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Publication Date

1983-06-01

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DIRECT LIQUEFACTION OF BIOMASS
FINAL REPORT AND SUMMARY OF EFFORT 1977-1983

H.G. Davis

June 1983

ENERGY
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DISCLAIMER

DIRECT LIQUEFACTION OF BIOMASS

Final Report and Summary of Effort 1977-1983

LBL Biomass Group

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EXECUTIVE SUMMARY

This report covers the work during the period 1977-1982 of the Lawrence Berkeley Laboratory Biomass Liquefaction Group. Emphasis is on the period from August 1980 to December 1982 when most of the experimental work discussed was carried out.

The early years of the group were largely devoted to developing the water-slurry (LBL) process including the prehydrolysis step which proved essential to achieving a concentrated pumpable slurry. This was, of course, the basis for the first yield of true wood-derived oil at the Albany PDU, and indeed of the highest quality oil (TR-7) produced. From FY81 on, the effort centered around operation of the bench-scale continuous liquefaction unit (CLU), used to identify the yields and problems of the water-slurry process. The continuous reactor program was supplemented by a batch autoclave effort and by an extensive effort to characterize products and identify the chemistry of reaction.

Liquefaction processes

Data were obtained indicating that dissolution in heavy recycle oil (solvolysis) is a superior front-end process for biomass liquefaction. When solvolysis at about 240°C is followed by hydrogenation over a commercially available catalyst a volatile product distilling largely in the gasoline range can be obtained. This process is strongly recommended for future development.

Of the existing processes, we conclude that the PERC process can indeed make a fairly high yield of heavy biomass oil (40 to 55% depending on how much oxygen is left in the oil). Very high recycle ratio of oil, effluent water and water- solubles, a sizable consumption of CO and the need for drying and grinding the feedstock make the economics questionable. The LBL water-slurry process avoids drying, grinding, and recycle, but results in higher yields of water solubles and therefore lower yields of oil. In both cases there is a water disposal problem (a worse one with the LBL process) and in both cases the product oil is unlike petroleum and is suited only as boiler fuel.

The potential advantages of solvolysis in heavy recycle oil over both PERC and LBL are many. Grinding and drying are avoided, large amounts of water do not have to be carried through the process, yields of water-dissolved organics are minimal and the basic product can be a distillate. While this distillate will contain some ketones and unsaturates and also phenols and aromatic ethers, the first two types can be removed by hydrogenation and the phenols can be alkylated. This procedure should produce useful automotive fuels -- potentially even octane improvers. Present indications are that the recycle ratios will be low (of the order of 4 to 1 oil with little or no aqueous recycle). Hydrogen, rather than CO, is consumed and probably in reasonable quantities (e.g. < 2000 SCF/barrel product). A hydrogenation catalyst will be required, but use of sulfuric acid can be avoided. So also can use of sodium carbonate as a catalyst.

Chemistry

The LBL group made substantial contributions to the understanding of the chemistry of oil products, and especially of the water-dissolved organics product, and of the roles of carbon monoxide and sodium carbonate in the process.

In the oil product we identified large numbers of individual compounds, supplementing the extensive effort at Pacific Northwest Laboratory (PNL). More importantly, methods of fractionating by polarity, acidity and molecular weight were developed. The picture of a typical wood-oil, with oxygen content in the range of 12-17 wt %, was formed. It contains a high percentage (70% or more) of compounds with one or more phenolic groups and has an average molecular weight in the 200-300 range. It contains 20% or more by weight of material which should be distillable at atmospheric pressure. Furthermore, if this is distilled off, additional lights can be formed from the residue by hydrogenation.

The water effluents contain substantial numbers of highly soluble organic compounds. About half are carboxylic acids and their anions, largely glycolic, acetic, and formic. The balance includes phenols, especially diphenols, and neutrals, including cyclic ketones. Effects of reaction temperature, process gas composition and pH on yields of these organics were identified. It was suggested that some of the CO consumed in the PERC process reacts with dissolved organics to form CO_2 and oil-soluble product.

It was shown that carbon dioxide formed in the CO-steam liquefaction processes arises from three sources. Largest is commonly the water gas shift reaction, whereby CO and H_2O are converted to CO_2 and H_2, a considerable economic loss. In PDU run TR-12, this loss was about 1.4 lb mols (500 SCF) per 100 lbs of dry wood fed. Pyrolytic CO_2 -- presumably formed by decarboxylation of intermediate carboxylic acids -- is of the order of 0.6 mol/100 lbs wood. And CO_2 formed by reaction of gaseous CO with oxygen in intermediate products is 0.0 to 0.7 lb mol /100 lbs wood depending on the reaction time, temperature and amount of recycle.

Many biomass substrates have been tested and found to undergo the liquefaction reactions. These include Douglas fir and aspen woods, agricultural residues like straws, walnut and coconut shells, and "energy" plants like euphorbia. We conclude that almost any biomass, not overly contaminated with ash, can be handled by direct liquefaction or the solvolysis route.

Of the constituents of woods, lignin is largely converted to biomass oil, while the cellulose and hemi-cellulose fractions give relatively high yields of water, carbon dioxide and water-solubles. In solvolysis a feed containing 45% cellulose, 30% hemicellulose and 25% lignin would be predicted to yield 45·0.52 + 30 · 0.44 + 25 · 1.0 = 61% of crude, net solvolysis product. Products from all three major wood components are highly aromatic with H/C atomic ratios close to 1.0. Crude solvolysis product still contains much of the biomass oxygen (over 20 wt %). When this is reduced to a desirable level, say 8-15%, yields in the range of 50 - 55% are the maximum possible.

1.0 INTRODUCTION

Efforts to generate a feasible process for liquefaction of biomass in an atmosphere of steam and carbon monoxide were initiated at the Pittsburgh Research Station of the U.S. Bureau of Mines in the 1960's.[1] Under the stimulus of a restricted petroleum supply ERDA and later DOE supported construction of a process development unit (PDU). This was designed and built at Albany, Oregon between 1974 and 1976. Initial efforts to operate the PDU as designed were frustrating. In 1977-78 a group was formed at Lawrence Berkeley Laboratory (LBL) to provide technical monitoring and to assist the PDU staff (Rust Engineering, a division of Wheelabrator Cleanfuel) in getting the PDU operational. The present report covers the achievements of the LBL biomass group from 1978 until the end of calendar year 1982, and especially from FY 81 to the present.

In the course of the work at Albany and at LBL, two modes of operation — incipient processes — evolved. The original process, as developed at the Pittsburgh Laboratory, involved feeding fresh Douglas fir as a slurry of dried, finely ground wood in a recycle oil. By 1976, the Pittsburgh Laboratories were known as PERC, and the process was dubbed the PERC process. The initial slurrying vehicle was coal-tar anthracene oil. Through 1979, no oil product which was not almost totally start-up oil had been made by this process.[2]

In 1978, the LBL group[3] began experimental studies of an alternate procedure. A prehydrolysis step was introduced. This allowed wood chips to be broken down in a pump refiner and slurried in water. After some indications of success in their runs 3, 4 and 6 (TR-3,4, and 6), Rust Engineering succeeded in TR-7 in producing five barrels of oil derived 100% from wood. In 1980, additional oil was produced from water-slurries in TR-10 and TR-11. The PDU was not well- adapted to operation in the LBL mode, and perhaps all that can be said for these runs is that they produced product and demonstrated the inherent operability of certain important steps in the process.

In 1979, the decision was made to build a bench-scale continuous unit at LBL. The was first called the PEU, for "process evaluation unit," and later the CLU, for "continuous liquefaction unit." The purpose was to get basic data on the liquefaction process, data which it was recognized could not be obtained satisfactorily from batch experimentation. The unit was completed in early 1980. First efforts to operate it were abortive and it was redesigned and rebuilt between August 1980 and January 1981.

The CLU was designed as a tubular reactor. However, at laboratory scale flow rates, presumably in a laminar flow regime, the 1/4" I.D. tubing plugged fairly rapidly. The reactor section was, therefore, replaced with a one-liter stirred autoclave [5] and operated thereafter as a CSTR. From mid-1981 on, the revised CLU operated successfully. Much of our present understanding of the possibilities and problems of the water- slurry liquefaction process comes from the CLU runs.

In the early period of the biomass liquefaction effort, relatively little attention was given to the chemistry of the process. The significance and chemical fate of the sodium carbonate "catalyst" used in both processes, were not understood. The size and nature of the substantial yields of water-soluble organics in both processes were not known. The overall stoichiometry of the processes was not established. This includes the quantitative usage of carbon monoxide as a reductant and by water gas shift, the amounts of pyrolytic carbon dioxide and water formed, and the distribution of product between oil, gases, and water-soluble organics. Characterization of the oil and water-soluble product fractions had barely been started.

Certainly, the state of the answers to the questions implied above has been greatly improved by the work at LBL. This will be covered in some detail in the body of the report.

As work progressed in 1981-82, it became progressively clearer that neither the PERC nor the LBL water-slurry approach to liquefaction had much chance of achieving commercial feasibility without drastic improvement. The limitations of these approaches will be discussed further below.

Both processes are efforts to solve the front-end problem: How do we get biomass into a liquefaction reactor at a high concentration and a high rate without fouling up the product distribution and without mechanical problems? A third possibility, referred to as "solvolysis," has been studied almost from the beginning of the LBL group.[6] When wood chips, or other biomass forms are heated with a phenolic solvent at temperatures in the range of 180-240°C, they disintegrate, forming a homogeneous solution or mixture with the solvent. While much of the basic work was done with phenol itself, the highly phenolic biomass product oil is the ideal solvent. Use of a hot recycle oil was therefore considered from the beginning[7,8]). It was demonstrated in early 1981[9]: unground (and undried, if desired) wood chips, with hot wood oil form a homogeneous product which is essentially completely soluble in such solvents as acetone.

To use solvolysis in a process we must have a method of regenerating a recycle solvent. This requires a cracking, or more probably hydrocracking step, in sequence with the solvolysis; i.e., a process sequence similar to that of several coal hydrogenation methods. During the final period covered by this report, hydrocracking with available commercial catalysts was studied briefly. The results can be termed promising but not definitive. They will also be covered in this report.

The work done here, primarily with Douglas fir wood as substrate, has been shown, by batch studies of both liquefaction and solvolysis, to apply to a variety of substrates. These include walnut and coconut shells, beet pulp, rye grass and rice straws, "energy" plants like euphorbia, calotropis and Jerusalem artichoke, and even peat. We suspect that both the water-slurry process and solvolysis apply to almost any biomass or biomass-like form of feedstock. Aspen, a hardwood, was found to be a superior feedstock in terms of yield and quality of oil.

The body of the report will follow the following general form: summary of the present state of the liquefaction effort, including a critique of the existing processes; discussion of CLU operation; summary of the work on solvolysis and hydrocracking; summary of the LBL work on characterization and analysis of product oil and water-solubles; and discussion of stoichiometry and chemistry. A brief history of the LBL project and a bibliography of reports, papers and presentations are appended.

2.0 SUMMARY OF PRESENT STATE AND CONCLUSIONS

From our present state of knowledge of liquefaction we can state with confidence that the existing oil recycle slurry and water slurry processes cannot be made commercial without substantial improvement. The most attractive approach to such improvement lies in a combination of solvolysis with a pyrolysis and/or reduction step.

In form, the ultimate process will probably look somewhat more like the present PERC process than like the LBL process. In fact, if in the PDU it had been possible to blend wood and recycle oil at an elevated temperature, many of the objections to the PERC process might have been countered.

In this section we give brief summaries of the strengths and weaknesses of the PERC and LBL processes and of the possibilities for a solvolysis process. Also a summary of our present understanding of the chemistry of the general process and the chemical make-up of the products, plus some recommendations for future work. A brief description of the two processes is given as an appendix to this section.

2.1 LBL or Water-Slurry Process

In the LBL process, a partial hydrolysis followed by pulp refining is used to break up the woody structure, shorten the fibers and promote slurry formation. Even 10 wt % slurries of wood flour, in water or in recycle oil, are very difficult to pump. After prehydrolysis pumpable slurries with as high as 30-35 wt % total organics have been made. About 20% is the highest concentration that has been fed continuously into either the PDU or CLU reactors.

Operation in the PDU has demonstrated that such slurries can be heated to reaction temperatures in a direct-fired preheater. Rust Engineering's success in heating slurry at 50 to 60 gal per hour in a 0.43" I.D. x 139 ft. long tube is a significant accomplishment. It indicates that the problems of indirect heating in the CLU's original 0.25"I.D. reactor are primarily problems of tubing size, flow rate and Reynolds number.

Yields of wood oil at the PDU were all lower than 30 wt %. In the CLU operation, after an initial period during which internal surfaces were coated with product, yields were in the mid-thirties. In the CLU some coke was always found in the stirred autoclave. We believe this to be largely the result of the high heat flux through the autoclave wall. Under a more ideal heating situation, as in the turbulent tubular heater of the PDU, coking should be a lesser problem. If this is so, the yields of oil should be 40 wt % or a little higher.

This is still significantly lower than the best PERC yields, about 53% at comparable severities in PDU TR-12. The discrepancy comes from the much greater yield of water-dissolved organics in the LBL process, about 25 wt % vs. about 8 wt % in TR-12.

Experiments showed[10] that much of the water-soluble product and very little of the oil comes from the dissolved pre- hydrolysate. Thus if the aqueous phase could be recovered and treated separately, perhaps fermented, there would be some advantage. An economical way of doing this without undue dilution is not available so far, and in any case removal of the hydrolysate would reduce the overall yield of oil -- say from 40% to 35%.

While recycle of aqueous effluent appears at first glance to be a possible solution to the problem of handling water- dissolved organics, this is probably not feasible. To recycle water to the prehydrolysis step, the large content of carboxylate ions must be converted to acids with sulfuric acid. More acid is then added to bring the pH to below 2. After hydrolysis, both sulfuric acid and the carboxylic acids must be neutralized with sodium carbonate. The usage of sulfuric acid and sodium carbonate is uneconomically high. Simulated recycle experiments were nevertheless run[11]. These indicate that the organic acids and/or their ions are stable during recycle and build up in the system. The severity level of the experiments was rather low (oxygen content of oils ~ 20%), and somewhat more decomposition would be expected under the conditions of PDU runs TR-8, 9 and 12 with their high recycle ratios.

The advantages and disadvantages of the LBL process may be summarized as follows:

Advantages	Disadvantages
1. Once through - no recycle	1. Much water must be heated, partially vaporized and cooled.
2. Grinding and drying not necessary.	2. Large yield of water dissolved organics at low concentration (~ 6% in aqueous phase).
3. Little or no reducing gas is consumed in the process.	3. Oil yields are at best about 40-42% and oxygen content of oil is high (12-17%).
4. Possibility of using hydrogen or an inert gas in place of CO,	

2.2 PERC or Oil-Recycle Process

In the PERC process, wood or other biomass is dried, ground to flour, then blended with recycle material and aqueous sodium carbonate. Slurries above about 11-12 wt % cannot be pumped. In practice, Rust Engineering[2,12] averaged only 7.5 wt % wood in their feed to their best runs, notably TR-12. Initially coal tar anthracene oil has been used as the slurrying vehicle. Because of the low concentration of wood, it requires many passes through the reactor system before high concentrations of wood-derived oil can be formed in the exit oil.

Products from TR-8 and TR-9 contain substantial amounts of anthracene-oil derived compounds -- principally polycyclic aromatics like phenanthrene. However, the final product from TR-12 is almost 100% wood-derived oil.

Product oil is recycled as recovered; i.e., with the aqueous phase unseparated. From the data given by Rust Engineering , a typical feed was about 7.5% wood, 25% aqueous phase (including recycled sodium salts and organics and added sodium carbonate) and 67.5% wood oil. If 0.52·7.5 or 3.9% new oil is made, the recycle ratio is 67.5/3.9 or 17/1. With slightly different assumptions on average feed composition, we have estimated ratios as high as 19/1. In any case the ratio is high and both oil and water are heated and cooled many times.

Despite this high recycle ratio, it proved possible to get excellent overall material balances. From the data we have been able to put together[13] acceptable atom balances. From these we calculated carbon monoxide consumptions of 0.3 to 0.7 lb Mol per 100 lbs dry wood feeds. At a severity sufficient to give an oxygen content of oil equal to 16% (achieved in the CLU water- slurry runs at about 350° C), the usage was about 0.5 Mol/100 lbs. A large amount of additional CO reacted by water-gas shift, typically about 1.4 lb Mol per 100 lbs dry wood fed. While this is not a net loss of synthesis gas (H_2 is formed in equivalent amount) it is nevertheless a severe economic loss if CO is the required reducing agent. The reverse shift, $H_2 + CO_2 \rightarrow H_2O + CO$, is not practicable.

Yields in TR-12 were about 52-53% of oil plus about 8% water-dissolved organics. The yields are compatible with the atom balances. Insolubles (char) were minimal -- about 1% of feed.

Besides establishing the yields and providing a basis for estimation of CO usage and other chemical features, TR-12 was particularly valuable for at least two reasons. First, it established that a wet-oil wood slurry could be heated to as high as 370°C in a small diameter direct-fired tubular heater without serious coking problems. Second, it established that wood oil could be recycled through the system many times without serious build-up of insolubles. Overall average residence times for the oil were of the order of five to seven hours. This indicates a degree of stability of the product oil that would not have been predicted, but which is also verified by tests run during TR-8.

Thus while the recycle ratios were inordinately high, TR-12 must be considered to offer promise of acceptable operability if an economic mode of operation can be established.

We have used somewhat less accurate balances[14,15] available for PDU TR-8 [2] to estimate PERC stoichiometry at a higher conversion severity (O in product oil (about 8%). For this run we concluded that slightly more pyrolytic water and CO_2 were formed than in TR-12 (0.7 mol and 0.7 mol/100 g dry feed, respectively, vs. 0.5 mol and 0.6 mol). Carbon monoxide usage was calculated to be somewhat less (0.4 mol/ 100 g dryfeed vs. 0.7 mol at the highest severities in TR-12). This lower usage of CO and higher formation of H_2O and pyrolytic CO_2 results in a

product of lower oxygen, but also of lower H/C ratio than resulted from TR-12. The yield of oil compatible with the admittedly approximate balance is 44 wt % (measured yield 43 wt %).

The advantages and disadvantages of the PERC process may be summarized as follows:

Advantages	Disadvantages
1. Relatively high oil yield.	1. Requires drying and grinding of feed.
2. Fair degree of operability established.	2. Low fresh feed concentrations. High recycle ratio of both product and water.
3. Aqueous organics are lower and at greater concentration (than in LBL).	3. Substantial net usage of synthesis gas.
	4. High conversion of CO to CO_2 and H_2 via shift reaction.
	5. Fairly large yield of aqueous organics to recover and/or dispose of.

2.3 CHEMISTRY AND STOICHIOMETRY OF THE PRESENT PROCESSES

In the overall process, biomass — typically 51% C, 5.8% H, 43.0% O, 0.1% N, 0.1% S — is converted to oil, which may be 76% C 7.8% H, 16% O, 0.2% other, assorted water-dissolved organics, estimated to average ~ 55% C, 7.5% H, 37.5 O, a little char, water, and CO_2. In TR-12 the distribution [13], when oil of 16% O is made, is as follows: oil 53% (including ~ 1% char or insolubles), water solubles 8%, water 7.2% (0.4 Mol/100 feed) and CO_2, 45% (1.02 Mol/100 lb feed). Of the CO_2, about half (0.55 mol) is pyrolytic, the rest (0.47 Mol) is formed by reaction of CO with O in the substrate. The CO_2 does not include that formed by water-gas shift, about 1.4 Mol/100 lb wood feed.

In the LBL process the stoichiometry has been much different. Yields are about 40% oil (including in the CLU runs 5% or more char), 25% water solubles, 9% H_2O (0.5 Mol) and 26% CO_2 (0.50 mol). Apparently little or no CO (or H_2) is consumed and all, or almost all the CO_2 is pyrolytic. We were not able to establish any dependence of yields or operability on the feed gas composition;* i.e., hydrogen was as good, or as bad, as CO. When CO is used, as expected, there is a large amount of

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* A minor exception, a small dependence of water-solubles yield and composition on feed gas analysis is discussed elsewhere in the report (Section 5).

shift reaction. When 100% H_2 is fed, a trace of CO is formed.

The water-solubles are roughly 50% carboxylic acids and 50% other (this is apparently true of the PERC water-soluble products also). 80-90% of the carboxylic acids from Douglas fir can be identified as formic, acetic, and glycolic (13, 16, 17), with glycolic the largest single product of the whole process and acetic acid second. Formic is relatively minor and its yield is strongly a function of pH and CO partial pressure. Clearly an important role of sodium carbonate in the liquefaction processes is simply to neutralize the acids formed. "Other" includes a large number of phenols, largely diphenols or other polyfunctionals, plus ketones, especially cyclic ketones and some furan- or furfural-derived products.

The oil products are highly oxygenated, only a few percent at most being classified as hydrocarbon. 70% or more of the molecules contain one or more phenolic groups, with ether functionality (mostly methoxy) common and some carbonyl. Qualitatively PERC and LBL oils appear to be similar.

The differences in CO consumption between LBL and PERC can be largely blamed on the differences in reaction time. Because of the high recycle, PERC products have been exposed far longer -- by a factor of 15 to 21 -- at reaction temperatures than have LBL products. If we compare LBL and PERC runs at the same O-content of oil, say 16%, we conclude that the LBL oil reached this O-level by the cracking out from the wood of CO_2 (about the same as in PERC), water (a little more than in PERC), and O-rich water solubles (much more than in PERC). We suspect that at least some of the CO which reacts in PERC, does so with water solubles to form CO_2 and oil.

Techniques[17] which have been useful in characterizing products and following the effects of reaction variables include the following: SESC (Sequential Elution by Solvent Chromatography[18,19], sequential solvent extractions to obtain phenolics and neutrals, GC and GC-MS, and a variety of high performance liquid chromatography procedures. These include HPSEC to obtain molecular weight distributions, HPIEC (ion-exchange) to measure the low-molecular weight carboxylic acids and other techniques.

2.4 SOLVOLYSIS

When biomass is heated with organic solvents containing hydroxyl groups, it tends to disintegrate and partially or completely dissolve in the solvent. It was found by Yu[6] that butanol and cyclohexanol are effective solvolytic agents and that phenol is particularly effective. The effect involves chemical reactions. Oxygen is lost from the biomass as water and carbon dioxide. Recovery of solvent by distillation is less than 100%. Phenol is incorporated to an especially high degree, as much as 75% of the weight of the dry wood. While we refer to the solvolytic agent as "solvent," it is obviously considerably more than a solvent.

It is equally obvious that the solvolytic agent, or an equivalent, must be regenerated; i.e., the process must involve an oil recycle. The recycle solvent must eventually approach some sort of heavy, highly phenolic, biomass-derived liquid. It makes more sense, therefore, to use an available biomass-derived oil as the initial solvent. In all our recent work [9,20,21], we have used TR-7 product, Douglas fir-derived oil from the 1979 LBL process run in the PDU. At about 240°C with ratios of oil to dry biomass as low as 2/1 or less, treatment with TR-7 gives essentially complete dissolution of Douglas fir or aspen wood chips, walnut shells and straws. We believe it will be effective with most forms of biomass. It is not necessary to add small amounts of mineral acid or to have particular ratios of water to biomass. This observation is contrary to Yu's findings with phenol or alcohols as solvent.

We have considered two possible process paths for converting the crude solvolysis mixture to product plus recycle. The most likely path involves a catalytic hydrogenation and hydrocracking step to reduce the molecular weight and remove part of the remaining oxygen. A schematic flow sheet is shown as Fig. 2.4-1. The recycle oil may be a portion of the whole product or a residue after a volatile product is withdrawn by distillation as shown in the figure. The alternate (Fig 2.4-2) is basically the PERC process with the solvolysis reactor replacing the lower temperature blender.

Batch experiments with several substrates [20,21] indicate that the hydrogenation scheme has a reasonable chance of working. Two extreme cases were used. In one, four parts TR-7 (or recycle) were added per part dry substrate (straw, walnut shells, aspen) and about 5% of a commercial copper chromite catalyst added. The mixture was heated in a 300 ml autoclave in hydrogen to 360°C and 4000 PSI, held for an hour then cooled. Overall reduction of oxygen content was high, with the product liquid typically having about 8 to 13% oxygen. The recovered liquids continued to be good solvolytic agents. In a second experiment with aspen chips, TR-7 topped to an IBP of 260°C was used as the starting solvent. The pyrolysis and hydrogenation steps produced low-boiling product equivalent to the expected yield from aspen. The solvolysis product was topped to 260°C and used as solvent. Again, low-boiling products were formed. However, excessive hydrocracking occurred, with formation of hydrocarbon gases and loss of solvent. The above runs are discussed further in Section 4.

In most of these experiments, consumption of hydrogen was low. Much of the reduction in oxygen content is due to pyrolytic action. In a continuous process the hydrogenation route is desirable provided an appropriate catalyst with an acceptable stability can be found. The advantages are (1) the use of H_2 and avoidance of CO and its losses by the shift reaction and (2) the probable avoidance of a need to use sodium carbonate. The sole advantage of the CO-steam route is the fact that -- if it works -- the findings at the PDU on the PERC process should be applicable.

FIGURE 2.4-1

SOLVOLYSIS / HYDROGENATION PROCESS SCHEMATIC

Wet biomass feed

Solvent recycle

Solvolytic reactor

To water treatment facilities

Hydrogen

To hydrogen & condensate recovery

Vent

Product oil

Process fuel

Oil/water separator

Hydrogenation unit

High pressure feed pump

Flash tank

Vacuum distillation column
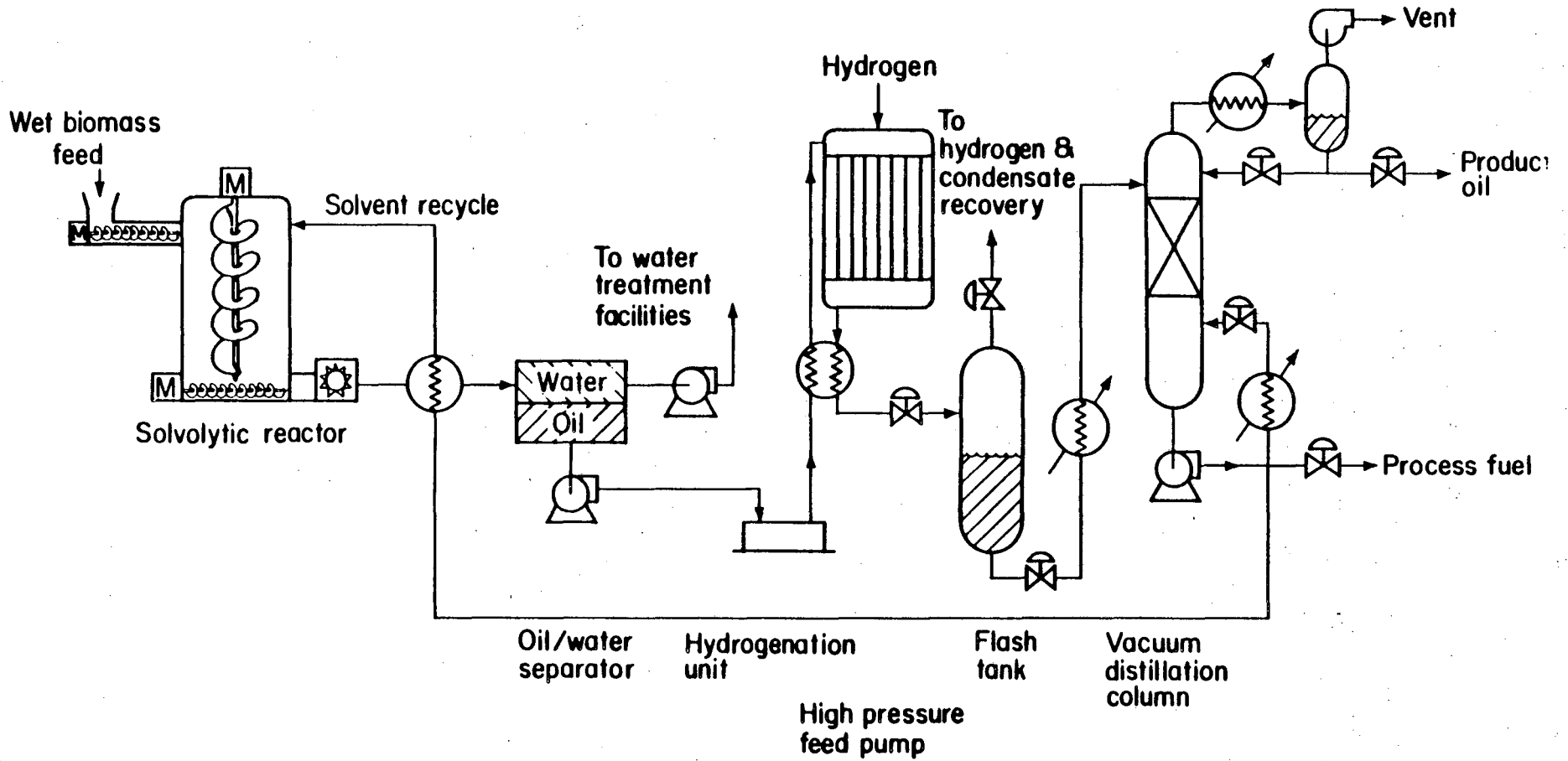
XBL 827-7096

FIGURE 2.4-2

SOLVOLYSIS / CO-STEAM PROCESS SCHEME

Wet biomass feed

Solvent recycle

Solvolytic reactor

To wastewater treatment facilities

$H_2(g)$
$Na_2CO_3(aq)$

To condensate & hydrogen recovery

Product oil

Oil/water separator

High pressure feed pump

Tubular reactor

Dissolver

Flash tank

Vacuum distillation column
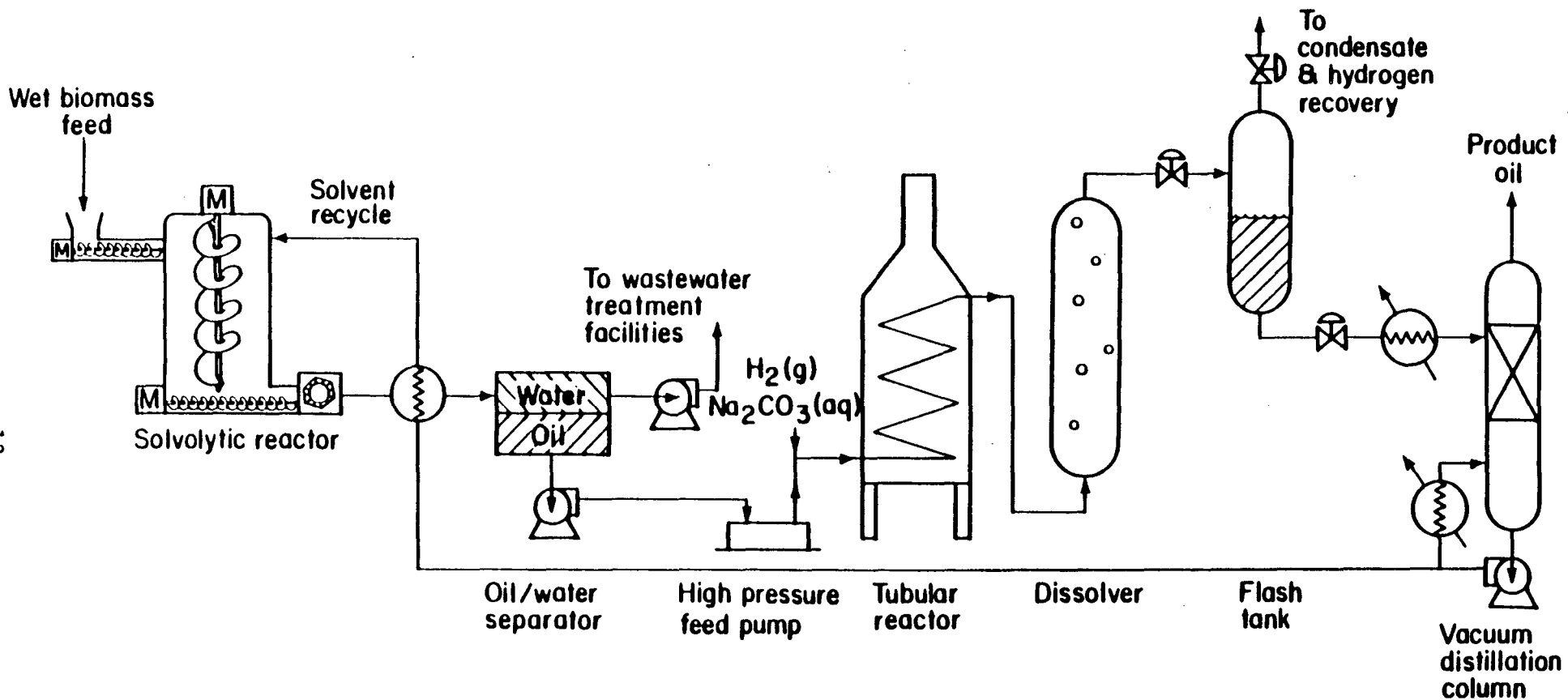
There was not time to carry out the experiment with 2:1 solvent: wood ratio through the needed number of simulated recycles. The results are, nevertheless, promising. A potential stoichiometry i.e., one reasonably compatible with the limited results available, is discussed in Section 4. It indicates probable yields of about 41% volatile oils (distillate at atmospheric pressure to head temperatures of 260-280°C) and about 10% fuel oil with hydrogen usage in the 1 to 2 wt % range (up to 2200 SCF/barrel of oil).

The volatile product from 100 lbs of biomass is mixed with 200 lbs of recycle solvent. Its concentration in the total effluent is therefore 16 wt %. From our experiments there is a reasonable probability that this percentage of volatiles can be recovered in a simple flash distillation — without recourse to vacuum. While the data are far from conclusive, they certainly point to a need to follow up the work at some time in the future. In practice some of the product would always have to be taken as heavy oil in order to purge insolubles from the system. The heavy purge oil would be used for plant fuel or to produce hydrogen or for both purposes.

2.5 CHEMISTRY OF SOLVOLYSIS

The chemistry of solvolysis is not well-established and deserves further study. Yu[6] concluded that phenol was incorporated into the solvolytic product in massive quantities — 75% by weight of dry feed. Alcohols (n-butanol, cyclohexanol, ethylene glycol) were also incorporated, but only at about 10% by weight of dry feed. He also concluded that oxygen was evolved from the feed primarily as water (with phenol as solvent about 1.3g mol/100 g feed). Only small amounts of CO_2 were evolved (0.1 mol/100 g).

Yu's work also shows that the H/C atom ratios of the crude product are low, ranging from 0.85 for the phenol product to 1.20 for the butanol product. After correction for solvent incorporation, under the assumption that the solvent is unchanged in composition, the residual H/C's are about 1.0 for the alcohol products, but only 0.74 for the phenol product. These results suggest (1) that the incorporated solvents, far from being unchanged, have lost hydrogen, as H_2O, perhaps as follows:

$$ROH + \acute{R}H \rightarrow R-\acute{R} + H_2O$$

or

$$ROH + \acute{R}OH \rightarrow R-O-\acute{R} + H_2O.$$
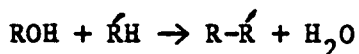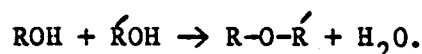
During summer 1982, we carried out[20] some exploratory experiments with phenol and elements of wood — alpha cellulose, xylan and kraft lignin.* The results show that each of these three materials, as would be expected, behaves quite differently.

At 240°C, for 45 minutes with a 2:1 ratio of phenol to dry feed, less phenol was retained than reported by Yu for whole Douglas fir. With cellulose, the retention was 57% of dry feed, with xylan (taken as representative of hemicellulose) 46%, with lignin 15%. If the whole (wood) can be taken as the sum of parts (say 45% cellulose, 30% hemicelluloses and 25% lignin) the average retention would be 43% — lower than reported by Yu, but still a very high number. Overall H/C ratios for the crude product were 0.8, 1.15 and 0.99 for cellulose, xylan and lignin, respectively. The H/C of the lignin product is not significantly changed from that of the feed (1.01), but the cellulose and xylan have obviously undergone profound change, forming highly aromatic mixtures.

Calculations based on mass and atom balances indicate that in the cellulose experiment 36g H_2O and 12g CO_2 were evolved per 100g dry feed leaving a net product of 52 wt %. With xylan 20g H_2O and 36g CO2 were evolved leaving 44% net product. With lignin, H_2O and CO_2 evolved were not significant within the accuracy of the calculation, so that the net yield is about 100%. If we calculate whole biomass as the sum of 45% cellulose, 30% xylan and 25% lignin, water evolved is 22g/100g feed (1.2 mol), CO_2 is 16g (0.37 mol) and liquid yield, phenol-free, is 62 wt %. The predicted elemental analysis is C – 72%, H – 5.6%, O – 22%. (H/C = 0.93.) From the H/C ratio it is clear that the solvolysis product is highly aromatic and that there must be some linkage of aromatic rings by direct ($C_A - C_A$ or $C_A - 0 - C_A$) bonding.

SESC fractionation indicates that most if not all of the retained phenol is bonded. Fraction 4, in which phenol is eluted, is a little higher than normal ("normal" is about 20 + or - 20% for CLU or PDU wood oils) in the xylan product, but lower than normal in the cellulose and lignin products. In all three cases there can be very little free

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phenol.

In summary, during solvolysis water is evolved, especially from the cellulose and hemi-cellulose components and CO_2 is evolved, especially from hemi-cellulose. As a result, a highly aromatic product, with some C_A-C_A or C_A-O-C_A inter-ring bonding, is formed. There is considerable depolymerization of the wood components, but there is chemical interaction between substrate and solvolytic agent, especially with the cellulose and hemicellulose components.

2.6 BRIEF DESCRIPTION OF PERC AND LBL PROCESSES

PERC (Fig. 2.6-1): Wood is dried, ground to flour and slurried in a blender with a wet recycled product oil. Sodium carbonate catalyst (4 to 6% of the weight of wood) and additional water are added. The mixture is heated rapidly to a reaction temperature of 330 to 370 °C in a directly fired tubular heater, with a flow of reducing gas (3 to 6 kg mols CO + H_2 per 100 kg wood), then passed through a tubular or stand-pipe reactor with volume sufficient to allow a space-time of 10 to 30 minutes. Reactor pressure is about 200 atmospheres. After cooling and pressure let-down, a portion of the exiting wood oil is withdrawn as product and separated from the aqueous effluent. The remaining oil is recycled, without separation of water, to the wood-flour blender. In the absence of an existing stock of satisfactory wood oil, coal tar anthracene oil is used as the initial slurrying medium. Yields of wood oil from Douglas fir are in the range of 40 to 55%, depending on the severity of operation, i.e., on the degree of reduction of the oxygen content from the 40-45% level of wood. There are also substantial yields of water-soluble organics, including carboxylic acids or their anions. The remainder of the wood is lost as carbon dioxide and water.

LBL (Fig. 2.6-2): Wood chips with only incidental air drying, mixed with water, are brought to pH 1.9 (about 0.075% sulfuric acid). The mixture is heated at 180°C for 45 minutes to prehydrolyze the hemi-cellulose content and greatly weaken the structure of the wood. Sodium carbonate is added to bring the mixture to a pH of about 8 and it is homogenized by passage through a refiner. Slurries of total organic content in the range 20 to 30% or higher are obtained. Slurry is heated to reaction temperature with reducing gas in a direct-fired tubular heater as in the PERC process. Additional residence time is obtained by passage through a turbulent tubular reactor or other well-stirred reactor. The effluent mixture, after cooling and pressure let-down, is separated into aqueous and oil phases. Total oil plus water-soluble product is about the same as in the PERC process, but there is a higher proportion of water-solubles, at least partly because of the lack of recycle. While the "turbulent tubular reactor" is desirable, it was not available in either PDU or CLU runs.

FIGURE 2.6-1

PERC LIQUEFACTION PROCESS

DRY WOOD FLOUR

BLENDER
100°C

SYNGAS — SODIUM CARBONATE IN WATER SOLUTION

GAS-FIRED HEATER

330-370°C

PLUG FLOW REACTOR

300-340°C

COOLER, PRESSURE LETDOWN

FLASH TANK

WET RECYCLE OIL

OIL PRODUCT RECOVERY

CONDENSATE RECOVERY

OIL

AQUEOUS EFFLUENT

LIGHT LIQUID

OFF-GAS

XBL 823-195
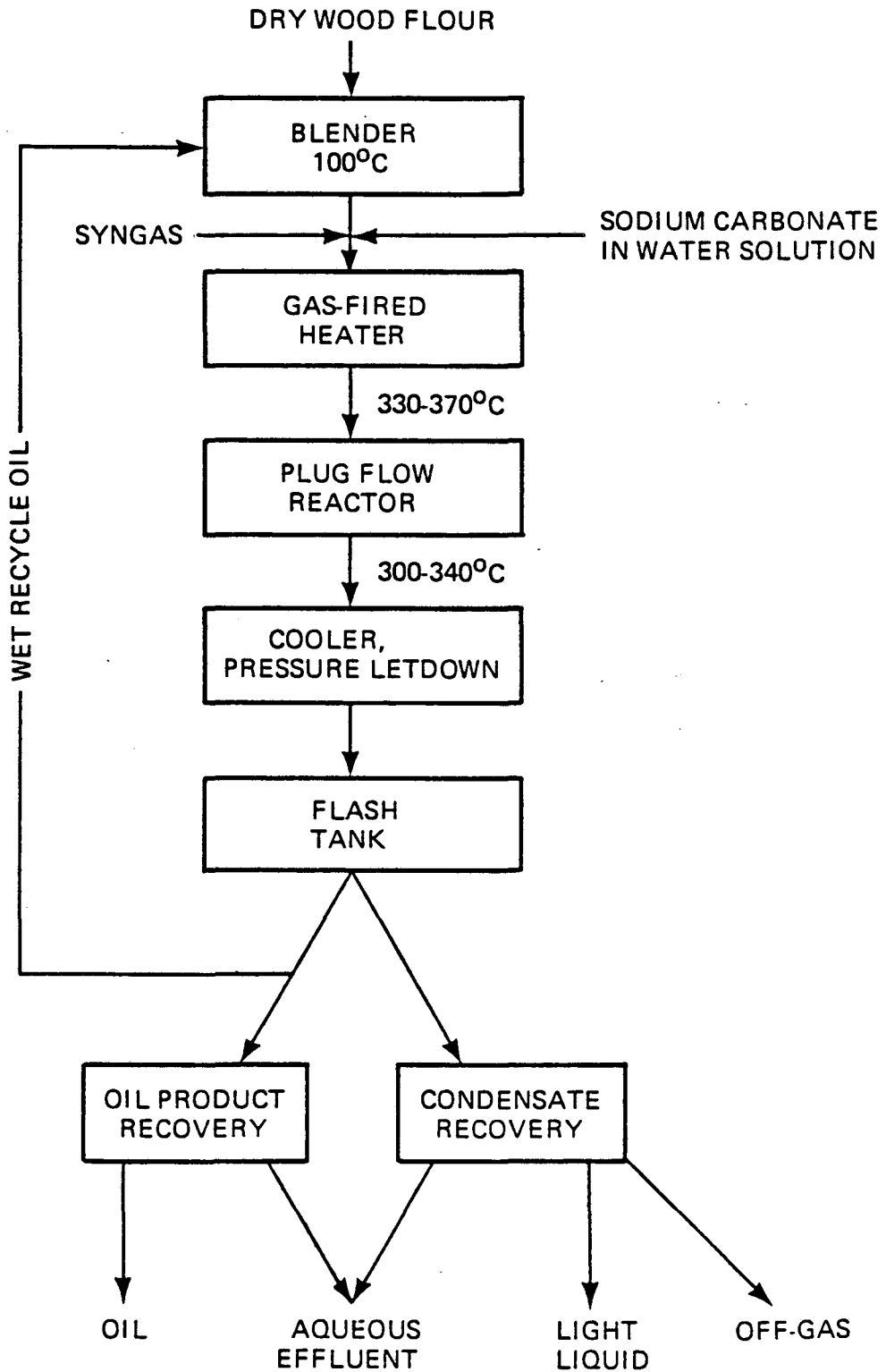
FIGURE 2.6-2

LBL LIQUEFACTION PROCESS

WOOD CHIPS

0.07% Sulfuric acid
in water

PREHYDROLYSIS
180°C
pH 1.9
45 min

Sodium carbonate

MECHANICAL
REFINING

Water slurry   (20-30%) Solids

REACTOR
330-360°C
2500-3500 psig
5-60 min

REDUCING GAS
(CO, H_2, or SYNGAS)

HEAT RECOVERY
AND COOLING

PRODUCT RECOVERY
AND
CRUDE SEPARATION

AQUEOUS EFFLUENT   OIL   OFF-GAS

XBL 8111-1529

-18-
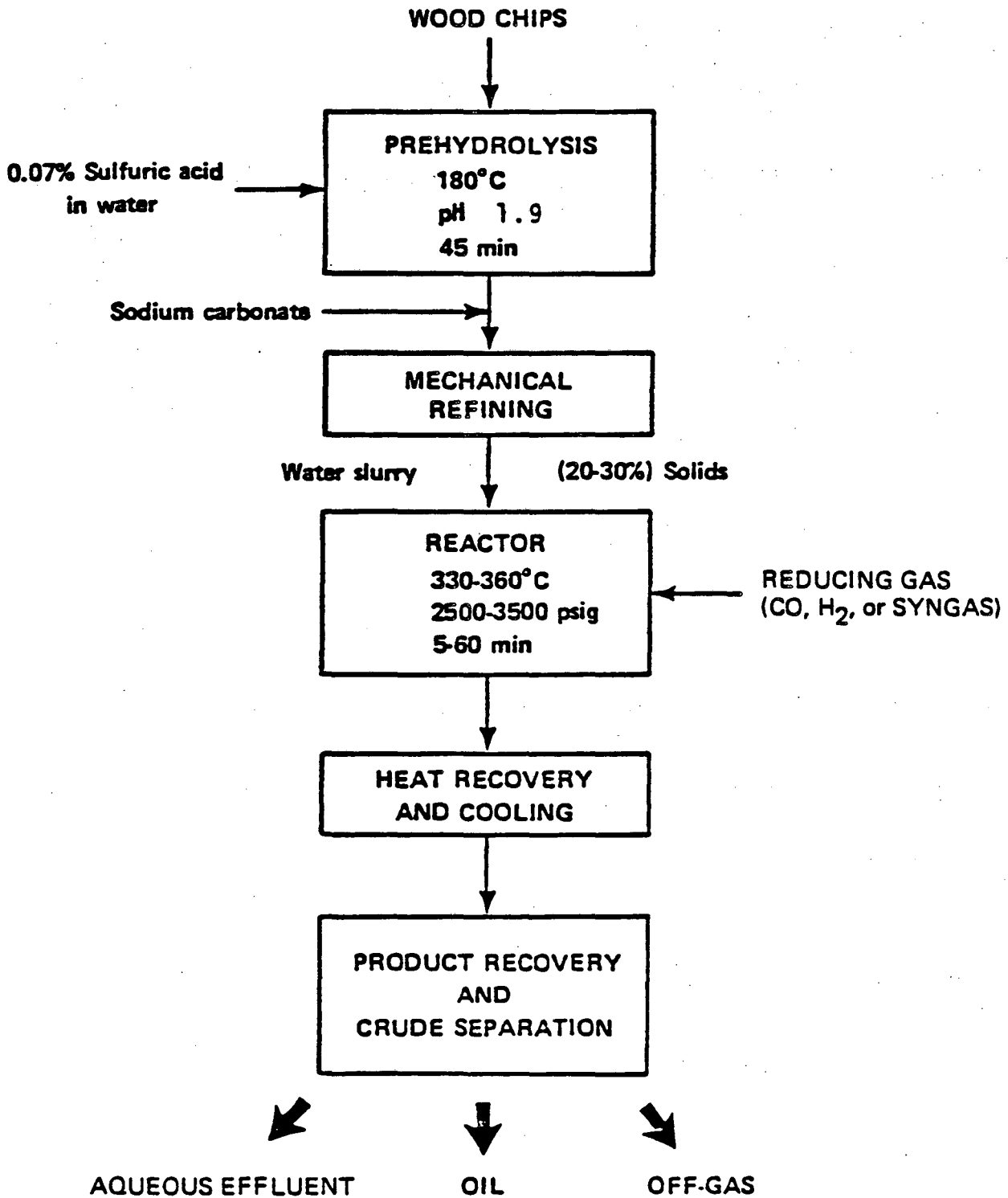
3.0 CONTINUOUS LIQUEFACTION UNIT (CLU)

Summaries of the CLU results have been given in numerous presentations and reports, especially references 13, 16, 20, 22 and 23. Operation of the CLU was successful in demonstrating the typical product yield distribution in the single-pass water slurry process, including the unfortunately large yield of water-dissolved organics. An insensitivity to the process gas, CO, H_2 or synthesis gas, was demonstrated and effects of temperature and pH were determined. Aspen was found to be a substrate preferable to Douglas fir, in that the former yielded more oil and less water-solubles.

3.1 OPERATION WITH DOUGLAS FIR WOOD SLURRIES

In the initial efforts to operate the CLU, a tubular reactor was employed (Fig. 3.1-1). Because of the small size of the equipment (the reactor was made of 1/4" I.D. tubing), and the flow regime, believed to be laminar, there was a serious problem of plugging. Runs were of short duration. Data from the runs which lasted long enough to be granted a run number are given in Table 3.1-1. The product collection system and reactor controls worked reasonably well. Problems of plugging by the heavy oil product downstream of the reactor were solved, but it was finally concluded that the scale was too small for a tubular reactor to work reliably. Since the operation at Albany had shown that a tubular heater does work at a scale where turbulent flow conditions can be maintained, it seemed inadvisable to spend further time trying to make the tubular reactor work at bench scale. It was therefore replaced with a one-liter autoclave, installed on-line as a stirred back-mixed reactor or CSTR (Fig. 3.1-2). The feed, product recovery, and pressure let-down systems remain essentially as they were.

After the changeover the runs were much more successful. Data are given in Tables 3.1-2 and 3.1-3.

Results of Tubular Reactor Runs

Some data for the runs made with the tubular reactor in place are given in Table 3.1-1. These experiments were primarily useful in teaching us how to run a small scale reactor. The conclusions can be summarized as follows:

o Wood oil products similar to those made in the PDU (Run TR-7) or in autoclaves can be made at 350°C outlet; minimum residence times should be greater than about 10 minutes.

o A down-flow tubular rector is less likely to plug rapidly than an upflow reactor.

o Any downstream line that has a slope below about 70°C is likely to plug with liquid product. Product cooling should be gradual -- air cooling is safer than use of a water condenser -- to avoid over-cooling.

FIGURE 3.1-1
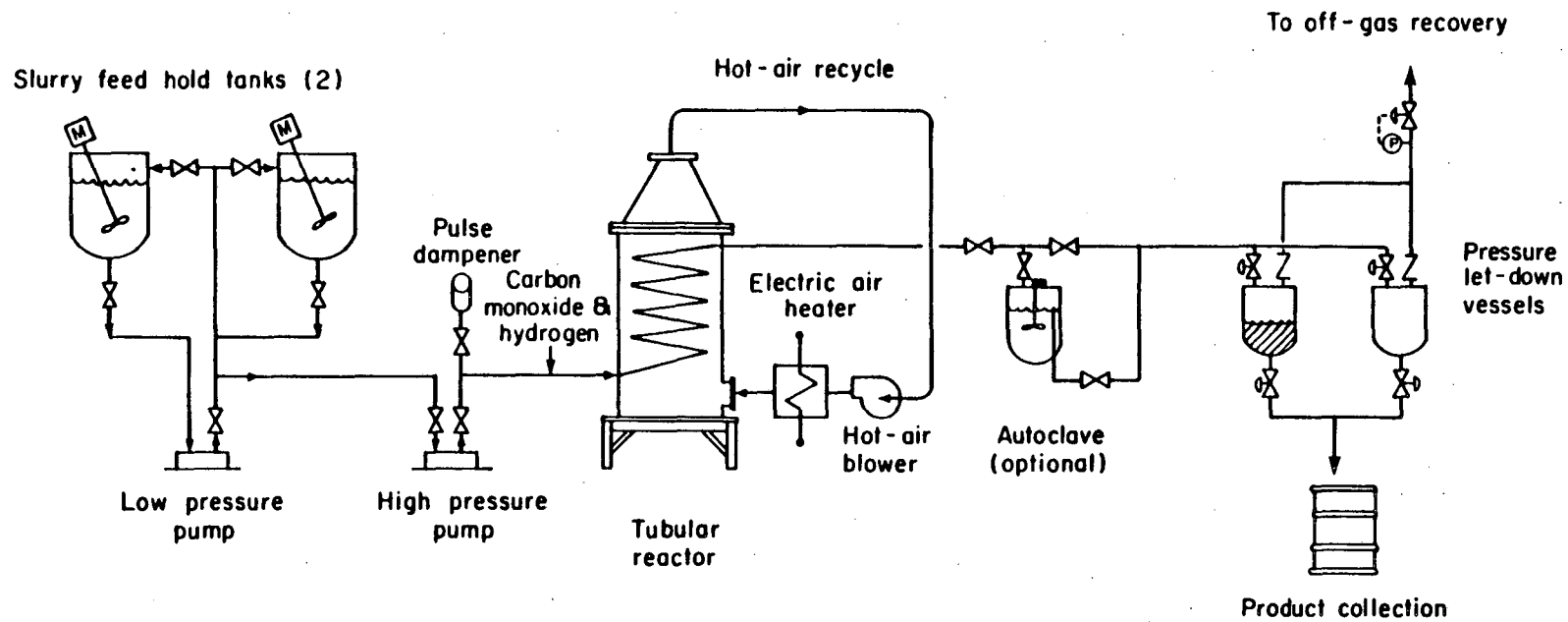
Biomass liquefaction process evaluation unit

LBL process

XBL 7910-4293

FIGURE 3.1-2

LAWRENCE BERKELEY LABORATORY
CONTINUOUS BIOMASS LIQUEFACTION UNIT (CLU)
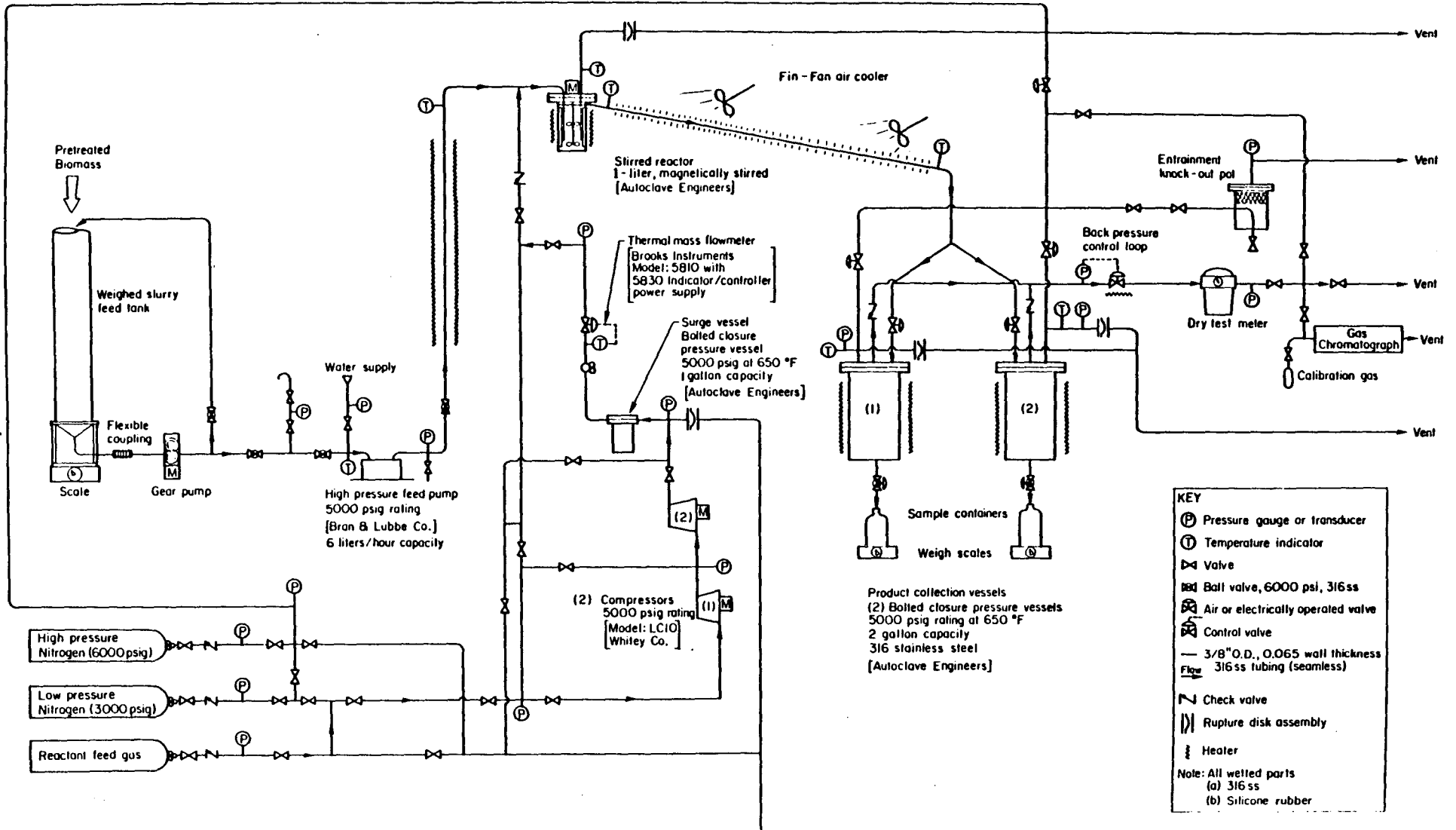
TABLE 3.1-1

CLU: SUMMARY OF RUNS WITH TUBULAR REACTOR

Run No.	Date	Total Duration, Hours	T°C	PSIG	Reaction time * t (min)	Reason for Termination	Comments
A	6/28/80	0.5	340	3000	18	Gas leak	After second attempt, 7/80, decision made to rebuild.
B	3/13/81	1.0	345	3000	18	Reactor plug	Yield of recovered oil 26 wt %.
C	5/6/81	2.0	350	3000	9	Reactor plug	
D	5/15/81	1.0	350	3000	12	Reactor plug	
1	5/22/81	0.5	350	3000	7	Reactor plug	Down-flow reactor Plug in exit lines.

* Reaction time estimated as $\dfrac{\text{Reactor Volume}}{3 \text{ X slurry feed rate}}$

In Runs B through 1, evidence of intermittent plugging: pressure drop swung at roughly 1 minute intervals from a low range of 30 to 100 psi to a high range of 80 to 300 psi.

TABLE 3.1-2

CLU: SUMMARY OF RUNS WITH BACK MIXED REACTOR

Run No.	Date '81	Run Time (hours)	$T°C$	P (atm)	Reactor Time (min)	Slurry Feed (kg/hr)	Gas Type (Ratio)	Gas Feed (L/min)	% Mass Recovery	Oil Yield (wt %)	Reason for Termination	Operating Equipment Modifications	Comments
2	6/28	1.5	350	205	13	1.8	CO/H_2 1:1	1.8	-	-	Plug	Slurry preheater installed	Poor temperature control on inlet and outlet reactor lines. Better control of line temperatures improved operation in later runs.
3	7/1	1	350	205	13	1.8	CO/H_2 1:1	1.8	-	-	Plug	-	
4	7/7	2	350	205	17	1.4	CO/H_2 1:1	1.6	80	24	Plug	Lowered slurry preheat temperature to 100°C	
5	7/16	15	345	205	18	1.3	CO/H_2 1:1	1.6	92	20	Plug		
6	8/4	5	354	205	29	0.8	CO/H_2 1:1	1.6	~100	15	Gas leak	Installed air cooler on reactor outlet line to replace water cooled exchanger.	High water vaporization rate noted
7	8/24	10	350	205	15	1.6	CO/H_2 1:1	2.2	91	31	Off-gas line plugged.		Oil foams upon depressurization.
8	9/2	24	330	205	26	0.9	CO/H_2 1:1	1.6	~100	32	Voluntary	Installed separate off gas vent line	New gas line avoids common vent pressure surges.
9	9/25	4	350	232	23	1.0	CO	1.0	-	-	Check valve failure	Replaced all viton o-rings with silicone	
10	9/29	10	350	232	21	1.1	CO	1.0	95	27	Feed sparger plugged.	Feed sparger line shortened to reduce effect of coking in line	Off gas composition: 32% H_2; 9% CO, 59% CO_2
11	10/15	24	340; 360	232	20	1.2	CO	1.0	98	33	Voluntary		Off gas composition: 22% H_2, 22% CO, 56% CO_2
12	11/4	24	340, 360	232	20	1.2	H_2	1.0	98	27	Gas leak	KO pot installed to collect foam.	Off gas composition: 70% H_2, 30% CO_2

TABLE 3.1-2 (Continued)

Run Number   13

Date   11/24/81

Run Time, Hours   20

Temperature, °C   340, 360

Pressure, ATM.   232

Reactor Time, Min.   20

Slurry Feed Rate, kg/hr.   1.0

Gas Type H_2 (100%)

Gas Feed, l/min.   1.04

Mass Recovery, %   97

Overall Oil Yield, %   33

Reason for Termination   Temperature Control at 360° poor

Operating Equipment   Same as Run 12

Comments   Off gas: 77% H_2
                                               22% CO_2
                                                1%   CO
                                             Trace CH_4

TABLE 3.1-3

CLU RUNS -- ADDITIONAL YIELD AND ANALYTICAL DATA

| Run No. | Elemental Analysis of Oil (maf) | | | Average Molecular Weight Recovered Oil[a] | | Aqueous Phase | | | Char Estimated Yield wt % |
| | | | | | | Estimated Yield Soluble Organic, wt % | pH | | |
	C	H	O	$\overline{M}_n$	$\overline{M}_w$		Slurry	Effluent	
4	74	7.5	19	271	483	26	6.1	4.5	7.1
5	77	7.9	15	213	319	23	6.1	5.0	9.0
6	78.5	8.2	13	176	232	20	6.1	3.9	3.9
7	76	7.4	17	242	384	27	7.5	4.5	11.3
8	74.5	6.8	18.5	282	364	33	7.5	4.1	0.3
9	-	-	-	-	-	26	8.9	4.5	-
10	77	7.5	16	272	344	22	8.9	5.1	1.6
11A	76	7.2	17	323	400	28	7.7	4.3	3.7
11B	77	7.3	16	254	336	25	7.7	4.5	
12A	76	7.0	17.5	271	349	25	8.0	4.2	5.0
12B	77	7.3	16	246	336	23	8.0	4.5	
13	75	7.1	18	295	389	25	9.0	5.0	7.0

a

$\overline{M}_n$ and $\overline{M}_w$ are number and wight average molecular weight, respectively.

Results of Back-Mixed Reactor Runs

Runs numbered from CL-2 on were carried out in the back-mixed continuous reactor. The first really successful run was CL-5 (July 16, 1981) and the first runs in which we felt sure that agitation was satisfactory were CL-9 (September 24, 1981) and CL-10 (September 29, 1981). The results of individual runs were instructive enough so that we should discuss them separately or in groups.

CL-2 to CL-4

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

CL-5

The overall run time was about 16 hours. Good samples were obtained and the overall material balance was fair (about 92%). It was found that over-rapid let-down of pressure from the product recovery vessels leads to a loss of oil product by a foaming mechanism. Hence, in CL-5 a disproportionate amount of oil was contained in the 8% overall loss. A series of improvements in the let-down procedure corrected the foaming loss problem, especially from run 8 on. The magnitude of the problem of hold-up on surfaces, reflected in the time needed to achieve steady state, was not realized until later (see discussion on runs 14 to 20).

CL-6

While CL-6 was a short run, aborted because of a system gas leak, there were interesting results. The aqueous effluent was found to be very low in titratable anion and, therefore, in sodium salts in general. This suggested that little or no water had exited from the reactor as liquid -- on the contrary, that it had left almost totally as vapor, leaving the sodium salts behind. Calculation showed that at reaction conditions (3000 PSIG, 354°C, 0.8 kg/hr slurry feed, 1.6 l/min synthesis gas) total vaporization of water would indeed be expected. Further, the small amount of oil product obtained had the lowest molecular weight and was the most fluid of any wood oil made in either the CLU or the PDU. Presumably, we were only recovering the vaporized lighter ends. Most oil remained in the reactor and coked.

CL-7

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

This was the best run to date. It showed us that at the reaction times available in the CLU (the liquid space-time was 60 minutes and the residence time about 30 minutes) the $330^{\circ}C$ product is heavy, viscous and probably under-reacted. If these are undesirable qualities, the range of temperatures which should be studied is fairly narrow, about 340-$360^{\circ}C$. Because of the problem of vaporization, pointed out above, it is best to use 100% CO rather than synthesis gas and to raise the total pressure somewhat for temperatures above about $340^{\circ}C$. These two steps reduce the ratio of fixed gas flow at reaction conditions to water flow, and, therefore, the percentage of water which exits the reactor as vapor.

CL-9, CL-10

A single upward thrust propeller was used for stirring in these runs and the feed gas was 100% CO. Shortly after the start of CL-9, the check valves on the gas product line were found to be stuck open. The run was stopped, double check valves in series were installed and run CL-10 was started. With 100% CO as the gas feed, it was immediately apparent that the water gas shift was occurring to a considerable extent. Also substantial amounts of formate ion were formed in the aqueous layer. The molar gas composition lined out, shortly after start-up, at 10% CO, 35% H_2, 55% CO_2. $H_2 \cdot CO_2/(H_2O \cdot CO)$ is estimated to be about 1, as compared to an equilibrium constant at $350^{\circ}C$ of 20, so that water gas shift equilibrium is approached but not reached. Some additional carbon dioxide, calculated for run 10 to be about 2/3 g-mol/hour, is dissolved in the liquid phases. This is significant in the material balance but not in the shift reaction pressure ratio.

CL-11, 12, 13

These were successful runs with two reaction temperatures (340 and $360^{\circ}C$) explored in each. Product gas flow measurements and analyses for CL-11 showed that little or no carbon monoxide was used up except by shift reaction. We therefore replaced carbon monoxide with hydrogen for CL-12 and CL-13.

CL-12 and CL-13 demonstrated no observable operating differences with pure hydrogen as the reactant feed gas. Analytical results of the oil produced also suggest no significant differences caused by the change in reactant feed gas. CL-13 was terminated after a short time at about $360^{\circ}C$ because of temperature runaways related to coking. Controlling at $360^{\circ}C$ or higher is difficult.

The pH was varied among runs CL-10 to 13 with higher levels in 10 (CO) and 13 (H_2) and lower in 11 (CO) and 12 (H_2). We could not observe any significant operating effect. However, minor effects on the yields of formate and other water-solubles are discussed elsewhere in the report (Section 5).

Runs CL-14 through 20.

These runs were primarily efforts to improve oil yields and reduce coke yields. They were designed to test a number of working hypotheses. With one exception the results were negative. (See Table 3.1-4).

It has always been observed, even in most successful runs, that product oil recoveries are 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.

CL-17

This run was purposely allowed to proceed for only three and a half hours to test the above 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%. Also the char yield, at 5%, was not excessively high, compared to that observed in earlier runs.

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

Finally, looking for further evidence that the important cause of initial low oil recoveries was system hold up, we looked at the yields by sampling periods in several of our runs. Results are shown in Table 3.1-5. 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 CL-13-6). Based on the analysis of Table 3.1-5 and of 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 remaining steadier parts:

CL-10   39%

CL-11   41%

CL-12   32%

CL-13   38%

TABLE 3.1-4

CLU - ADDITIONAL 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 (slpm)	Feed gas Type	Oil yield wt %	Off-gas concen. %	Char Yield	Overall mass Recovery	Reason for run termination	Observation
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 plugges 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	6.4	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		-	-	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 buildup.	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.

TABLE 3.1-5

Period	Receiver	g oil/100 g organics fed (kg slurry in parentheses)		
		CL-11	CL-12	CL-13
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)	

Average oil yield 37.5 + 2.0% (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 3.1-4, 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 again about 40%. Run 20 was made with the first pumpable slurry made after a prehydrolysis 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 the product, however, we found it was largely partially reacted slurry solids which had bypassed the coke-filled reactor.

3.2 STATUS OF PRESENT PROCESSES (ASPEN AS A FEED MATERIAL)

Two final runs which bear on the status of the water slurry process were carried out before shutting down the CLU. These were with slurries prepared in this laboratory from Minnesota aspen (populus tremuloides). Considerable time had to be spent in finding out how to make a pumpable slurry, probably because our small-scale equipment is somewhat less than adequate. However, acceptable batches of 20 wt % slurry were finally made. We believe that in commercial continuous equipment, such as the Asplund defibrator, more concentrated slurries could be prepared. In run CL-24, an extensive gas leak occurred and the data are deemed worthless. Data on run CL-21 are shown in Table 3.2-1 and further data on the products in Tables 3.2-2 and 3.2-3.

If we treat this run as we have found it necessary to treat earlier runs with Douglas fir -- i.e., ignore the first several kgs of slurry feed while a steady recovery system is set up, we estimate yields of 43 to 57 wt %.

Total oil plus char becomes 50-64%, the higher end becoming unbelievably high. Since, from an oxygen balance, the carbon dioxide plus water yields must be of the order of 35% and there are also water-dissolved products, the oil plus char cannot be much above 50%.

The water effluent contains only 50-60% as much carboxylic acid as found with Douglas fir. This is verified by titration of water layer samples for CL-24, which gave 0.36-0.38 Eq/kg. The yield of water-dissolved organics can, therefore, be estimated at about 60% of the amount found with Douglas fir, or about 15%.

TABLE 3.2-1

LIQUEFACTION OF 20% ASPEN SLURRY

RUN CL-21

Conditions:

350°C, Hydrogen feed gas (1.0 l/hr), 3400 psig, slurry feed rate 1.25 kg/hr.

Period	Slurry Fed, kg	Oil Recovered, kg	Aqueous Recovered, kg
1	2.7	0.0	2.1
2	1.35	0.0	2.4
3	5.05	0.221	4.5
4	5.0	0.649	5.4
5	0.0	0.0	3.1
TOTALS	14.1	0.87	17.5

(Includes water collected during final flush.)

Char recovered 205 g (7% of dry wood).

Overall yield oil 31% of dry wood.

Yield based on periods 3 and 4, 43% of dry wood.

Yield eliminating first 6 kg of slurry ∿ 57%.

TABLE 3.2-2

ACIDS AND ANIONS IN AQUEOUS PRODUCT, CL-21

Sample	pH	Eq/kg aqueous		
		acid	anion	Total
CL 21-2	4.58	0.17	0.21	0.38
CL 21-3	4.60	0.12	0.15	0.27
CL 21-4	4.75	0.11	0.13	0.24

At this point therefore, we estimate the yield distribution for aspen to be substantially better than that from fir:

Product, g/100g dry wood	Douglas fir	aspen
oil + char	40	50
$CO_2 + H_2O$	35	35
water dissolved organics	25	15

The product of run CL-21 is also a superior product. By its high fluidity at room temperature, its oxygen content, its SESC fractionation and its molecular weight distribution it is substantially better than CLU or PDU Douglas fir products. Table 3.2-3 shows some comparisons.

From the table, it is observed that the lighter SESC fractions, 1-4, which contain the neutrals and monophenols, are larger than in typical Douglas fir runs. The total in fractions 1-4 is 59.9% for CL-21, 42.7% for CL-11 and 32.2% for TR-12. Similarly, the average molecular weights for CL-21 oil are much lower than those of CL-11, made from Douglas fir slurry at comparable conditions, or of the PDU's TR-12. The oxygen content of the CL-21 oil is almost 3% lower than the CL-11 Douglas fir oil made under similar CLU conditions, and almost as low as the PDU oil made under much more severe conditions.

3.3 SUMMARY

Operation of the CLU established the reality of the high yields of water-dissolved organics in single-pass slurry operation. Thereby, a limit on the yield of oil by this type of process was established. With Douglas fir, at an operating severity sufficient to give oil of 16% O content, oil plus coke yields cannot be much above 40%. I.e., to produce 40% oil we must limit the coke formation to the low levels of 0-2% found in the best PDU runs (TR-8 and TR-12). Water solubles will be about 25% and the balance CO_2 and H_2O.

With aspen, yields of 50% oil (plus coke) are possible. Furthermore, the quality of oil from aspen is better (oxygen ~ 13%, molecular weight lower, proportion of SESC fractions 1-4 higher). Other observations, including effects of pH, temperature, and process gas are discussed in the section (5) on product characterization.

As of December 1982, the CLU remains in stand-by condition. It is capable of operation as a CSTR liquefaction unit (as in the runs reported) or as a CSTR or trickle-bed catalytic hydrogenator (see Figure 3.3-1).

TABLE 3.2-3

CHARACTERISTICS OF WOOD OIL FROM ASPEN AND DOUGLAS FIR

A - SESC FRACTIONS, WT %

	CL-24 (Aspen)	CL-11 (fir)	TR-12 (fir), PDU
1,2	4.7	2.9	4.1
3	14.8	15.2	14.0
4	40.4	24.6	14.1
5	19.9	39.2	37.7
6	13.1	12.2	18.2
7	0.5	0.4	0.5
8	1.5	2.4	8.4
9	5.2	3.0	3.0

B. MOLECULAR WTS BY GPC

	CL-24 (Aspen)	CL-11 (fir)	TR-12 (fir), PDU
Number Average	177	235	250
Weight Average	244	337	350
Polydispersity	1.52	1.43	1.40

C. ELEMENTAL ANALYSIS

	CL-24 (Aspen)	CL-11 (fir)	TR-12 (fir), PDU
C	78.6	76.5	78.9
H	7.8	7.2	8.3
O	13.4	16.3	12.3

FIGURE 3.3-1

biomass
derived-oil

hydrogen ⟶

3-zone tube furnace

maximum operating conditions:
2000 psi
460°C

packed
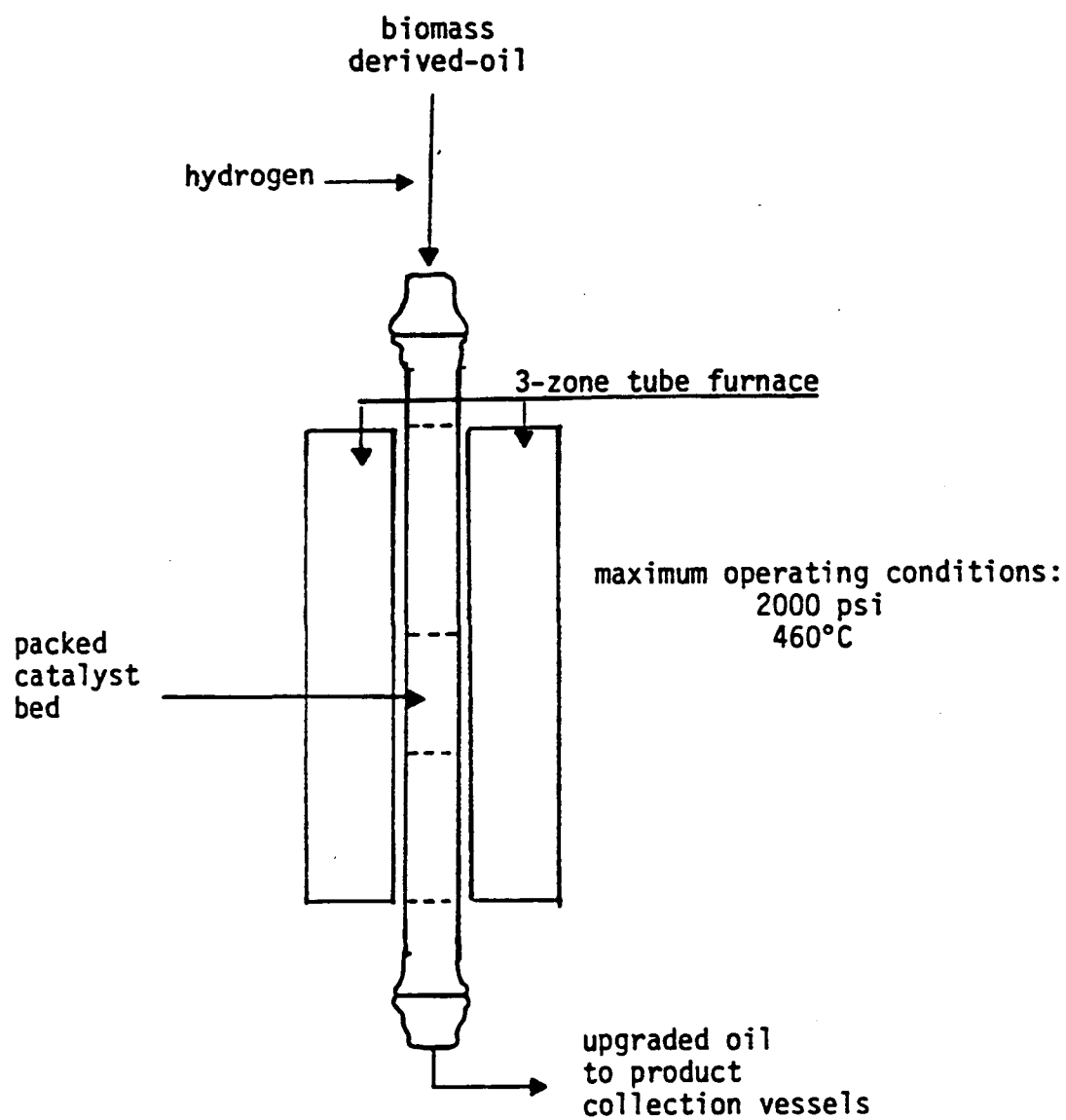catalyst
bed ⟶

upgraded oil
to product
collection vessels

Fig. 2 Trickle-bed hydrogenation reactor

4.0 SOLVOLYSIS AS A LIQUEFACTION PROCESS

Since we believe that solvolysis will be a part of the ultimate commercial liquefaction process, we have included a rather complete summary in section 2.4. Here we append recent laboratory data. Additional material can be found in references 6 and 8.

4.1 FUNDAMENTAL STUDIES OF SOLVOLYSIS

The work reported under this heading was carried out by a visiting graduate student -- Pierre-Yves Lamy of the University of Compiegne, France -- during a two and a half month visit during the summer of 1982, with help from the staff. Mr. Lamy chose to study some aspects of solvolysis of biomass by phenol (previously studied here by Yu).[6]

Samples of cellulose, xylan (from hemi-cellulose) and kraft lignin were heated with twice their weight of phenol, plus a small amount of water and a trace of sulfuric acid (see Table 4.1-1). After holding at $240^{\circ}C$ for 45 minutes, the mixture was neutralized with $NaHCO_3$, and freed of water by decantation plus evaporation. Such phenol as could be distilled from the organic phase was distilled and the remaining oil analyzed. Analyses performed included C, H, N, S (O by difference), SESC and molecular weight by GPC. From the elemental analyses of the dried feedstock and the oil product and the recovery (ratio of weight of oil product to weight of feedstock) it is possible to calculate the following: (1) % phenol incorporated into the product, (2) % CO_2 evolved during treatment and (3) percent H_2O evolved during treatment. It will be obvious that some assumptions are required to make this calculation: the elemental analyses and recovery ratios must be sufficiently accurate for good atom balances to be made, other products (e.g. water solubles other than phenol) must be negligible, and other volatile products generated must not be significant. These assumptions appear to be reasonable. The calculated results are shown in Table 4.1-2.

There is a very large retention of phenol in the products from cellulose and xylan. Also there is a large evolution of water. Taking the monomer weight of cellulose as 162, we estimate 58.6g H_2O or 3.25 mols/per monomer and 18.8g or 0.43 mol CO_2 per monomer. The net yield of solvolytic product in the final mix is only 52 wt % of the dry cellulose feed. Xylan behaved similarly, retaining somewhat less phenol and evolving more CO_2 and less H_2 and and giving a net yield of only 44%.*

Lignin, on the other hand, retained relatively little phenol (15%) and evolved no significant amounts of CO_2 or H_2.

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* For the sake of product quality, more O lost as CO_2 and less as H_2O is preferable. From other experience a very rapid heat- up to solvolysis temperature and perhaps a shorter holding time may move the reaction in this direction.

TABLE 4.1-1

SOLVOLYSIS OF BIOMASS FRACTIONS WITH PHENOL

Conditions: 240°C, 45 min., Phenol/substrate = 2/1 by wt.
              Water and H_2SO_4 added to make phenol phase 88% phenol and
              0.1% H_2SO_4. 30g substrate in 300 ml autoclave.

Biomass Fraction		Cellulose	Xylan	Lignin
Elementary	C	43.1	40.08	63.45
Analysis	H	6.3	5.6	5.39
wt %, dry basis	O	50.50	54.24	26.45 (Ash = 3.1)
	N	0.1	0.08	0.50
	S	-	-	0.99
% H_2O in substrate as used		7.2	8.8	5.5
% yield of solvolysis product. After phenol distillation g/100g dry substrate		113	95	114
Molecular wt by GPC				
weight average		442	311	491–511
number average		337	217	392–403
polydispersity		1.31	1.43	1.32–1.28
SESC Fractions				
1-2		0	1	0
3		3	2	2
4		11	35	6
5		23	8	17
6		45	29	37
7		2	0.4	11
8		3	1	22
9		13	22	6
Product	C	79.18	68.67	66.14
elementary	H	5.18	6.61	5.48
analysis, wt %	O	17.33	19.22	26.22
	N	0.02	0.07	0.65
	S	0.09	0.23	0.11
Ash or residue		3.2	5.2	1.4

TABLE 4.1-2

CALCULATED PHENOL RETENTIONS AND CO_2 AND H_2O
EVOLUTION DURING SOLVOLYSIS WITH PHENOL AT 240°C

Feedstock	Phenol Retained		CO_2 Evolved	H_2O Evolved
	g/100g dry feed	g/100g total product	g/100g dry feed	g/100g dry feed
Cellulose	57.3	52	11.6	36.2
Xylan	45.5	51	35.9	19.8
Lignin	14.8	13	(-2.14)	0.75

The SESC fractionations and GPC analyses are of some interest. The broad distribution among the SESC fractions indicates that little of the retained phenol is retained as unreacted phenol. This is also indicated by the number average molecular weights and the polydispersity. It would not be possible to obtain MW ⁓ 340 and polydispersity ⁓ 1.3 from a simple mixture of 52 wt % phenol with 48 wt % of a high molecular weight material.

4.2 PROCESS RELATED STUDIES -- SOLVOLYSIS PLUS CATALYTIC HYDROGENATION

Batch experiments were carried out with several substrates. Apart from Douglas fir and aspen, these included several agricultural residue materials. TR-7 oil was used as the initial solvent in all experiments, and at around 240°C it appears to be universally effective. Commercial copper chromite and sulfided nickel tungsten catalysts are appropriate hydrogenation catalysts.

Simulated recycle experiments were carried out with rice straw, rye grass, and walnut shells,calotropis weed and aspen. Fresh substrate (one part) was in each case heated to 360°C in a 300 ml stirred autoclave with TR-7 (4 parts) or total product oil, plus catalyst (5-6% copper chromite) and held for about 45 minutes. The oxygen content of the mixture at the solvolysis temperature of 240°C should be about 12-16%. After hydrogenation it was in general ⁓ 9% (see Table 4.2-1). Average molecular weights of whole product were about 215 -- much like the Douglas fir liquefaction products.

The whole product remained a good solvolytic agent during these experiments and there was no evidence of serious coking. However, even with seven such recycles, the final recycle solvent can be calculated to be at least 40% TR-7. The results can be called encouraging, but certainly more work is needed. The oil yields from walnut shells and aspen appear to be acceptable, around 50 wt %. However, the yields from the other feeds are probably lower. The use of a high solvent to substrate ratio made quantitative analysis of the runs very difficult.

Most recently (November-December 1982), recycle experiments in a one liter stirred autoclave were started with aspen as substrate. Again TR-7 was the initial solvent and commercial copper chromite was the catalyst. The solvent/dry substrate ratio was reduced to 2/1.

Since the most desirable final product is light distillate, we topped the initial TR-7 in an ASTM-like atmospheric pressure rapid distillation to about 260°C IBP. The residue was used as solvent. Again the whole hydrogenated product was topped to about 260°C and the residue used as solvent. The whole product was again topped to 260°C.

Unfortunately, time ran out before further runs could be made. The data obtained are shown in Tables 4.2-2 and 4.2-3. The feed to the first pass was 80g dry aspen, 162g TR-7 oil previously topped in a rapid one-plate atmospheric pressure distillation to about 260-280°C, and 12g of commercial copper chromite catalyst. The mixture was brought to about 360°C in a one-liter autoclave and held for about an hour at about 4000 psi.

TABLE 4.2-1

ELEMENTAL ANALYSES OF FEEDS AND OIL PRODUCTS, DRY BASIS

FEED	C	H	O	N	ASH
Rice Straw	35.7	4.9	40.6	1.1	17.7
4th Cycle Oil	82	8.3	9	0.8	--
Rye Grass	44.1	5.5	45.6	0.7	4.1
4th Cycle Oil	81.6	8.1	9.6	0.7	--
Calotropis	39.7	5.3	43.8	2.1	9.1
6th Cycle Oil	79.4	8.6	9.7	2.3	--
Walnut Shells	49.1	5.7	40.9	1.0	3.4
7th Cycle Oil	82.2	8.6	9	0.3	--
Aspen	51.0	5.7	42.2	0.1	1.0
6th Cycle Oil	81.5	8.6	10	0.1	--

Note: Cycle oil includes remains of initial TR-7 solvent plus oil
       made from biomass feeds. Samples analyzed contained some water
       and an approximate correction has been made to account for this.

TABLE 4.2-2

HYDROGENATION OF ASPEN WITH LOW SOLVENT FEED RATIO

A. ELEMENTAL ANALYSES

SAMPLE	C	H	N	O
SOLVENT (TR-7)	79.9	7.86	0.10	12.1
CRUDE PRODUCT 1	82.0	7.5	0.09	10.4
STILL RESIDUE 1	83.7	6.95	0.10	9.2
LIGHT FRACTION 1	75.5	9.52	0.04	14.9*
CRUDE PRODUCT 2	86.1	7.6	0.07	6.2
LIGHT FRACTION 2	88.2	11.2	0.01	0.6
STILL RESIDUE 2	85.6	6.70	0.09	7.6

B. SESC FRACTIONATION OF SOLVENT AND OF WHOLE CRUDE PRODUCTS

FRACTION	WEIGHT PERCENTAGE IN FRACTION			
	TR-7	HYDROGENATED-TR-7	PRODUCT 1	PRODUCT 2
F-1,2	3.5	8	4.4	8.9
F-3	16.8	24.7	19.5	11.9
F-4	44.1	52.8	40.0	32.9
F-5	21.1	4.5	12.6	22.6
F-6	6.5	1.	2.7	3.4
F-7-9	7.7	9.	21.2	20.4
F-1-4	64.4	85.5	63.9	76.3

---

* From the oxygen content, light fraction 1 may have been incompletely
  dried.

TABLE 4.2-3

HYDROGENATION OF ASPEN WITH LOW SOLVENT FEED RATIO YIELD INFORMATION

FIRST PASS	REACTANTS		CRUDE LIQUID	DISTILLATE	
	TOPPED TR-7	162g		AQUEOUS	18.5g
	DRY ASPEN	80g	198.1g	LT. OIL	38.8g
	CU CR CAT.	12g			

SECOND PASS					
	RESID. OIL	110g		AQUEOUS	20.9g
	DRY ASPEN	55g	112.0g	LT. OIL	19.2g

HYDROGEN CONSUMPTION FROM PRESSURE CHANGES, WT. % OF DRY ASPEN

FIRST PASS -- 4.4%, SECOND PASS -- 5.7%

HYDROCARBON GAS YIELDS, WT. % OF DRY ASPEN

FIRST PASS -- 4%, SECOND PASS -- 31%

The encouraging results of this experiment include the following observations:

(1) Volatile products were formed equal in weight to about 50% of the fresh feed; i.e., more than enough was generated to allow a 40% yield of distillate product.

(2) Hydrocarbon gas formation was relatively minor. As a result, the hydrogen consumption was probably much less than the 4% estimated from pressure changes — probably not over 1-2%, based on the water and hydrocarbon gas yields and the hydrogen in the net increment of oil.

The results of the second pass experiment were very poor. There was excessive hydrocracking to form methane and higher hydrocarbons and the high measured hydrogen uptake (over 5%) was probably real. Volatile liquids -- apparently almost oxygen-free -- were formed, but the net production of oil was very low or negative. The experiment shows that control of the hydrogenation is tricky. Trickle bed hydrogenation, or some other continuous technique should be an improvement. (See Tables 5, 5B).

The SESC fractionation results given in Table 5-B show the development of volatiles. Hydrogenation of TR-7 oil (at the higher temperature of 400°C) substantially increased the percentage in fractions 1 to 4 where the bulk of the potential atmospheric pressure distillable resides. Topping the initial TR-7 solvent must have removed nearly all the F-1-3 and much of the F-4. The SESC's of the two whole crude products show that these light fractions are regenerated during the solvolysis/hydrogenation sequence, and that the total in F-1 to F-4 is high — probably higher than necessary. The percentage in the three heaviest fractions, F-7-9, is higher than in TR-7 oil. Tests to see whether there is a steady build-up are required.

We conclude that the solvent-recycle, solvolysis and hydrogenation route can indeed lead to an acceptable, practicable way to convert biomass to distillable liquids. The present work barely scratches the surface and a substantial research and development program is needed. Some of the desirable content of such a program is outlined below.

The chemistry and stoichiometry of solvolysis with a phenolic recycle oil should be studied in detail. Solvolysis should be tested under conditions of rapid heat-up comparable to those possible in a continuous operation. One way of accomplishing this is to use two autoclaves in series. The first is used to preheat the solvent oil to a temperature above the solvolysis reaction temperature and the second contains substrate at a lower temperature. Solvolysis is initiated by forcing the hot solvent with pressure into the second autoclave while adding heat rapidly to maintain solvolysis temperature.

Hydrogenation, with available catalysts, should be studied in a similar manner. Conditions for maintaining steady solvent composition must be established. This then permits accurate assessment of the stoichiometry of both solvolysis and hydrogenation and accurate calculation of the hydrogen consumption.

Detailed characterization of the volatile hydrocrackate should be carried out.

The rate of heavy polymer and char formation during solvolysis and hydrogenation should be determined. Conditions simulating continuous operation must be achieved, or, if possible, continuous experiments run.

The possibility of decanting water formed during the solvolysis step at solvolysis temperature should be tested.

Studies of the stability of available commercial catalysts under reaction conditions should be initiated. Tests with possible inexpensive catalysts like FeS should be run.

Conditions for alkylating phenols in the distillate product should be established.

In the absence of the results of such an extensive program, we can only conjecture about the answers to important questions about yields and hydrogen usage. Within the boundaries of the present limited information, we can develop a yield and hydrogen uptake pattern which is at least possible, as shown below.

Hydrogen consumption is determined by the proportion of oxygen removed as water rather than carbon dioxide, by the amount of hydrocarbon gas formed, and by the degree of saturation of the product oils. All of these factors can be expected to be controlled to some extent by the catalyst chosen and by the choice of conditions. A reasonable goal might be to reduce the hydrogen usage to as little as 1.0 percent ($\frac{1}{2}$ mol per 100g biomass feed). At that level hydrogen requirement, in petroleum industry terms, is a little over 1000 SCF per barrel of product. At 2% hydrogen it is about 2200 SCF/bbl. These numbers are low compared to coal hydrogenation requirements (5000 to 10,000 SCF/bbl to produce distillate hydrocarbons).

5.0 PRODUCT CHARACTERIZATION

Methods of product characterization which have proved particularly useful to us include a modified version of Mobil Oil's SESC sequential elution analysis, GC-MS, an acid-base extraction procedure for high and low molecular weight phenolics, and two high performance liquid chromatographic (HPLC) techniques. The HPLC methods are HPSEC (size exclusion for molecular weight distribution), and HPIEC (ion-exchange column separation for quantitative analysis of the low molecular weight acids in the water-solubles. Elemental analyses, total organic carbon on aqueous samples, and direct acid-base titration have, of course, also been useful.

5.1 ANALYSIS OF OIL PRODUCT

5.1.1 SESC FRACTIONATION

The SESC procedure and results were updated as recently as October 1982.[21] We therefore reproduce here, with only minor modification, the entire section on SESC from the October paper.

Method Development

While the original SESC technique [19] was developed for coal-derived liquids, especially SRC (solvent refined coal), it required only slight modification for our purpose. Since wood oil is virtually devoid of aliphatic hydrocarbons, the first step, elution with hexane, was omitted. Whatever amount of this fraction, F1, does exist, is eluted along with the aromatic hydrocarbons by 15% benzene-hexane in the present technique. This hydrocarbon fraction is designated F1,2. Also, we have found acetic acid to be superior to pyridine for removing the last wood oil residues from the column. The complete sequence of solvents is shown in Table 5.1-1.

A further improvement was the use of the low pressure preparative liquid or "flash" chromatographic technique [24,25]. This employs small, irregularly-shaped particles of silica gel (40 μm) and low positive pressures (20 psig) to afford speedier analysis and improved resolution with reduced consumption of solvent.

One sample of wood oil, TR-7, produced from Douglas fir at DOE's Albany, Oregon liquefaction test facility by LBL's water-based process, was fractionated four times, including once with an anhydrous sample, in order to check repeatability and the effect of water. The presence of 8% water in the sample did not alter the results (Table 5.1-1).

Fraction	Solvent	Amount(%) Std. Dev.
F1,2	15% Benzene-Hexanes	3.5 ± 0.4
F3	Chloroform	16.8 ± 2.3
F4	6% Ether-Chloroform	44.1 ± 3.7
F5	4% Ethanol-Ether	21.1 ± 3.0
F6	Methanol	6.5 ± 1.3
F7	4% Ethanol-CHCl$_3$	1.0 ± 0.4
F8	4% EtOH-THF	2.5 ± 1.7
F9	Glacial acetic acid	4.2 ± 0.6

TABLE 5.1-1
SESC FRACTIONATION OF TR-7 OIL

Characterization of SESC Fractions

Several dozen biomass-derived oil samples have now been subjected to SESC as modified for wood oil. Information regarding the chemistry of various fractions has been provided by gel permeation chromatography (HPSEC) for molecular weight distributions, GC-MS for specific compound identification, infrared spectroscopy, elemental analysis and solubility classification.

In Table 5.1-2 we show the ranges of the percentages found in each fraction of the oils tested, typical average molecular weights, the typical percentage of oxygen in the fraction and an average molecular formula.

Table 5.1-2
CHARACTERIZATION OF WOOD OIL SESC FRACTIONS

Fraction	Wt%	$\overline{M}_n^a$	$\overline{M}_w^b$	%O	Average Molecular Formula
1,2	0-6	140	160	5	$C_{11}H_{14}O_{0.5}$
3	1-20	170	210	11	$C_{13}H_{15}O_{1.3}$
4	5-45	170	210	16	$C_{12}H_{14}O_2$
5	5-55	210	290	21	$C_{15}H_{16.5}O_{3.3}$
6	5-35	350	600	23	$C_{30}H_{30}O_7$
7	1-3	180	210	46	—
8	2-20	690	900	—	—
9	0-10	—	—	—	—

[a] Number-average molecular weight. [b] Weight-average molecular weight.

Molecular weight distributions of fractions and whole oil samples were obtained by gel permeation chromatography. The predominant band in the infrared spectra of most fractions was that due to hydroxyl stretching, except that this band is absent in F1,2 and weak in F3. Other bands included the carbonyl stretching band (F3-F6 and F8) and those

characteristic of the aromatic ring.

Fractions 1-5 are liquid while 6, 8 and 9 are solid. Fraction 7, always minor, is usually solid. Capillary gas chromatography indicates that the distillable components reside exclusively in fractions 1-5 with the suggestion that F5 also contains material of very low volatility. Fractions 4-6 dissolve rapidly and almost completely in 5% aqueous sodium hydroxide.

Fraction 1,2 contains aromatic hydrocarbons. GC-MS analysis of one F1,2 sample gave the following tentative identifications: alkylated benzene derivatives (C_8H_{10}, C_9H_{12}, $C_{10}H_{14}$, and $C_{11}H_{16}$); substituted indanes or alkenylbenzenes (C_9H_{10}, $C_{10}H_{12}$ and $C_{11}H_{14}$); 2-methylnaphthalene, biphenyl and a tetramethylphenanthrene isomer. In the biomass oils we have analyzed, F1,2 has been small.

According to Farcasiu,[19] the constituents of F3 include nonhydroxylic polar aromatics and oxygen heterocycles. Anisole, a variety of cycloalkanones, a butyrophenone (1-(p-methoxyphenyl)-1-butanone) and a hindered phenol (2, 4, 6-trimethylphenol) were found by GC-MS in this study. Standards were used to show that anisole, guaiacol and eugenol also elute with F3. These methoxyphenols can also be considered to be hindered.

The present work reinforces the conclusion that F4 consists largely of monophenols [19]. Phenol and 5-indanol elute cleanly with 6% ether-chloroform.

Fractions 5 and 6 are also phenolic in nature as evidenced by solubility in aqueous caustic, infrared spectra and elemental analyses. From thin-layer chromatography (TLC) data,[19] it is expected that 1-naphthol, 2,3-naphthalenediol, salicyclic acid and chrysin, $C_{15}H_8O_2(OH)_2$, would be found in F5. We find that 3,4-bis (p-hydroxyphenyl)-3,4hexanediol appears in F5. The average molecular formula can be fairly well represented by the structure,
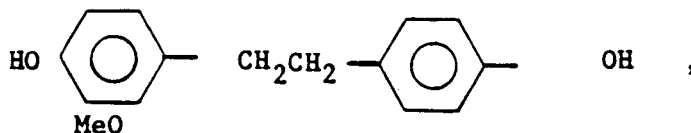
a fragment conceivably derivable from softwood lignin. Although there is probably considerable overlap between F4 and F5, it can be inferred that monophenols prevail in the former and phenolic dimers (e.g., bisphenols) in the latter. Single-ring aromatics with two strongly polar functional groups are also to be expected in F5. The bisphenol structure pictured above is therefore only one of many types to be expected here.

Methanol, the F6 eluent, marks the approximate line between asphaltenes (benzene-soluble pentane insolubles) and preasphaltenes in SESC. The sixth fraction elutes sharply as a dark brown band with little or no contamination by the tail end of F5. This material is involatile,

highly polar and phenolic in nature. The major components of SRC-derived F6 have been termed "highly functional molecules" having greater than 10 wt % heteroatoms. In the case of wood oil, F6 would seem to be polyphenolic material, in part degraded lignin.

SESC Profiles of Wood Oils

SESC profiles of eight biomass oils are shown in Table 5.1-3. These runs are described in Table 5.1-4, along with additional product information. The oils identified as TR-7, TR-10, and TR-12 were produced in the PDU at Albany, Oregon. TR-7 and TR-10 were made by the LBL water-slurry process. TR-12 oil is a product of the oil recycle or PERC process. The TR-12 used in the present study was judged to be at least 99% wood-derived, with very little residue of start-up anthracene oil.

TABLE 5.1-3
SESC PROFILES OF SELECTED WOOD OILS

Fraction Oil:	TR-7	TR-10	TR-12	CL-8	CL-10	CL-11B	CL-12B	CL-21[a]
1,2	4	1	4	1	3	4	3	5
3	17	7	14	3	18	16	15	15
4	44	19	14	6	8	20	25	40
5	21	40	38	44	50	41	39	20
6	6	21	18	31	14	12	12	13
7,8,9	8	11	12	15	6	7	5	7
1-4	65	27	32	10	29	40	43	60
4-6	71	80	70	81	72	73	76	73

[a] From aspen. All others were from Douglas Fir.

TABLE 5.1-4
OPERATING CONDITIONS AND ANALYTICAL RESULTS FOR SELECTED RUNS

	TR-7	TR-10	TR-12	CL-8	CL-10	CL-11B	CL-12B	CL-21
Temperature ^{o}C	~350	~350	330-370	330	350	360	360	350
Steady-state yield,%	~25	~26	53	40	39	41	32	43
Residence time, hrs.	5	0.3	0.3[a]	0.4	0.35	0.3	0.3	0.3
% Oxygen	14	17	13	18.5	16	16	16	13.5
M_n	220	290	240	280	270	250	250	180
M_w	310	470	370	360	340	340	340	270

[a] TR-12 (PERC process) used two reactors in series at two temperatures. The residence time given here must be multiplied by a large factor to allow for recycle. See discussion of stoichiometry in Section 6.

The CL oils were produced in the LBL continuous liquefaction unit (CLU). They were made by the LBL process using 18% to 20% aqueous slurries of prehydrolyzed wood. Except for CL-21, from aspen (Populus tremuloides), all of the oils of Table 3 were derived from Douglas fir.

Quality of Wood Oils

Desirable process goals for biomass liquefaction can now be cast in terms of these SESC profiles of oil quality. From the standpoint of fuel quality (especially volatility) the ideal wood oil would consist entirely of fractions 1-3. However, from the results shown in Table 4 (4 to 21% in F1-F3) this appears to be unrealistic with the current generation of liquefaction processes. A more practical process goal would be to maximize fractions F1 to F4 at the expense of F5 and F6. Although a well-defined index of reaction severity* is not available, severity does appear to be the most significant factor affecting the proportion of F1-4. The effect of reaction severity is most evident in comparisons of TR-7 (65%) with TR-10 (27%), and of CL-8 (10%) with CL-10, 11B or 12B (29-43%). In general it appears that the CLU oils are somewhat less reacted than the products of TR-7 or TR-12. This can be attributed to the fact that residence times in the CLU were of the order of 20 min., a constraint imposed by the operating characteristics of the system and the lack of oil recycle.

Other uses of the SESC results have been discussed elsewhere in the report. A further example is the analysis of samples of TR-7 oil before and after hydrogenation ($400^\circ C$, 2000 psig H_2, 2% Cu-Cr, 1 hr). The analyses shown in Table 5.1-5, indicate a substantial degree of hydrocracking to form fractions 1-4 at the expense of 5-6 (see table 5.1-5). Fractions 5 and 6 have been substantially depleted, but the heaviest fractions, 7-9 were resistant to cracking.

	TABLE 5.1-5	
FRACTION	UNTREATED OIL	HYDROGENATED OIL
	wt%	wt%
F 1,2	3.5	8
F 3	16.9	25
F 4	44.2	53
F 5	21.2	4
F 6	6.5	1
F 7-9	7.7	9
	100.0	100.0

---

* In comparing LBL products with PERC products and CLU or autoclave products with PDU products, we have generally used oxygen content of whole, dry product oil as the best available measure of severity.

5.1.2 FRACTIONATION OF OILS INTO PHENOLICS AND "NEUTRALS:"

Because of multiple oxygen functionality and fairly wide molecular weight range, product biomass oils must be termed chemically complex. Although a completely satisfactory group separation scheme has not yet been developed, some progress was made. A fractionation scheme for removing high molecular weight phenolics is shown in Figure 5.1-1.

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).

TABLE 5.1-6

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

FRACTIONS	TR-7	TR-8*	TR-10
	weights in grams		
High MW Phenols (HMP)	3.8	1.4	6.8
Non-Acidic Materials (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, 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

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 three PDU samples, together with some elemental analyses, are given in Table 5.1-6.

In comparing the results for TR-10 and TR-7, both LBL-process runs, we observe that the higher severity of TR-7 has resulted in increased low molecular weight phenols (fractions F & G) and neutrals (fraction E) at the expense of high molecular weight phenols. An increase of severity appears to have resulted in depolymerization as well as removal of oxygen.

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* The available sample from TR-8 contained much anthracene oil.

FIGURE 5.1-1

FRACTIONATION SCHEME FOR WOOD DERIVED OILS

XBL 816-10283
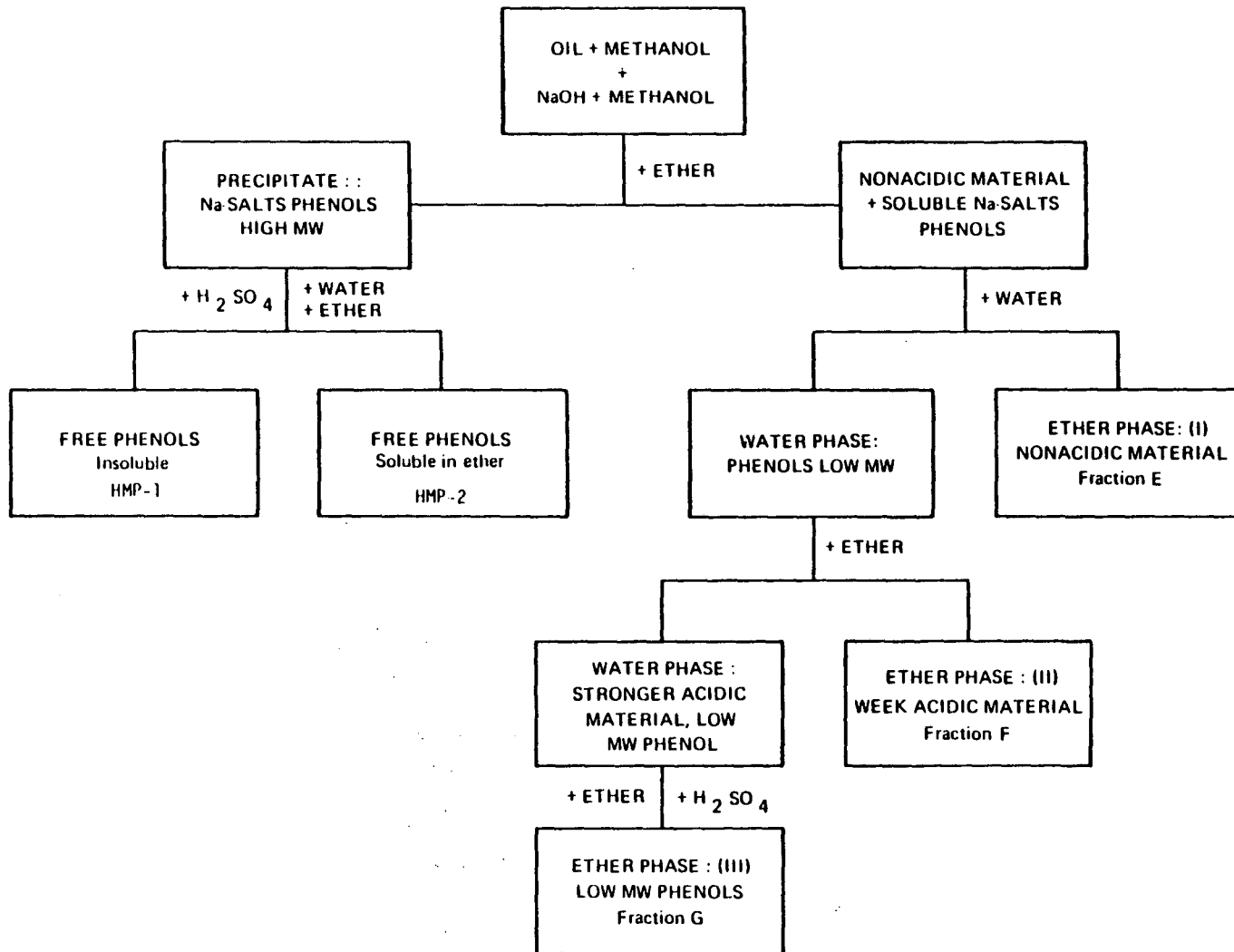
Gel permeation chromatograms of the fractions from TR-7 are compared with a chromatogram of whole oil in Figure 5.1-2. Separation of the high molecular weight phenolic fraction of TR-7, shown in the figure, appears to have been good. This simple and fast extraction procedure makes it possible to divide the oil into a non-acidic fraction and phenolic fractions of two different molecular weight ranges, without getting involved in sticky resinous materials, which always appear when organic solutions of the oils are extracted by alkaline water solutions.

From our other studies — especially the SESC results — we believe the high percentage of phenolic material found for the PDU TR-7 and TR-10 runs to be typical. Normalizing to 100%, we have, for TR-7, phenolics 64%; "neutrals" 36%; for TR-10, phenolics 84%, neutrals 16%; for TR-8 (PERC process, high recycle ratio, high severity of operation, contamination with anthracene oil), phenolics 45%, neutrals 55%. In the order of increasing reaction severity, TR-10 is lowest, TR-7 much higher and TR-8 much higher yet. Phenolics are removed as reaction proceeds. However, a substantial, but not quantitatively measured portion of the TR-8 neutrals were hydrocarbons remaining from the anthracene oil start-up solvent, and in all cases phenolic content is quite high.

5.1.3 MOLECULAR WEIGHT DISTRIBUTION

Average molecular weights and distribution curves were determined by typical HPLC procedures. As work proceeded, the calibration curve was improved by using model compounds of types expected to be in the biomass oils. Calculating techniques were also improved. The average molecular weights given elsewhere in this report should be consistent with each other, i.e. valid in a relative sense. The absolute values are certainly in somewhat greater doubt and the <u>caveat</u> not to take them overly seriously should be borne in mind.

Some other typical HPSEC curves — on four SESC fractions from CLU run 6 — are shown in Figure 5.1-3. The combination of SESC fractionation and HPSEC is a powerful tool. It has been a major factor in pushing us towards a solvolysis (hydrogenation process) route, as discussed elsewhere in the report.

5.1.4 GC-MS

Most of the detailed knowledge about individual components of wood oil stem from GC-MC studies. D.J. Kloden, during the period he was with this group, undertook an extensive study of the composition. First he did a rough distillation into several volatile fractions and a distillation residue. Each fraction was then separated by gas chromatography. and at least tentative identification of all peaks above about 1% (by area) made in the LBL MS group. Unfortunately, this work was terminated, because of funding and staffing problems, before final resolution of the many uncertainties in identification could be made. The list of compounds identified (Table 5.1-7) is presented for whatever light it may throw on the composition of typical wood-derived oils.
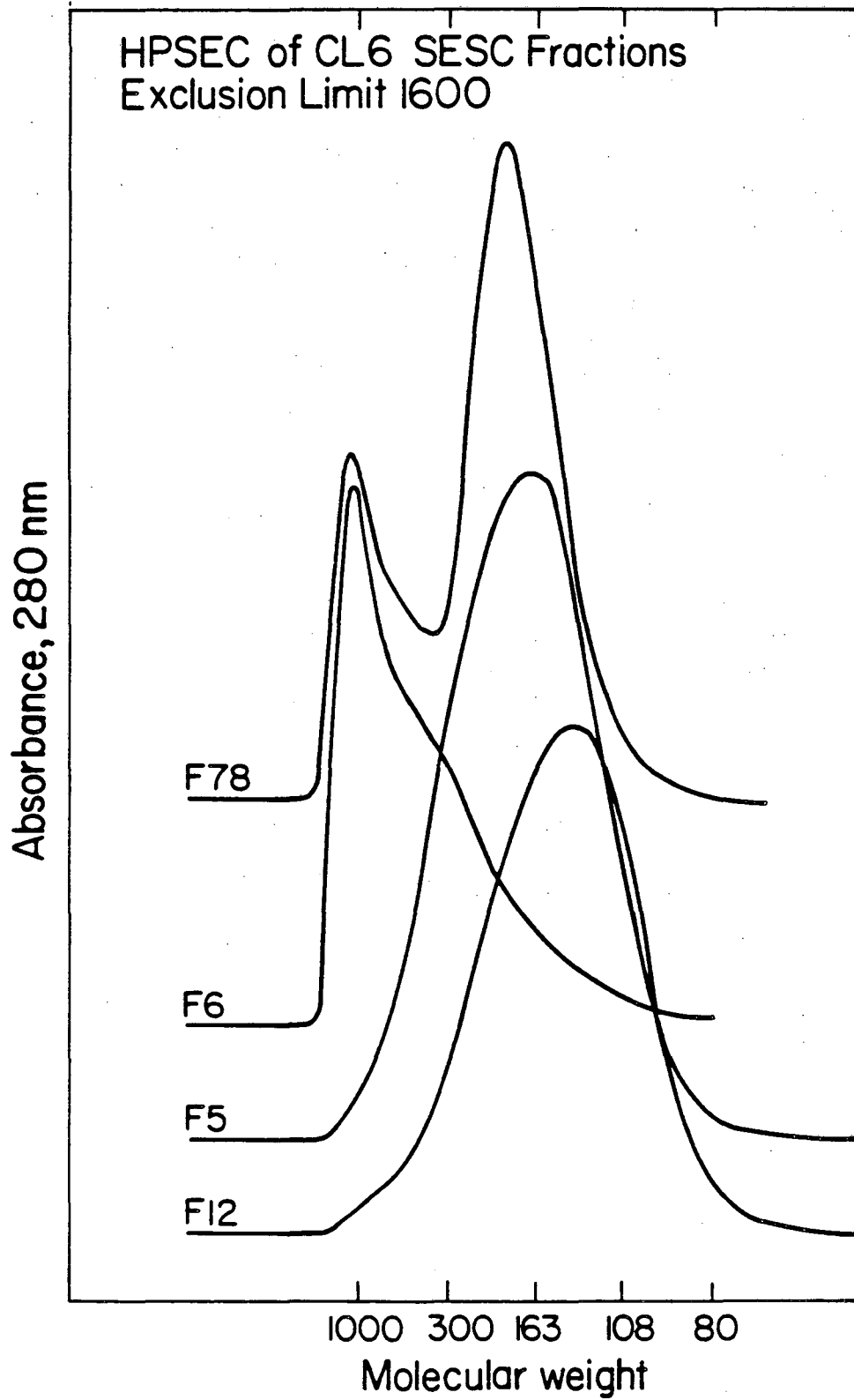
FIGURE 5.1-2

Gel permeation chromatograms
of TR7 oil fractions
UV 254 nm

Gel permeation chromatograms of TR7 oil fractions UV 254 nm

XBL 815-811

FIGURE 5.1-3

HPSEC of CL6 SESC Fractions
Exclusion Limit 1600
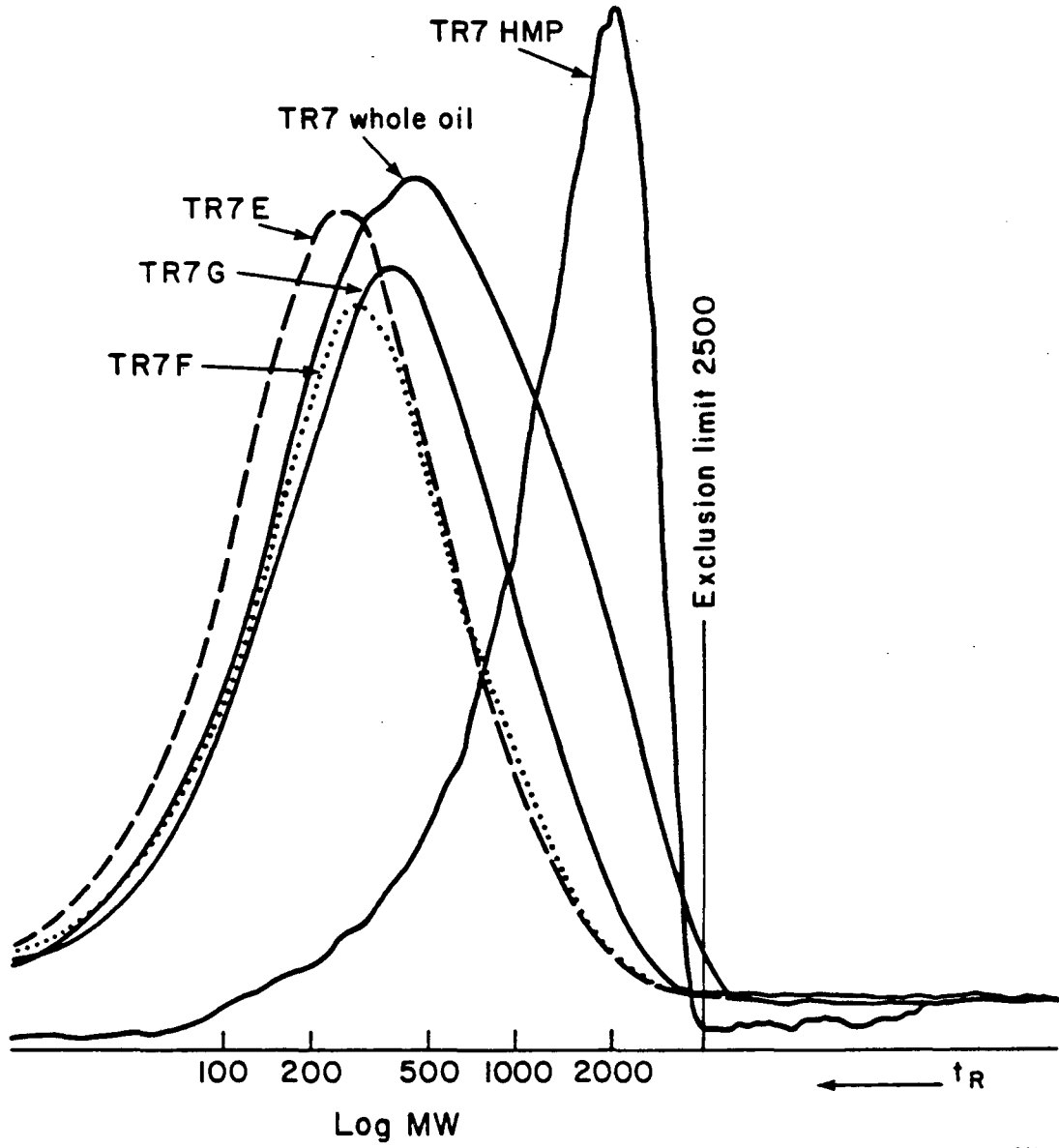
XBL 8110-1421

TABLE 5.1-7

MAJOR COMPONENTS OF TR-7 AND TR-12 WOOD OILS BY GC-MS

No.	M.W.	FORMULA	IDENTIFICATION	TYPE
1	85	C_5H_8O	cyclopentanone	ketone
2	98	$C_6H_{10}O$	3-mecyclopentanone	ketone
3	94	C_7H_{12}	cyclopentylethylene	HC
4	110	C_8H_{14}	dimecyclohexane	HC
5	108	C_8H_{12}	1,6-dimecyclohexene	HC
6	124	C_9H_{16}	propylcyclohexene	HC
7	"	"	methylethylcyclohexene	HC
8	"	$C_7H_8O_2$	2-methoxyphenol (guaiacol)	ether-phenol
9	122	$C_8H_{10}O$	2-ethylphenol	phenol
10	138	$C_{10}H_{18}$	CP-Menthelene	HC
			1-Me-4-i-propylcyclohexene	
11	122	$C_8H_{10}O$	3,4-dimephenol (xylenol)	phenol
12		$C_8H_{10}O_2$	1,2-dimethoxybenzene	diether
13	136	$C_9H_{12}O_2$	2,4,6-trimephenol	phenol
14	152	$C_9H_{12}O_2$	4-ethylguaiacol	ether-phenol
15	166	$C_9H_{14}O_2$	4-propylguaiacol	ether-phenol
16	138	$C_{10}H_{18}$	perhydroindene	HC
17	110	C_8H_{14}	3-propylcyclopentene	HC
18	152	$C_9H_{12}O_2$	4-eth,5-me-1,3-benzenediol	diphenol
19	166	$C_{10}H_{14}O_2$	propylguaiacol or	diphenol
			butylresorcinol	
20	150	$C_9H_{10}O_2$	4-(1-propenyl) resorcinol	diphenol
21	136	$C_9H_{12}O$	4-propylphenol	phenol
22	152	$C_9H_{12}O_2$	4-i-propylcatechol	diphenol
23	166	$C_{10}H_{14}O$	4-prop,5-mecatechol	diphenol
24	166	$C_{10}H_{14}O_2$	diethylcatechol	diphenol
25	162	$C_{12}H_{18}$	dipropylbenzene	HC
26	176	$C_{12}H_{16}O$	3-ethyl, 4-i-propenyl,	phenol
			6-mephenol	
27	166	$C_{10}H_{14}O_2$	4-propyl, 5-mecatechol	diphenol
28	166	"	3-me,4-ethylguaiacol	ether-phenol
29	166	"	3,4,5-trimethylguaiacol	ether-phenol
30	180	$C_{10}H_{12}O_3$	4-(1-propanone-2)-5-mecatechol	ketone-diphenol
31	166	$C_9H_{10}O_3$	4-(1-propanone-2) catechol	ketone-diphenol
32	152	$C_9H_{12}O_2$	4,5-trimecatechol	diphenol
B-1	124	$C_8H_{12}O$	2,3,4-trime-2-cyclopentanone	cyclic ketone
2	108	C_7H_8O	3-mephenol	phenol
3	122	$C_8H_{10}O$	2,5 dimephenol	phenol
4	136	$C_9H_{12}O$	methylethylphenol	phenol
5	"	"	i-propylphenol	phenol
6	"	"	3-ethyl-5-mephenol	phenol
7	"	"	2-ethyl-5-mephenol	phenol
8	"	"	2,4,5-trimephenol	phenol
9	150	$C_{10}H_{14}O$	2-sec-butylphenol	phenol
10	"	"	5-me-2-propylphenol	phenol (thymol)
11	"	"	3-me-4-propylphenol	phenol
12	"	"	4-i-propyl-1-methoxybenzene	ether
13	150	$C_{10}H_{14}O$	2-sec-butylphenol	phenol
14	"	"	diethylphenol	phenol
15	"	"	diethylphenol (isom)	phenol
16	164	$C_{10}H_{12}O_2$	4-methoxyphenylethylketone	ether-ketone

No.	MW	Formula	Name	Type
17	174	$C_{12}H_{14}O$	4-i-propenylphenylmethyl methylketone	ketone
18	164	$C_{11}H_{16}O$	3-pentylphenol	phenol
19	180	$C_{10}H_{12}O_3$	2-methoxy-4(I-propan-2-one) phenol	phenol-ketone
20	178	$C_{12}H_{18}O$	2,4-dipropylphenol	phenol
21	150	$C_{10}H_{14}O$	5-me-2-i-propylphenol	phenol
22	150	$C_{10}H_{14}O$	3-me-4-propylphenol	phenol
23	138	$C_8H_{10}O_2$	4-ethylcatechol	diphenol
24	164	$C_{11}H_{16}O$	3-ethyl-4-propylphenol	phenol
25	178	$C_{12}H_{18}O$	3,5-dipropylphenol	phenol
26	178	$C_{11}H_{14}O_2$	1,2-dimethoxy-4-(i-propenyl) benzene	diether
27	162	$C_{12}H_{18}$	hexamethylbenzene?	HC
28	166	$C_{10}H_{14}O_2$	4-propyl-5-methylcatechol	diphenol
29	166	$C_{10}H_{14}O_2$	2-methyoxy-4-ethyl-5-me-phenol	ether-phenol
30	166	$C_{10}H_{14}O_2$	4-sec-butylcatechol	diphenol
31	192	$C_{13}H_{20}O$	methyldipropylcatechol	diphenol
32	138	$C_8H_{10}O_2$	4-methoxyphenylmethanol	ether-alcohol
33	138	$C_8H_{10}O_2$	4-ethylresorcinol	diphenol
34	152	$C_9H_{12}O_2$	2,3 dime-5 methoxylphenol	phenol-ether
35	178	$C_{12}H_8O$	3,4-dipropylphenol	phenol
36	152	$C_9H_{12}O_2$	4-propylresorcinol	diphenol
37	166	$C_9H_{10}O_3$	methyl-(4-hydroxyl-3 methoxyphenylketone	phenol-ketone-ether
38	152	$C_9H_{12}O_2$	3-me-4-ethylcatechol	diphenol
39	166	$C_{10}H_{14}O_2$	2-me-4-propylresorcinol	diphenol
40	166	$C_{10}H_{14}O_2$	4-t-butylcatechol	diphenol
41	176	$C_{12}H_{16}O$	3(1-propenyl)-4-propylphenol	phenol
42	176	$C_{12}H_{16}O$	3-propyl-4(1-propenyl) phenol	phenol
43	176	$C_{13}H_2O$	1,2,4-trimethyl-5-mebenzene	HC
44	180	$C_{10}H_{12}O_3$	4-(i-propanone-2)-5-mecatechol	diphenol-ketone
45	180	$C_{11}H_{16}O_2$	3,5-dime-4-propylcatechol	diphenol
46	180	$C_{11}H_{16}O_2$	2-methoxyl-3-me-4 propylphenol	phenol
47	194	$C_{11}H_{14}O_3$	1-(2,4 dimethoxyphenyl)-1-propanone	diether-ketone

SUMMARY, TABLE 5.1-7

Hydrocarbons	11
Ketones	4
Phenols	28
Diphenols	18
Phenol-ketone	1
Diphenol-ketones	3
Phenol-ethers	7
Diether-ketone	1
Ether	1
Diethers	2
Ether-ketone	1
Ether-ketone-phenol	1
Ether-alcohol	1
TOTAL	79

The most impressive result of the work is the fact that about 80% of all compounds identified contain at least one phenolic hydroxyl. It is also of interest that there are quantitative differences between samples with different histories (e.g. TR-7, LBL process, and TR-12, PERC Process). But when we examined chromatographs of a variety of samples we found no outstanding qualitative differences: the same major peaks were found in all samples.

5.2 WATER-SOLUBLE ORGANIC PRODUCTS

A serious difficulty with the water-slurry process, and even with the PERC oil-slurry process, is the production of large amounts of water-dissolved organics. Roughly half of these are carboxylic acids and their anions, while the balance includes low molecular weight ketones and phenols (especially diphenols and other di- or trifunctional aromatics).

The characterization work at LBL has been especially useful in elucidating the nature of these water-soluble products. As recently as 1980, this was by no means generally understood. Witness of this is reference to plugging of reactors by "catalyst" or talk of recycling catalyst (26). In both cases "catalyst" refers to the sodium carbonate added to make the initial pH high. It is now clear that as soon as any significant reaction takes place, in either PERC or LBL process, enough carboxylic acid is formed to lower the pH below the point where significant carbonate remains. Evaporation to dryness gives a mixture of sodium carboxylates.

Characterization of the water-dissolved organics proceeded in the order (1) determination of total carboxylic acid and carboxylate ion by acid-base titration; (2) identification of specific acids by GC-MS plus quantitative determination of the low molecular weight acids by HPSIEC and (3) identification of phenols and neutrals by GC-MS, either directly or after derivatization.

5.2.1 CARBOXYLIC ACIDS AND ANIONS

The presence of large amounts of carboxylic acids, or, depending on pH, their anions, was first established by titration with standard alkali and/or acid. Figure 5.2-1 shows the type of curve obtained. Since the samples are from PDU run TR-12 (high recycle ratio, PERC process), concentrations found are high.
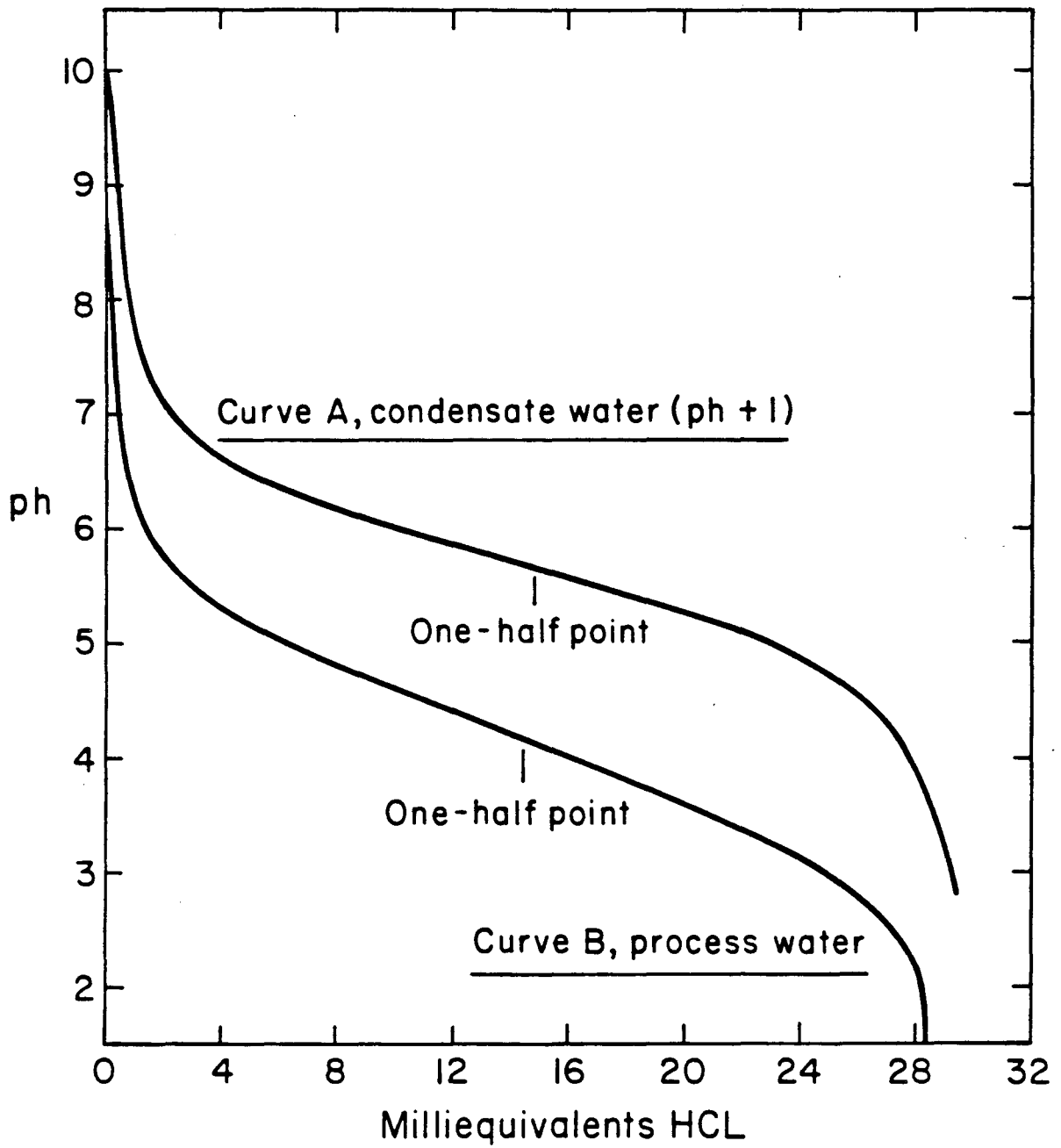
Overhead water or condensate, was acidic before adjustment to pH 8-9. The pK_a indicated by the half titration point is about 4.7, compatible with the major components being acetic and other mono-acids volatized at the effluent water pH of about 7.

The bottom water, on the other hand has an average pK_a of about 4.1. This suggests the presence of substantial amounts of acids much stronger than acetic. All samples of water from CLU runs had similarly low pK_a's. Following up on this observation led to determining that glycolic acid (pK_a 3.83) was a major component of the water-soluble fraction, in fact the largest single product of Douglas fir liquefaction. It also led to establishing formic acid (pK_a 3.75) as a moderately important, though very variable, product.

Figure 5.2-2 shows a chromatogram of aqueous effluent from run CL-12. All other process waters display comparable HPLC traces. It was established that aromatics, like, phenol and guaiacol are not eluted within the 25-min time frame of Figures 5.2-2. 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 Figures 5.2-2. Moreover the retention times of formic and glycolic acids were identical.
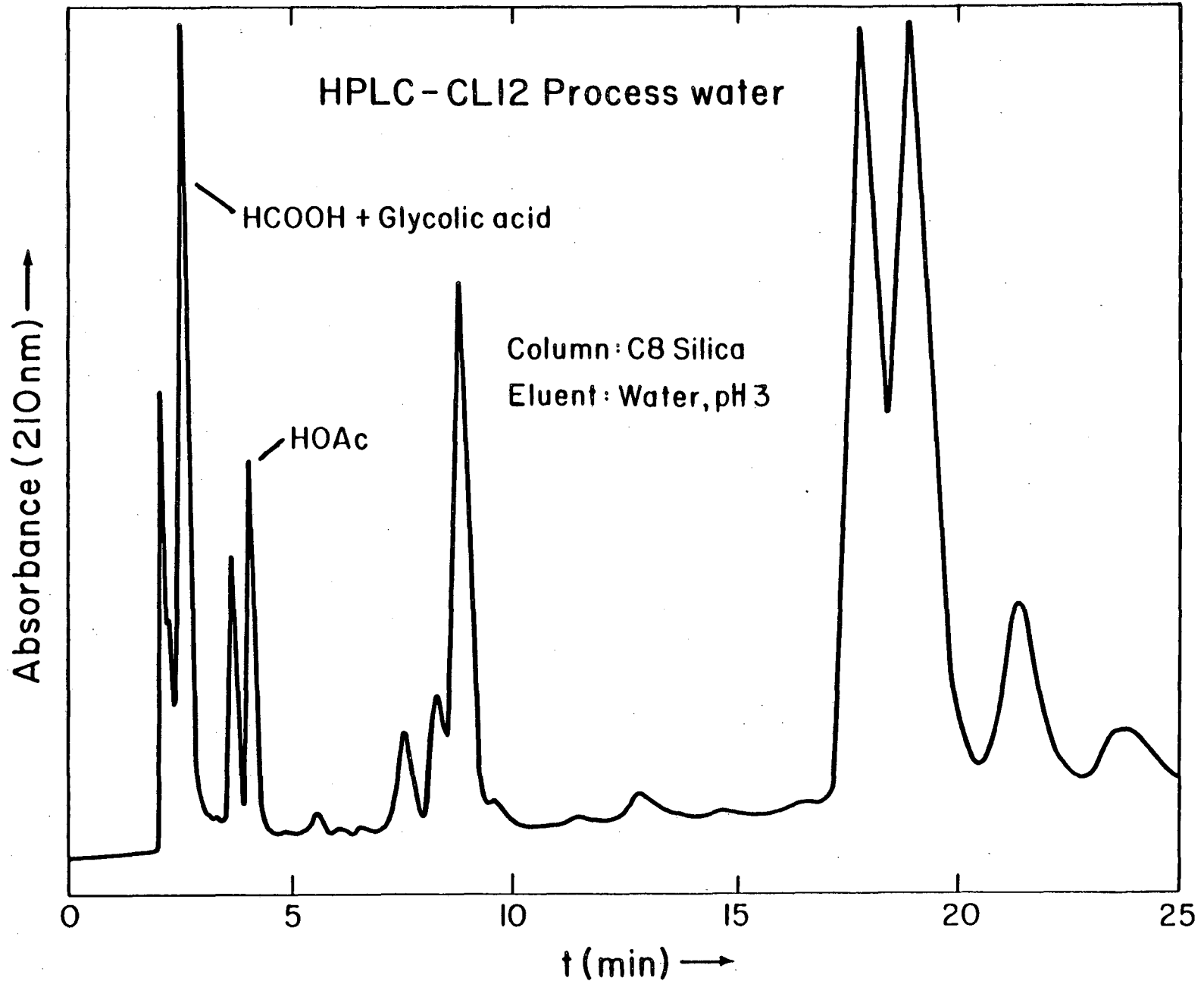
Formic and glycolic acids were resolved by high-performance ion exchange chromatography (HPIEC). A Wescan anion exchange column was used with an eluent of 0.001 $\underline{M}$ phthalate buffer at pH 3.0. Interpretation of chromatograms was simplified through the use of a Wescan Model 213 conductivity detector which selectively monitors ionic species.

FIGURE 5.2-1

Curve A, condensate water (ph + 1)

One-half point

One-half point

Curve B, process water

XBL 815-810

-59-

FIGURE 5.2-2

Absorbance (210 nm) →

HPLC – CLI2 Process water

HCOOH + Glycolic acid

HOAc

Column : C8 Silica
Eluent : Water, pH 3

t (min) →

The ion chromatograms of 1 μl samples of prehydrolyzed wood slurry water and CL-12-3 process water are compared in Figures 5.2-3 and 5.2-4. Glycolic acid is cleanly separated from formic and acetic. Levulinic acid appears between acetic and glycolic as a minor component of slurry water.

A great deal of chemistry is exemplified in these figures. 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 in effluent water is higher because of the reaction between CO and hydroxide ion or water. Reference to Table 5.2-1 shows that glycolic acid concentration undergoes a very large increase upon liquefaction. This increase occurs when either CO or H_2 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 phenols. The possibility that these water-solubles represent the major intermediate stage 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. The possibility that some oil is formed upon repeated recycle of water-solubles cannot, however, be excluded, and is indeed one probable explanation of the difference in yields of water solubles of the PERC and LBL processes.

Glycolic acid has now been established (at least, for Douglas fir) 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 -- a higher concentration but smaller yield. A sample of TR-12 water analyzed for 9.7% glycolic acid, 10.9% acetic and 2.7% formic. 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. It should be noted that increased severity reduces the yield of glycolic acid. This is in contrast to acetic acid which increases. Here the observation that acetic acid is more important than glycolic in TR-12 effluent water is consistent with the higher severity of operation because of recycle.
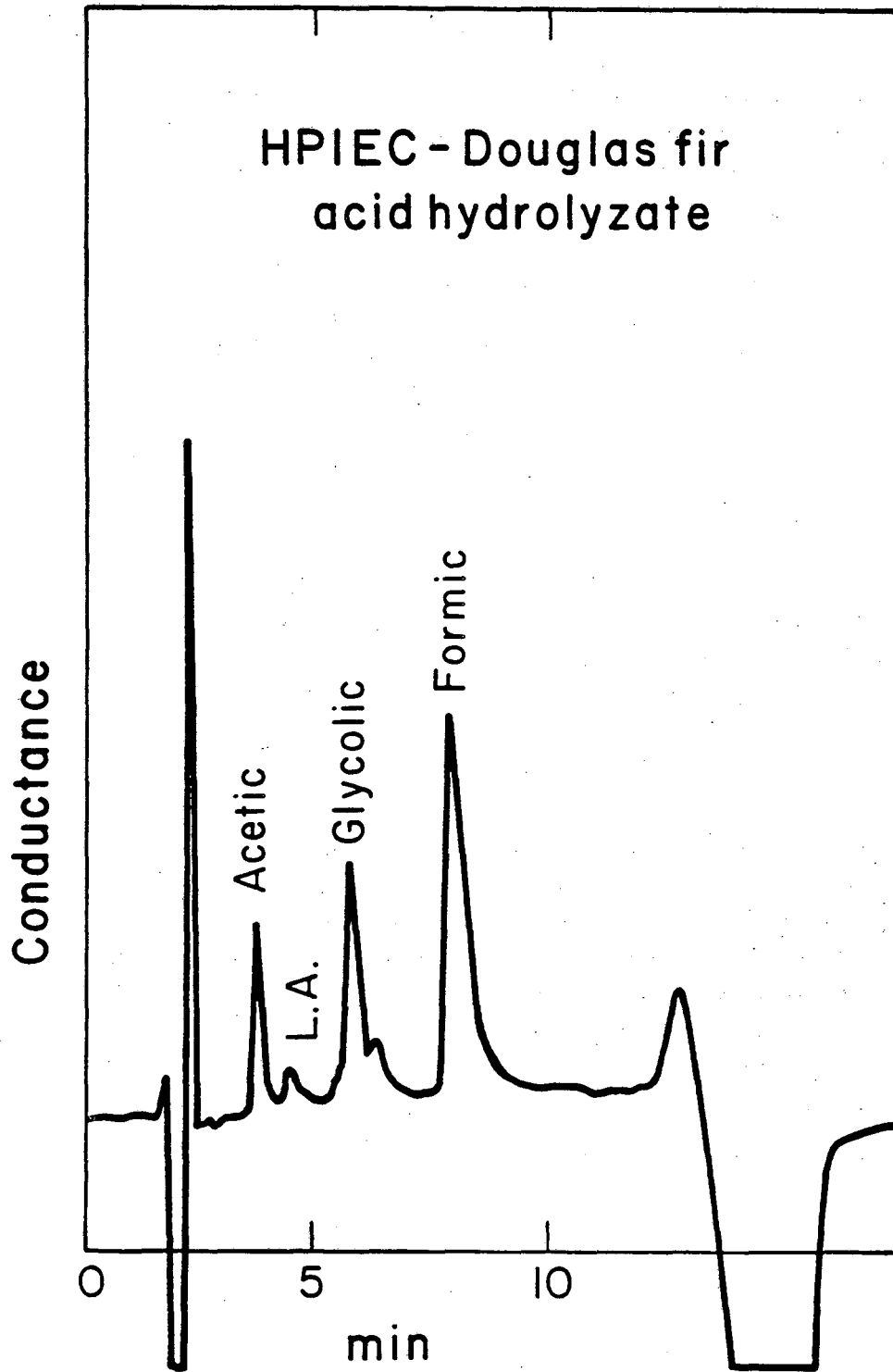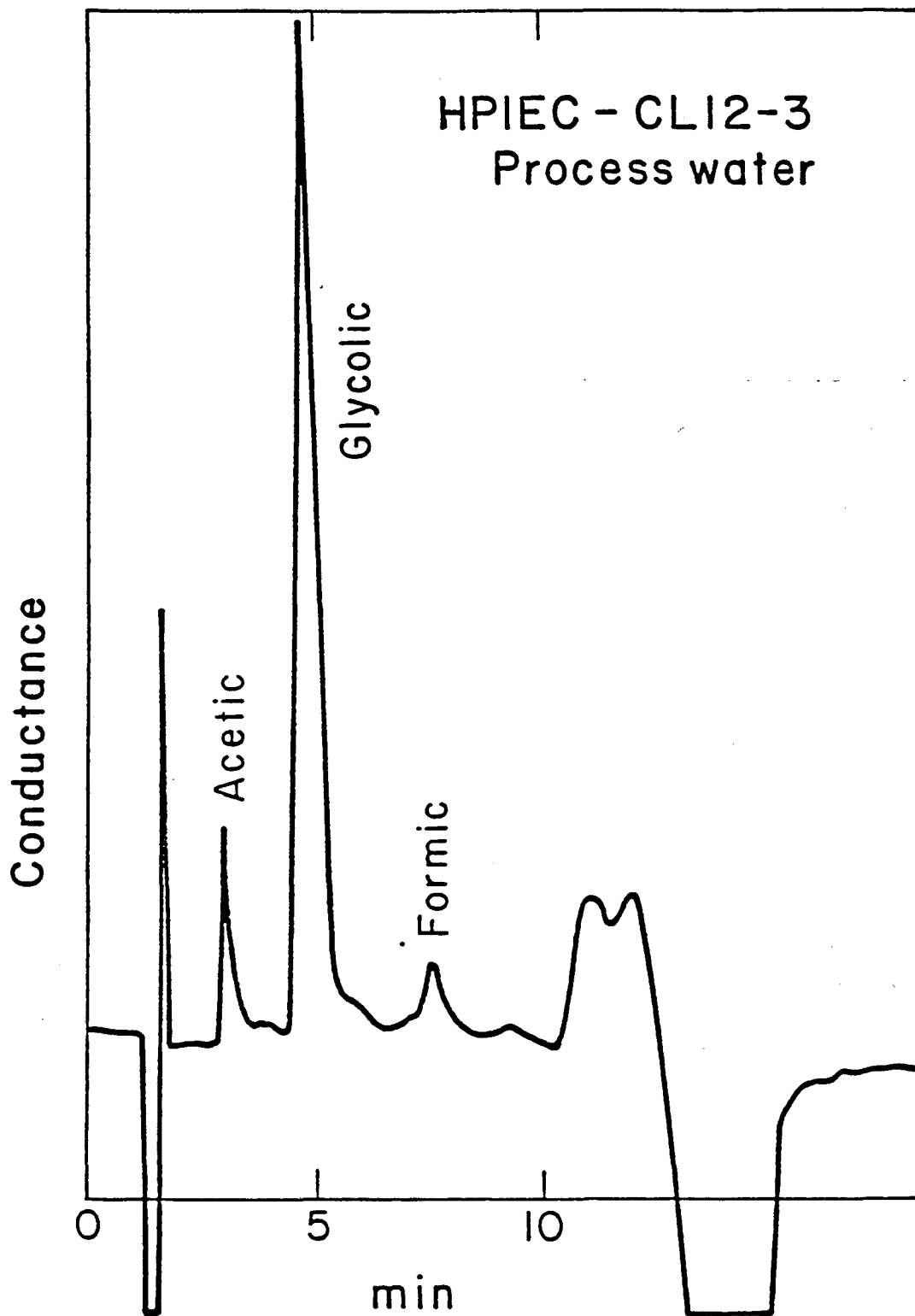
FIGURE 5.2-3

HPIEC – Douglas fir acid hydrolyzate

FIGURE 5.2-4

FIGURE 5.2-4

HPIEC - CL12-3
Process water

Conductance

Acetic

Glycolic

Formic

0   5   10   min

TABLE 5.2-1					
EFFECT OF REACTION CONDITIONS ON CONCENTRATIONS OF CARBOXYLIC ACIDS IN PROCESS WATERS FROM DIRECT LIQUEFACTION OF DOUGLAS FIR					
Slurry Water	Glycolic[a]	Acetic[b]	Formic[a]	Levulinic[a]	Total[b]
(180°, 45 min, pH 2)	.04N	.10N	.11N	0.02N	.26N
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 large number of individual acids were identified by GC-MS. The total list is given in Table 5.2-2. It should be remembered that formic, acetic and glycolic account for a very high percentage of the total yield of acids. The remaining acids split up about 10% (or perhaps at most 20%) of the total.

[a] Determined by HPIEC, [b] Measured by acid-titration.

TABLE 5.2-2

CARBOXYLIC ACIDS IN AQUEOUS PHASE

	FORMULA	IDENTIFICATION	MW
1.1	CH_2O_2	formic	46
2.1	$C_2H_4O_2$	acetic	60
2.2	$C_2H_4O_3$	glycolic	76
3.1	$C_3H_6O_2$	propionic	74
4.1	$C_4H_6O_2$	methacrylic	86
4.2	$C_4H_6O_2$	crotonic	86
4.3	$C_4H_6O_4$	methylmalonic	118
4.4	$C_4H_6O_4$	succinic	118
4.5	$C_4H_8O_2$	isobutyric	88
4.6	$C_4H_8O_2$	butyric	88
5.1	$C_5H_6O_5$	2-oxoglutaric	146
5.2	$C_5H_8O_2$	3-methyl-2-butenoic	100
5.3	$C_5H_8O_2$	2-pentenoic	100
5.4	$C_5H_8O_2$	3-pentenoic	100
5.5	$C_5H_8O_3$	levulinic	116
5.6	$C_5H_8O_4$	methylsuccinic	132
5.7	$C_5H_8O_4$	glutaric	132
5.8	$C_5H_{10}O_2$	2-methylbutanoic	102
5.9	$C_5H_{10}O_2$	pentanoic	102
6.1	$C_6H_8O_2$	2-methyl-2,4=pentadienoic	112
6.2	$C_6H_{10}O_2$	4-methyl-3-pentenoic	114
6.3	$C_6H_{10}O_2$	3-methyl-4-pentenoic	114
6.4	$C_6H_{10}O_2$	3-hexenoic	114
6.5	$C_6H_{10}O_3$	2-ethyl-3-oxobutanoic	130
6.6	$C_6H_{10}O_3$	4-oxohexanoic	130
6.7	$C_6H_{10}O_3$	5-oxohexanoic	130

	FORMULA	IDENTIFICATION	MW
6.8	$C_6H_{10}O_4$	2,2-dimethylsuccinic	146
6.9	$C_6H_{10}O_4$	ethylsuccinic	146
6.10	$C_6H_{10}O_4$	2-methylglutaric	146
6.11	$C_6H_{10}O_4$	3-methylglutaric	146
6.12	$C_6H_{10}O_4$	adipic	146
6.13	$C_6H_{12}O_2$	2-methylpentanoic	116
6.14	$C_6H_{12}O_2$	3-methylpentanoic	116
6.15	$C_6H_{12}O_2$	hexanoic	116
7.1	$C_7H_6O_2$	benzoic	122
7.2	$C_7H_6O_3$	4-hydroxybenzoic	138
7.3	$C_7H_6O_4$	2,3-dihydroxybenzoic	154
7.4	$C_7H_{12}O_2$	4-heptenoic	128
7.5	$C_7H_{12}O_3$	2-methyl-5-oxohexanoic	144
7.6	$C_7H_{12}O_3$	4-methyl-5-oxohexanoic	144
7.7	$C_7H_{12}O_4$	2,3-dimethylglutaric	160
7.8	$C_7H_{14}O_2$	2,4-dimethylpentanoic	130
8.1	$C_8H_8O_2$	pehnylacetic	136
8.2	$C_8H_8O_3$	p-hydroxyphenylacetic	152
9.1	$C_9H_{10}O_2$	3-pehnylpropanoic	150
10.1	$C_{10}H_{12}O_4$	3-(4-hydroxy-3-methoxyphenyl)propanoic	196

5.2.3 WATER DISSOLVED NEUTRALS AND PHENOLICS

A gas chromatograph of a sample of liquefaction aqueous effluent shows the presence of a host of organic compounds. Many of these are carboxylic acids, and these have largely been identified. If the pH of the water is adjusted to about 9 or 10, the carboxylic acid peaks disappear, but a very large number of peaks remain. These are neutrals or phenolics, which are weakly acid and largely present as the unionized component at these pH's. The effect of pH is indicated in the chromatograms shown as Fig. 5.2-5.

In our early work[4] on these organics, using straight GC-MS, we identified a number of compounds, primarily cyclic ketones and simple monophenols or methoxyphenols. Similar compounds were found in a steam distillate from TR-7 oil. While a distribution of such compounds between the oil and aqueous phases is to be expected, it is probable that some of the material steam-distilled was actually dissolved in the roughly 7% water present in the samples of TR-7. The following compounds were of significance in both materials: cyclopentanone, cyclohexanone, methylcyclopentanones, methylcyclopentenones, di- and tri-methylcyclopentenones, guaiacol (2-methoxyphenol), and methylguaiacols. In later direct GC-MS studies of extracts from water effluents, phenol, cresols, xylenols, and several diols were identified. In addition we identified methoxy-diphenols, 3-methylfuran, 2,5-hexanedione, and furanol and furanone derivatives.

More recently, a new study of the water-soluble components after derivatization was initiated. The work has not and will not be completed. However, even incomplete, the data are the most extensive reliable data on the water- solubles available so far. They are summarized in Table 5.2-3. In this effort water-dissolved phenolic components of water from run CL-12 were converted to acetates, which greatly aided in the ease of separation and identification.
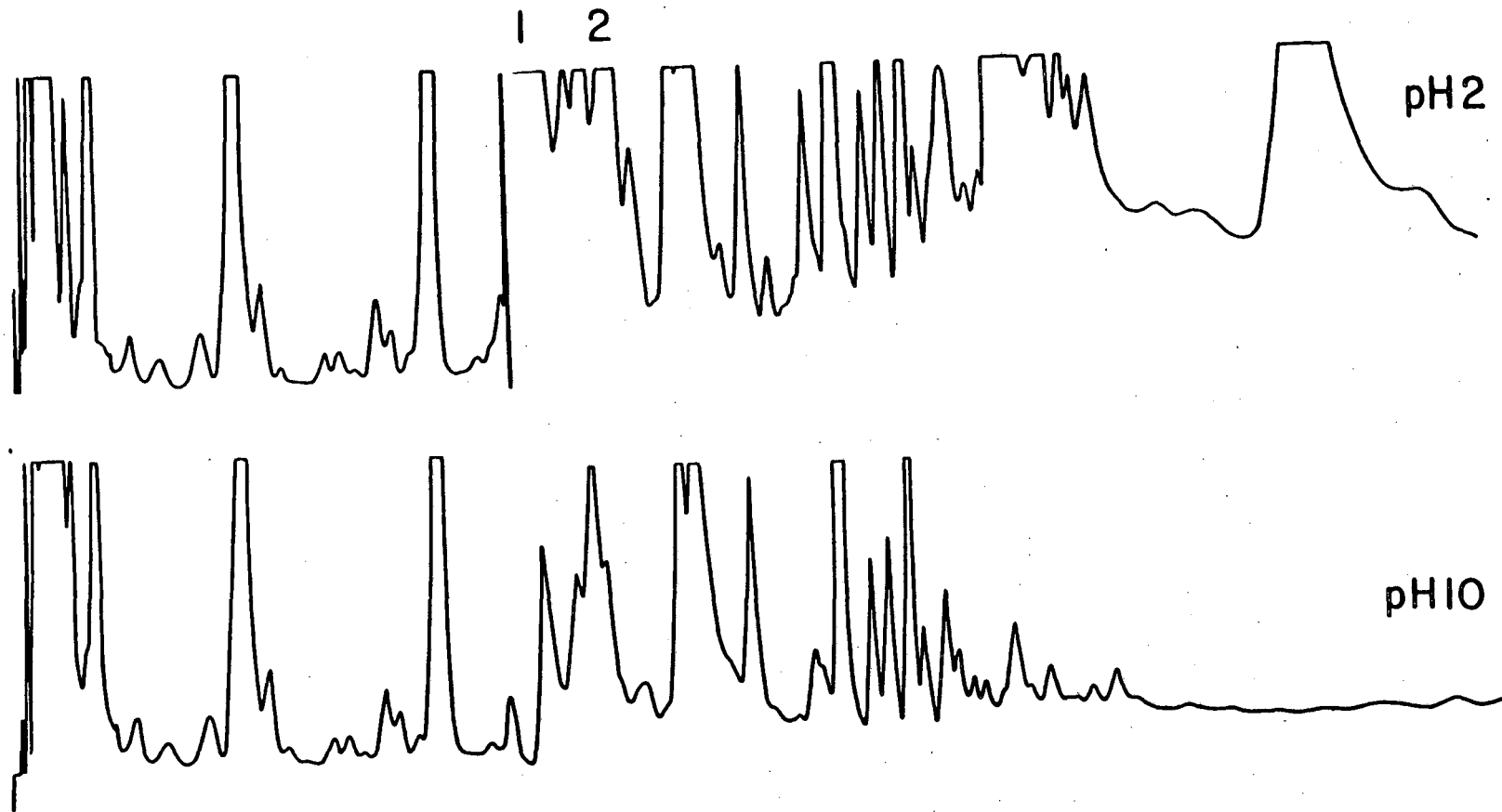
FIGURE 5.2-5

Fig. 5.2-5 Gas chromatograms of aqueous phase from batch autoclave run RA-23 (Douglas fir water slurry 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. At pH 10, many or all phenols will act as "neutrals."

TABLE 5.2-3

IDENTIFICATION OF WATER SOLUBLE ORGANICS AFTER ACETYLATION

Elution Order	Time Seconds	Mass	Identification	Comment
1	540	84	Cyclopentanone	
2	625	98	Unidentified	Me Cyclopentanone
3	770	96	Me Cyclopentenone	
4	826	110	Unidentified	Dime(orethyl-) cyclopentenone? ?
5	907	96	Me Cyclopentenone	
6	958	110	Dimecyclopentenone	
7	1054	110	Dimecyclopentenone	
8	1086	136	Phenol (as acetate)	
9	1147	124	Trimethylcyclopentenone	
10	1230	150	Cresol (as acetate)	
11	1280	150	2-cresol (as acetate)	
12	1292	150	3-cresol (as acetate)	
13	1494	166	Guaiacol (as acetate)	
14	1524	152	Unidentified	
15	1542	126	Unidentified	
16	1668	180	4-methylguaiacol (as acetate)	
17	1810	152	Unidentified	
18	1893	208	Methylcatechol (as acetate)	Probable identification
19	1940	208	Isomer of 18 (propyl-guaiacol?)	
20	1967	152	Possibly vanillin	
21	1984	222	Ethylcatechol (as acetate)	
22	2008	222	Isomer of 21 (as acetate)	
23	2031	180	Methylguaiacol (as acetate)	
24	2070	222	Isomer of 21 (as acetate)	
25	2106	194	Ethylguaiacol (as acetate)	Possible only
26	2119	236	Propylcatechol (as acetate)	
27	2166	194	Isomer of 25 (as acetate)	
28	2232	194	Isomer of 25 (as acetate)	
29	2272	194	Dimethylmethoxyphenol (as acetate)	
30	2302	224	Unidentified (one OH)	
31	2383	224	Unidentified (one OH)	
32	2403	196 (?)	$C_{10}H_{12}O_4$ as monoacetate	
33	2505	266	2-hydroxypropylguaiacol (as acetate)	
34	2547	210 (?)	Unidentified	
35	2659	252	Unidentified	Similar to 33?

5.2.4 GENERAL OBSERVATIONS

5.2.4.1 Process considerations

The water-dissolved organics are a major product of either of the existing processes, but especially of the water slurry process. While there is some tendency for these to decompose on recycle, recycling in general is ineffective as well as very costly. Also, many of the most important components, such as glycolic, acetic and formic acids, and the diphenols, are highly hydrophilic and therefore difficult and uneconomic to extract.

Preliminary results with solvolysis indicate that only very small amounts of water-solubles are formed. In any case the quantity of water to be treated is small. This is a major factor in pushing the development towards solvolysis as the front-end process.

5.2.4.2 Concentration in Various Waters

Table 5.2-4, from data available in early 1981, gives some typical estimated concentrations of acids and neutrals (including phenols) in several aqueous streams. As stated in the table, percentages of acids and anions are calculated from titration values, assuming an equivalent weight of 80 (see below). Then to estimate the percentage of neutrals from the total organic carbon, we have assumed that the acids have average carbon percentages of 48 and the neutrals and phenols 50. From the footnote to table 5.2-4, it will be seen that the portion of acids readily extracted (with chloroform) was about 6.3% higher in carbon than the average. We have assumed that the same difference applies to the extracted and total neutrals.

TABLE 5.2-4

LIQUEFACTION OF DOUGLAS FIR WOOD

ANALYSES OF SOLUBLE ORGANICS IN AQUEOUS STREAMS

SAMPLE	Total Organic Carbon, wt %	Acids + Anions*		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

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

† Sample 7 - <u>Extracted</u> acids (1.9% of sample) had C - 53.5, H - 6.8, 0 - 39.7%
Sample 8 - Total acid from sodium salt had   C - 47.2, H - 6.9, 0 - 45.9%
Sample 7 - <u>Extracted</u> neutrals (0.8% of sample) C - 56.6, H - 6.65, 0 - 36.7%

The three batch autoclave runs analyzed indicate that in the low severity range studies, an increase in severity does significantly reduce the content of both acids and neutrals.

We can test how much control we have in a continuous unit over water-solubles by looking at results in the series CL-7 to CL-13. Here we systematically varied the pH, gas feed type and reactor temperature. We show the results below, with O-content of product oil used as an additional severity indicator.

A rise of $20^{o}C$ in reactor temperature gives the following change (The observed value of percent O and equivalents/kg in the first run named are subtracted from those for the second run to give the differences shown):

CL-8   vs. CL-7;   0% - 1.5, Eq/kg, - 0.09

CL-11A vs. CL-11B;   0% - 1,   Eq/kg, - 0.04

CL-12A vs. CL-12B;   0% - 1.5, Eq/kg, - 0.06.

CL-13A vs. CL-13B;   0% - 1.5 (assumed) Eq/kg,- 0.06.

Similarly the effect of pH can be seen.

CL-10A vs. Cl-11 (ave); Eq/kg, - 0.08 (-0.10)*

CL-13(ave.) vs. Cl-12A; Eq/kg, - 0.11 (0.09)*

There are significant effects when process gas is changed::

$CO \rightarrow H_2$

    CL-11 (average) vs. CL-12 (average); Eq/kg, - 0.10

    CL-10 vs. CL-13B;   Eq/kg, - 0.04 (-0.08)*

$CO \rightarrow$ Syn Gas (50% H_2, CO)

    CL-11A vs. CL-7;   - 0.06.

Apparently by raising reactor temperature $20^{o}C$, we reduced the acid plus anion content of the water phase by about 0.06 Equivalents/kg (about 0.5 wt % of the water), while dropping the % O of the oil phase by about 1.5. By raising pH about 1 unit, we raised the acid/anion content about 0.10 Eq/kg (about 0.8 wt %). By changing process gas from CO to syngas (1 : 1, H_2 : CO) and then to 100% H_2, we dropped the acid plus anion content, probably about 0.05 eq/kg for each of those two steps (0.4 wt % or 0.8 wt % for the full change from CO to H_2).

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* Values in parenthesis are corrected to allow for slightly different severities based on O-content

Part, but certainly not all, of the effect of CO lies in increasing the formate formation (or decreasing its loss). Increased pH can also be associated with increased formate, but again the amounts of formate found are not large enough to account for the differences (cf. table 5.2-1).

We may conjecture how much of the lower yield of acids and anions produced in the PDU-PERC runs may be attributed to changed conditions. The effective pH's are somewhat higher than in the CLU-LBL runs. The process gas is syngas. The severity, because of the high recycle, is considerably higher. During most of TR-12, the oxygen in the oil product was in the range 12-13.5 wt %.

If we compare TR-12 with CL-10, we expect to lose about 0.04 Eq/kg because of the gas difference and about 0.06 x (16-13)/1.5 = 0.12 for the severity shift. The overall loss should be about 0.16/0.56 or 29% of the whole yield. Apparently the higher severity in the PERC runs, due to recycle, is partly, but not wholly responsible for the change in water-solubles yield. It is, of course, possible that the effect of recycle and therefore of long residence time, is greater on the water-soluble products than on the oil.

6.0 STOICHIOMETRY AND CHEMISTRY OF LIQUEFACTION

Despite the lengthy history of the U.S.-supported liquefaction project and parallel work in other countries, many features of the chemistry have remained in doubt. The question of the role of the sodium carbonate "catalyst" has been referred to above. Even the role of CO in a process generically referred to as "CO-steam" has been questionable. Apparently, when the PDU was first initiated (cf ref. 27, p. 4-4), operators assumed that both CO and H_2 would be consumed from synthesis gas. It was assumed that solubles were formed but in small yield (about 3%) and with the unlikely empirical formula $CH_3O_{0.045}$ (76% C, 19% H, 5% O). At various times others have claimed that CO was or was not consumed and was or was not necessary.

By having ascertained an approximate elemental analysis for typical water-soluble organics, and by having available the excellent material balances obtained by Rust Engineering Co. in runs TR-8 and TR-12 — especially the latter — we have been able to throw considerable light on the general stoichiometry.

We conclude that CO is indeed consumed in the PERC process, largely because of the high oil and aqueous recycle. We conclude that considerably more CO is consumed by the water gas shift reaction.

Also we conclude that the sodium carbonate "catalyst" has its chief role in maintaining a pH near to neutral by neutralizing the carboxylic acids generated. Higher pH's increase the amount of CO reacting to form formate ion:

$$CO + OH^- \rightarrow HCOO^- \text{ (formate)}.$$

This reaction is definitely a step in the water gas shift reaction, by way of

$$HCOO^- + H_2O \rightarrow HCO_3^- \text{ (bicarbonate)} + H_2$$

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2.$$
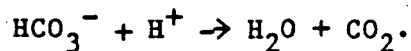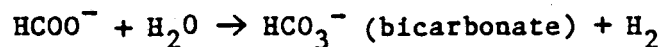
Since the role of formate ion as a reducing agent, though frequently suggested, has never been established, the finding of formate ion in water products does not prove that sodium carbonate is a necessary catalyst. However, by preventing the pH from going too low during liquefaction, it may inhibit coking reactions. Firm data proving even this are hard to find.

We found, from the CLU experiments, that little or no CO was consumed in the single-pass, water-slurry LBL runs. Hydrogen, CO, and synthesis gas appeared to be interchangeable as process gasses, except for small effects on the yields of water solubles (see Section 5). We discussed an analysis of PDU run TR-12 at length in Reference 13. This analysis is reproduced here essentially as originally written.

6.0.1 STOICHIOMETRY OF PERC PROCESS

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 technical reports[2] and in a paper presented in January, 1982[12]. 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 a primary objective and no analysis of these effects was made. Data given in the reports are not sufficient for such an analysis. However, Rust Engineering has kindly given us further data (primarily elemental analyses of oil produced and analyses of effluent gas corresponding to various temperatures). 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 (Table 6.0-1).

The independent variables tested were T_1, (outlet temperature $^{\circ}C$ of reactor 1), T_2 (outlet temperature $^{\circ}C$ 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. As the data are not sufficiently accurate to pick up quadratic effects, the two last can be eliminated. There was no significant dependence of anything, except one of the calculated variables, on F_{in}. There was no significant dependence on R_{flow} of 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.

The feed gas composition was kept throughout at 60.8 mol % CO and 39.2 mol % H_2. R is a function of this composition.

TABLE 6.0-1

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.	$49.8 \pm .5$*	-	-	-	-	-	-
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.	$1.54 \pm .04$*	-	-	-	-	-	-
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
$V_{CO_2, PYRO}$	none sig.	$0.66 \pm .03$*	-	-	-	-	-	-

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

   $V_{CO_2 PYRO}$ = Calculated Pyrolysis CO_2 variable, Mols CO_2 by Pyrolysis/100 lbs wood

2. T_1 = Outlet Temp °C, Reactor 1
   T_2 = Outlet Temp °C, Reactor 2
   $S = (T_1 1 \bar{T}_1 + T_2 - \bar{T}_2) + 355°C$
   F_{in} = Dry gas feed, Mols/100 lbs wood

* Standard error of mean.

The calculated dependent variables are estimates of the shift reaction, the CO consumed in reducing feed organics, and the CO_2 formed by pyrolytic decomposition of feed organics:

$$V_{sr} = \frac{(Mols\ H_2)}{100\ lbs}out - \frac{(Mols\ H_2)}{100\ lbs}in = Mols\ shift/100\ lbs\ wood.$$

$$V_{CO,ox} = \frac{Mols\ (CO + H_2)}{100\ lbs}in - \frac{Mols\ (CO + H_2)}{100\ lbs}out$$

= Mols CO oxidized by organics per 100 lbs wood.

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

= Mols CO_2 formed by pyrolytic decomposition per 100 lbs wood.

We can now discuss the dependence of each of the dependent variables on T_1, T_2, S and F_{in}: the actual coefficients of dependence and the statistical parameters are given in Table 7.

Oil Elemental Analysis

% C - increases with T_1 and T_2 but is equally well- represented as a function of S. % H - barely significant increases with T_1 or with S. % O - decrease with T_1 and T_2 or with S.

Gas Molar Analysis % H_2 - no significant dependence (t < 1). Mol % H_2 = 49.8 + 0.5 (standard error of mean) % CO decreases with T_1 and T_2 or S. % CO_2 increases with T_1 and T_2 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. For the 60 : 40 CO/H_2 mixtures:
R_{flow} = 1.540 + 0.04 (standard error of mean).

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

$$CO + H_2O \rightarrow CO_2 + H_2,$$

since H_2O is not counted as a gas, and

$$organics_1 + heat \rightarrow organics_2 + CO_2.$$

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. On the average 1.4 lb Mol CO was shifted per 100 lbs fresh dry wood feed.

$V_{CO_2,PYRO}$ (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 ± 0.03 Mols/100 lbs includes CO_2 formed from added Na_2CO_3, about 0.04 to 0.06 mol.

$V_{CO,ox}$ (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. 6.0-1 and the dependence of the outlet gas analysis is given in Fig 6.0-2. Fig. 6.0-3 shows the dependence of the net syngas consumption, by way of the reduction reaction, on temperature. In Fig. 6.0-2 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.

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 8·0.3 = 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

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

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). We believe that 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.
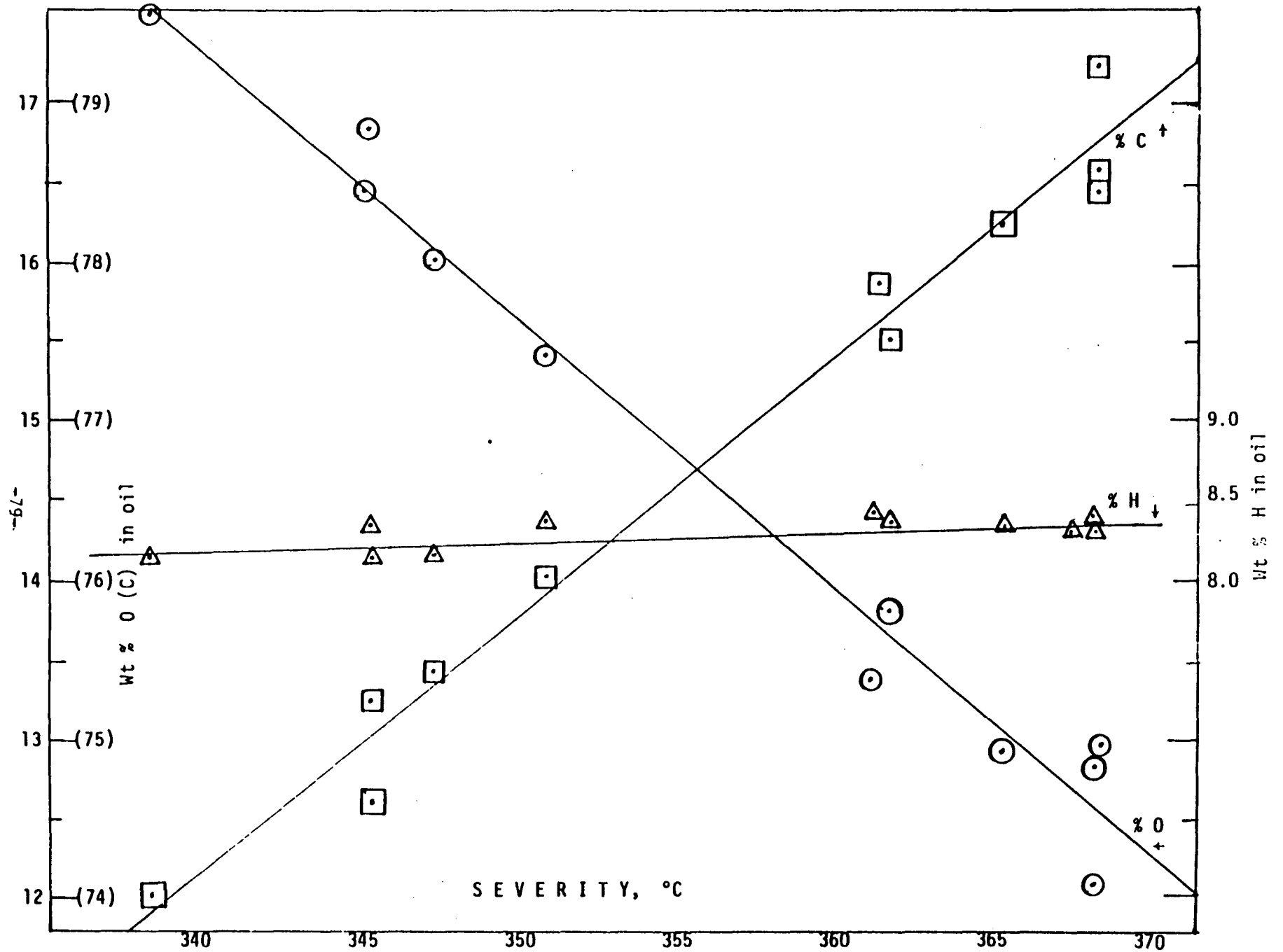
FIGURE 6.0-1
ELEMENTAL ANALYSIS OF OIL VS. SEVERITY

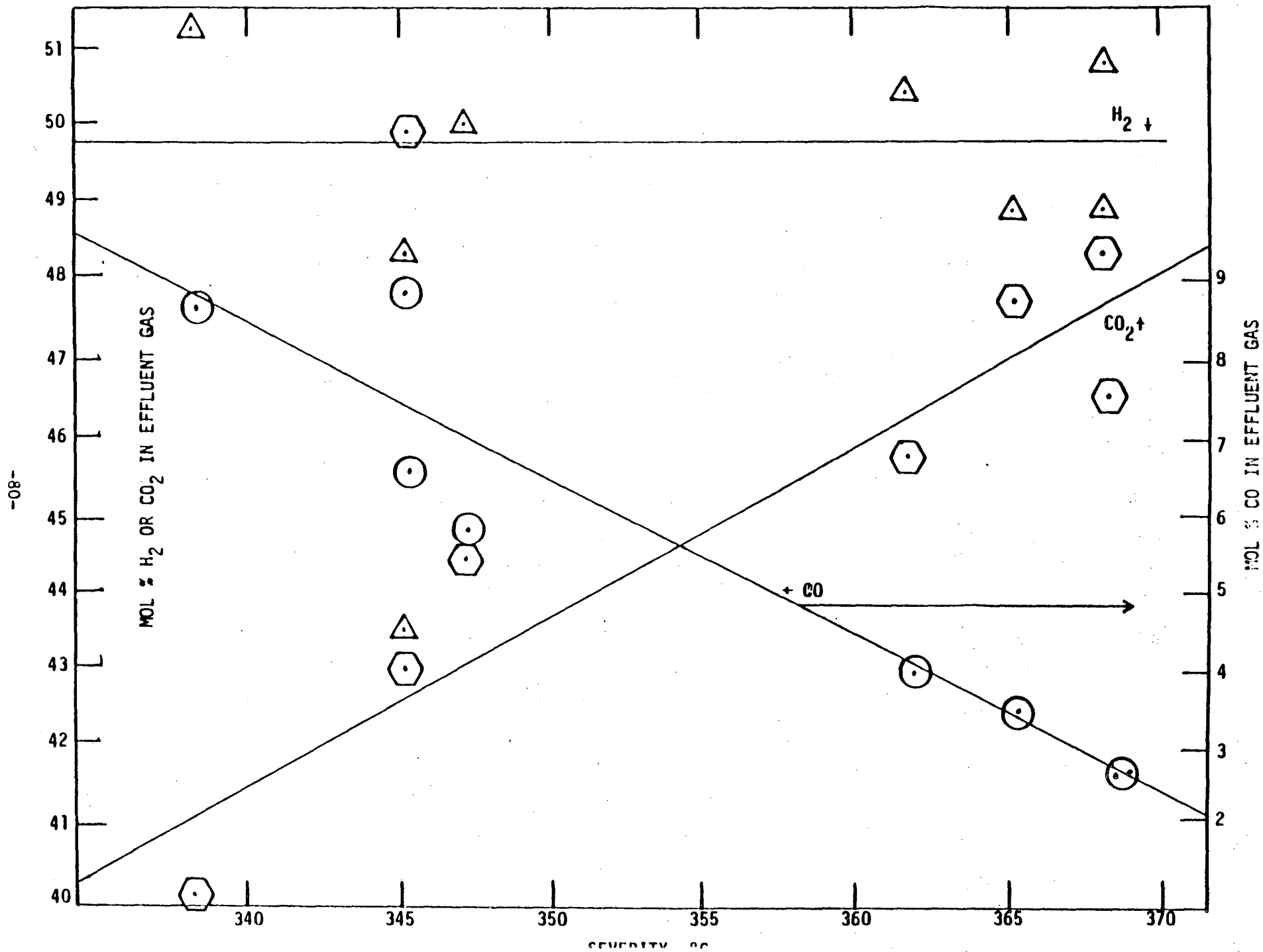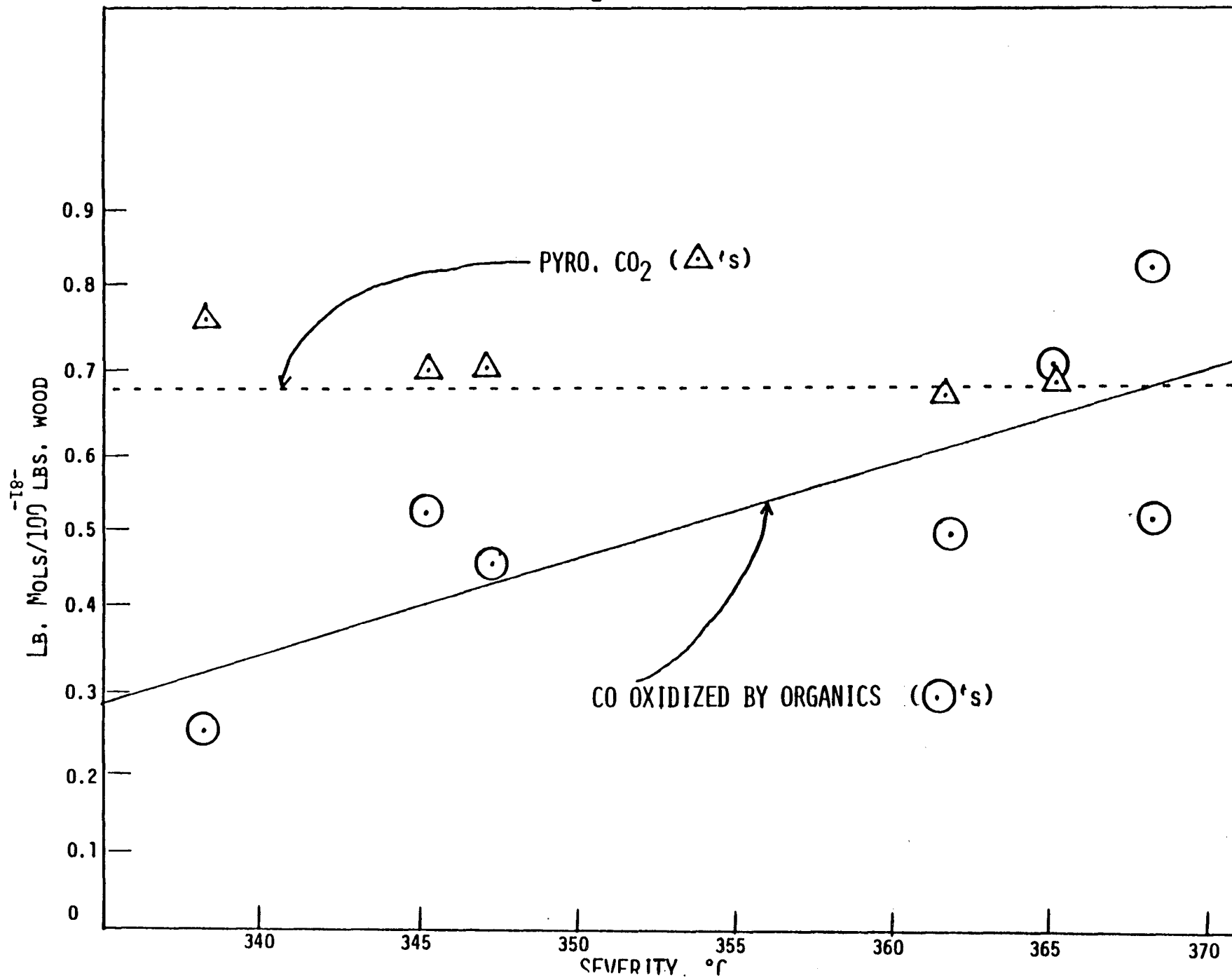FIGURE 6.0-2

MOLAR ANALYSIS OF MAKE GAS, PDU RUN TR-12

FIGURE 6.0-3
SOURCES OF CO_2 DURING LIQUEFACTION (PDU TR-12)

The above can be summed up briefly as follows:

at S = 338°:

100 lbs wood → 53 lbs oil + 0.6 mol CO_2 (26 lbs) + 0.3 atom O red. (5 lb) + 0.4 mol H_2O (7 lbs) + 9 lbs water solubles.

at S = 368°:

100 lbs wood → 51 lbs oil + 26 lbs CO_2 + 8 lbs O reduced + 8 lbs H_2O + 7 lbs water solubles.

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 not significant (i.e., too low to determine) in the CLU runs. The suggestion we make above, that part of the action of CO is on the water-solubles may help explain this observation. 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 at least part of 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.

APPENDIX

Brief History of the LBL Group

The Lawrence Berkeley Laboratory Biomass group was formed in 1977 to "provide technical and monitoring services"[27] for DOE's biomass liquefaction program. By the end of calendar year 1978 it included five technical people and a secretary. Two UCB Professors were available as consultants.

Experimental work, primarily on the formation of Douglas fir wood slurries by way of acid prehydrolysis, was initiated, originally in the laboratories of the Forest Products Department of the University of California, Berkeley. In early 1979, laboratory facilities were established in rented Building 155 of UCB's Richmond Field Station. The staff was increased to seven full-time technical people, plus a secretary and one graduate student.

A series of "directives" for operation of the PDU were issued. From these, and other interactions on a personal basis, came the first successful production of wood-oil at the Albany PDU, in runs TR-6 and especially TR-7. Because of these successes and because of the need for more basic information about the water-slurry process and the liquefaction process in general, a bench-scale continuous liquefaction unit (the CLU) was proposed. Also, studies of slurry properties[3,2] and batch liquefaction tudies[7, 4, 11] were undertaken. The CLU was designed and constructed[29].

During 1980, the group was reorganized and at the end of FY 1980, consisted of six technical people and a secretary. The CLU, as originally designed, was mechanically complete in early 1980. Efforts to run it, however, were disappointing. Rebuilding, with the objective of greatly improved operability and safety was undertaken in August 1980. This was not mechanically complete until early 1981. Laboratory facilities in the Dymo Building, begun in 1979, were also completed in early 1981.

During 1981, an analytically inclined organic chemist was added as a temporary employee. He proved very helpful in the product characterization program. Two part-time student technicians were also hired and were helpful im completing, maintaining, and operating the CLU. A graduate student joined the group to do an MS thesis on liquefaction of miscellaneous biomass types. The CLU, initially designed as a tubular reactor, could not be so operated at the small scale and with laminar flows. It was changed to a CSTR (back-mixed) mode and operated successfully from early summer 1981 on. As FY 1982 began, the available technical staff was reduced to three as funding was cut. By addition of a third student technician and a second MS candidate, a reasonable level of effort was, however, maintained.

In FY 82, the product characterization was continued and the CLU continued to run on Douglas fir slurries and finally on aspen slurries made in a 10-gallon autoclave. The decision having been made that the LBL and PERC processes had doubtful economic potential, more emphasis

was placed on solvolysis and hydrogenation. A study of fundamentals of solvolysis was initiated in summer 1982 and an MS thesis study of solvolysis as a process was carried out. A continuous hydrogenation unit was built, but little information could be obtained because of lack of funding as FY 83 started.

With extremely limited funds available in Fall 1983, work was limited to reporting, premature completion of the solvolysis thesis study and completion of analyses in process. At the end of the quarter, the group was — at least temporarily -- dissolved. Equipment remains available in stand-by condition.

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The efforts covered in this report are the results of the contributions of the members of the LBL Biomass Group. Besides the writer, these members include:

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