3. Gel permeation chromatograms of TR-7 oil fractions. See text for explanation. Conditions were the same as those indicated in Fig. 1.

Gel permeation chromatograms  
of TR7 oil fractions  
UV 254 nm

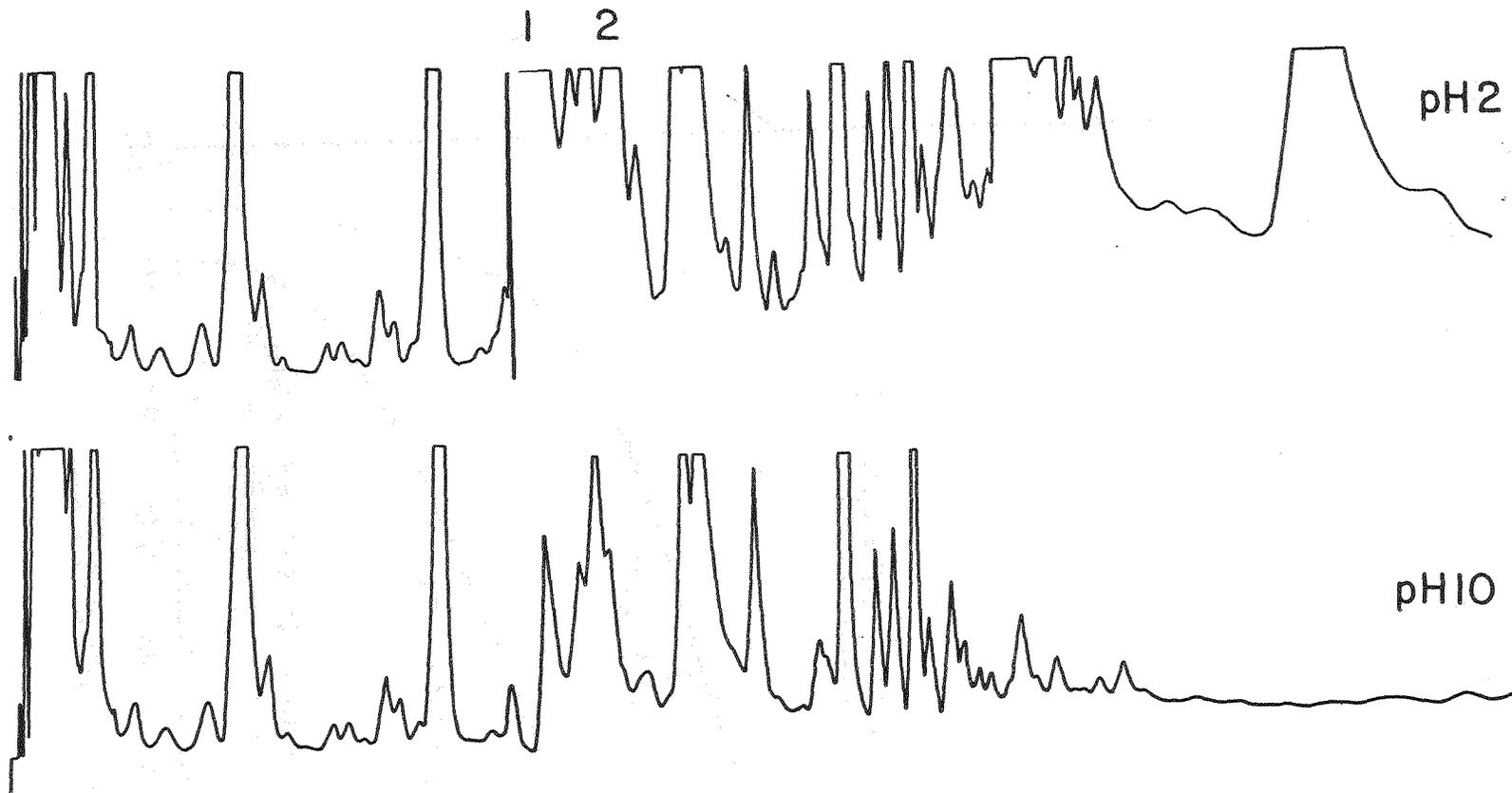


XBL 815-811

Fig. 4. Organic anion or acid content of aqueous product, PDU trun TR-12. Curve A - condensate from overhead vapor adjusted from pH 3.6 to pH 8.9 before titration with 1N HCL; 112-g sample; pH + 1 vs. meq HCL x 5. Curve B - liquid aqueous product, adjusted from pH 7.7 to pH 9.5 before titration with 1N HCL; 8.0 g sample; pH vs. meq HCL.



XBL 815-810



-34-

XBL 815-814

Fig. 5. Gas chromatograms of aqueous phase from batch autoclave run RA-23 (330°C for 30-min). A 4' x 2 mm i.d. column packed with AT-1000 was used with FID detection. The upper curve (pH 2) shows acids and neutrals while the lower curve (pH) shows only neutrals. Acetic acid (1) and propionic acid (2) are identified on the upper curve.

## BIBLIOGRAPHY

- (1) H. R. Appell, Y.C. Fu, S. Friedman, P.M. Yavorsky, and I. Wender, Bureau of Mines Report of Investigations 7560, U.S. Dept. of Interior, Washington D.C., 1971.
- (2) D. C. Elliott "Description and Utilization of Products from Direct Liquefaction of Biomass," This Symposium, Poster 40.
- (3) Rust Engineering Co., Birmingham, Alabama, Technical Progress Report, U.S. Dept. of Energy Contract DE-AC01-78-ET-23032, April-June 1980, Aug. 7, 1980.
- (4) Rust Engineering., Birmingham, Alabama, To be reported.
- (5) H. Davis, S. Ergun, C. Figueroa, C. Karatas, D. Kloden, L. Schaleger, and N. Yaghoubzadeh, Catalytic Biomass Liquefaction Quarterly Report, U.S. Dept. of Energy Contract W-7405-ENG-48, LBID-339, January 1981.
- (6) K.V. Sarkanen and C.H. Ludwig, "Lignins, Occurrence, Formation, Structure and Reaction," p. 55, also 639-694; Wiley-Interscience, New York, 1971.
- (7) D.C. Elliott, Preprints, Div. Fuel Science, Am. Chem. Soc., 25, No. 4, 257-263 (1980).
- (8) H. Davis, S. Ergun, C. Figueroa, C. Karatas, D. Kloden, L. Schaleger, and N. Yaghoubzadeh, Catalytic Biomass Liquefaction Quarterly Report to U.S. Dept. of Energy, Nov. 1980, LBID-314.
- (9) H. Davis, R. Djafar, S. Ergun, C. Figueroa, C. Karatas, L. Schaleger, M. Seth, J. Wrathall, N. Yaghoubzadeh, and G. Yu. Catalytic Biomass Liquefaction Quarterly Report to U.S. Dept. of Energy, Aug. 1980, LBID 272.
- (10) H. Davis, S. Ergun, C. Figueroa, C. Karatas, D. Kloden, L. Schaleger, and N. Yaghoubzadeh. "Research and Development Activities on Direct Liquefaction" Quarterly Report to Battelle Pacific Northwest Laboratories, LBL-12537, April 1981.
- (11) Rust Engineering Co., Birmingham, Alabama, Technical Progress Report, Oct.-Dec., 1980, U.S. Dept. of Energy Contract CE-AC01-78ET-23032, June 1981.
- (12) H. Davis, Lawrence Berkeley Laboratory Report, LBL-12331, UC-61, DOE Contract W-7405-ENG-48, March 1981.
- (13) H.R. Appel, Y.C. Fu, E.G. Illig, F.W. Steffgen, and R.D. Miller, Conversion of Cellulose Wastes to Oil. U.S. Bur. of Mines, Rep. of Investigations 8013, 1975.

- (14) E.J. Soltes, This symposium, paper 11; "Biomass Pyrolysis--Towards an understanding of its complexity, versatility, and potentials."
- (15) T.J. Elder, E.J. Soltes, Wood and Fiber, 12(4), 1980, "Pyrolysis of Lignocellulosic materials; Phenolic Constituents of a Wood Pyrolytic Oil."
- (16) J.A. Knight, Progr. Biomass Convers. 1979, 1, 87-115; "Pyrolysis of Wood Residues with a Vertical Bed Reactor."
- (17) J.A. Knight, U.S. Environ. Prot. Agency, Off. Res. Dev. (Rep) EPA 1979, EPA - 600/9-79-023b; "Pyrolysis Oils from Agricultural and Forestry Residues and Municipal Solid Waste."
- (18) J.A. Knight, Fuels Energy Renewable Resour., (Symp.) 1977, 169-95; Editor: Tillman, David A., Sarkanen, Kyosti V., Anderson, Carry, Academic, New York.