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Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

To be presented at the 13th Biomass Thermochemical
Conversion Contractors Meeting, Washington, D.C.,
October 27-29, 1981

CATALYTIC LIQUEFACTION OF BIOMASS

Hubert Davis, Carlos Figueroa, Cihan Karatas,
Dieter Kloden, Larry Schaleger, and
Nasser Yaghoubzadeh

October 1981

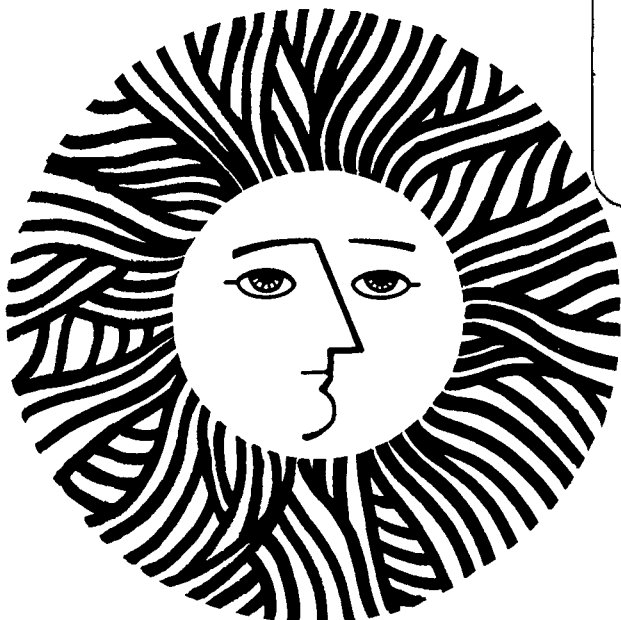
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ABSTRACT

The bench-scale continuous liquefaction unit or CLU is in operation as a back-mixed reactor. Its capabilities include temperatures up to 370°C, reaction times of about 10-30 minutes and pressures up to 4000 PSIG. It is in use exploring a factorial experiment in temperature, time, slurry pH, gas to slurry feed ratio and other variables. From early runs at times of about 20 minutes, temperatures of 350°C or higher and slurry pH's above 8 are desirable. The reactor has been used only on Douglas fir wood slurries. However, it is available for a wide range of biomass or even fossil feedstocks.

New methods of characterizing oil and water-soluble products have been developed and applied to CLU products. Conditions under which formate ion, probable intermediate in both water gas shift reaction and reduction of biomass oxygen by CO, is formed in large quantities have been found.

Raw wood chips have been shown to undergo "solvolysis" -- total dissolution -- when mixed with wood liquefaction oil and heated under certain conditions. This phenomenon must occur to some degree in the initial stages of the PERC process. Solvolysis is suggested as a possible way to get the benefits of oil recycle without the uneconomically high recycle ratios of the PERC process.

Presented at the 13th Biomass Thermochemical Conversion Contractor's Meeting
October 2, 28, and 29, 1981, Washington, D.C.

INTRODUCTION

There are several cogent reasons why a successful biomass liquefaction process is needed. The long-range reasons, of course, stem from the fact that biomass is the ultimate organic feedstock, after most of the fossil fuels are used up. There are also more immediate reasons.

In many parts of the world, various forms of biomass -- wood or plants -- can be grown on marginal land or are available as waste materials. Some of these materials can be used directly as fuel, but others, because of their high water content, or low bulk density, or for other reasons are not suitable for this. In any case, solids are often difficult or inconvenient to feed into a reactor, be it a gasifier, a boiler, a chemical unit, or a carburetor. They are also costly to store and to transport. Liquefaction offers a chance to dewater and concentrate the diluted calories of biomass into a dense material which can be pumped as a liquid. This primary crude liquid is then available as a boiler fuel, a feed to a gasifier, or a feed to a refinery producing automotive fuels, solvents, and chemical feedstocks. In every case, the biomass oil replaces petroleum or natural gas, thereby reducing our dependence on imports.

So far, the emphasis has been almost entirely on methods of producing the crude liquid economically. Indeed, the emphasis in the United States has been on producing crude biomass oil from a single feedstock -- Douglas fir wood, and liquefaction of Douglas fir is the subject of this report. Extension of the findings to other woods and other forms of biomass, agricultural wastes, energy plants, should, however, be a relatively easy job.

The recent history of wood liquefaction by the carbon monoxide-steam process can be dated from the decision in 1974 to construct a process development unit at Albany, Oregon. The PDU, under the auspices of ERDA, was designed by the Rust Engineering Co. Division of Wheelabrator-Frye and constructed by Maecon Inc. The process was based on experiments carried out at the Pittsburgh Energy Research Center (PERC), now PETC, by Appell et al. (1)

Early efforts by the Bechtel Corporation and after 1976, by the Rust Engineering Co. showed that there were serious flaws in the original design. In 1978, the Lawrence Berkeley Laboratory (LBL) group was set up to monitor and give technical advice to the operation. In 1979, through the combined efforts of LBL and Rust Engineering, a modified mode of operation, termed the LBL process, was tested.^(2,3) This resulted (Run TR-7⁽⁴⁾) in the first production of substantial quantities of wood oil. By late 1979, most of the mechanical and design problems of the original PDU had been identified. While it was not possible to change over to an ideal LBL or PERC process, adaptations could be made so that technical feasibility could be demonstrated and preliminary economic evaluations made.

In 1979, it was decided to build a continuous bench scale liquefaction unit (CLU) at LBL. The purpose of this unit was to obtain chemical and engineering data on the process not possible in the larger, less flexible PDU. It was also felt that process improvements could be best identified at the smaller scale. The CLU was initially completed and tested in June-July 1980. Improvements in operability and safety were found to be necessary and the unit was rebuilt and ready for retesting in early 1981. Starting in June 1981, runs of increasing reliability have been carried out on a regular basis.

During 1980, Rust Engineering was able to operate the PERC process at Albany and made many drums of wood oil in runs TR-8 and TR-9. They also made drums of oil by the LBL process in runs TR-10 and TR-11. In the latter two runs, Rust demonstrated the capability of heating slurries of wood in water to reaction temperature in a direct-fired tubular reactor. This was a substantial process achievement. The tubular reactor was also used successfully with slurries of wood flour in wet oil by the PERC process in run TR-12, February-March 1981.⁽⁵⁾ From the viewpoint of smooth operation and material balance, this has been the best run to date. From TR-12 we can deduce, that if an economic process can be devised, a technically feasible engineering embodiment of it can almost certainly be designed.

The PERC and LBL processes, as they have evolved during the past two years, have been described by Elliott.⁽⁶⁾ Briefly, we update these here.

PERC process: wood is dried, ground to flour and slurried with a wet recycled product oil in a blender. It is also mixed with sodium carbonate catalyst (4 to 8% of the weight of wood). The mixture is heated rapidly to a reaction temperature of 330 to 370°C in a directly fired tubular heater, then passed through a tubular or standpipe reactor with volume sufficient to allow a space-time of 10 to 30 minutes. After cooling and pressure let-down, a portion of the existing 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, largely carboxylic acids or their anions. The balance of the weight of wood is lost as carbon dioxide and water.

LBL process: Wood chips, with only incidental air drying, are mixed with water, brought to pH 1.7-1.8 with about 0.075-0.1% 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 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, probably because of the lack of recycle.

The major deficiency of the PERC process is the need for an extremely high oil recycle. In the PDU, wood flour contents of 11% or more have caused plugging in blenders, lines, and pumps. In the most operationally successful run, TR-12, the average wood content of feed was only 7-1/2%. If we assume the feed slurry was 1 part wood, 2.8 parts aqueous phase and 9.5 parts recycle oil, the new oil formed was only 5% of the total oil effluent and the oil recycle ratio was 19 to 1.

As a single-pass process, the LBL process avoids the oil recycle problem totally. Since the heat capacity of water is high, it is necessary to maximize the wood content of feed slurry, preferably to 30% or more. However, some heat can probably be recovered from the process. The major economic stumbling block of the PERC process is thus spoken to. Operational problems are, however, introduced. These are now being studied in the CLU and will be discussed in the body of this report.

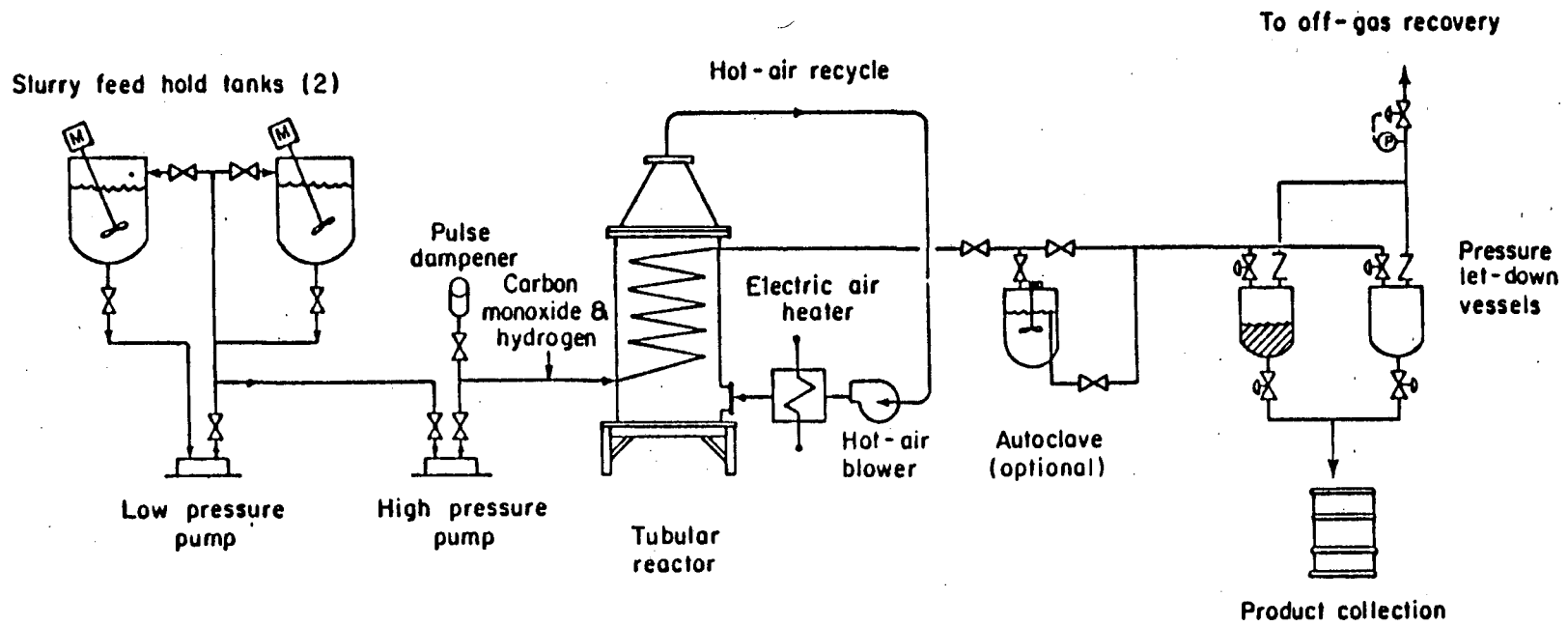
EXPERIMENTAL PROGRAM

In FY 81 the LBL experimental program centered around the rebuilding, operation, and maintenance of the continuous liquefaction unit. In support of this we mounted an intensive effort to characterize both the oil and the water-soluble products of liquefaction. This resulted in a much-improved knowledge of the chemical properties of the products. Most importantly, it resulted in advanced analytical techniques which permit us to follow quantitatively the effects of process changes on product quality. Batch liquefaction experiments were carried out in stirred autoclaves to screen ideas, test thoughts on mechanism, and to determine the effect of process water recycle, among other things. Efforts to study the prehydrolysis step were initiated. The phenomenon of "solvolysis" (dissolution of wood by appropriate solvents) was further studied. The results obtained at the Albany PDU were followed and analyzed for ideas about the chemistry of the liquefaction process.

Operation of the CLU

In the initial efforts to operate the CLU, a tubular reactor was employed (Fig. 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

FIGURE 1



Biomass liquefaction process evaluation unit

LBL process

XBL7910-4293

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 I. 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 (Fig. 2). The feed, product recovery, and pressure let-down systems remain essentially as they were.

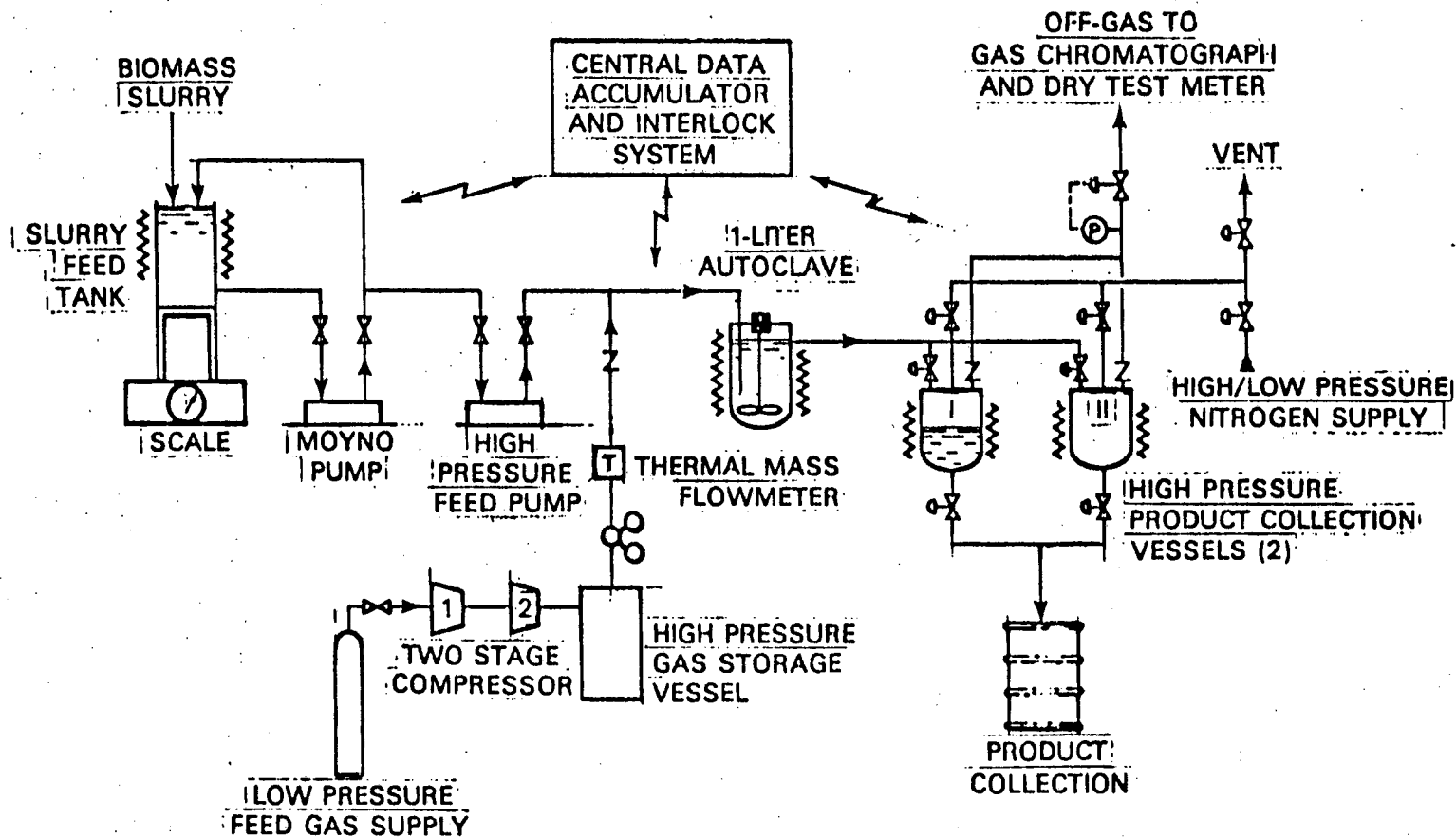
The runs since the changeover have been eminently more successful. Data are given in Table II. Some characteristics of oil products are given in Table IV.

Before discussing the detailed results, however, we need to make some qualitative observations. There is clearly phase separation in the reactor. The ratio of water to crude, heavy wood oil product is 10 to 1 or higher. To avoid a build-up of oil in the reactor and a resulting long residence time, it is necessary to have violent agitation. The object is to maintain an oil-in-water emulsion with the oil droplets small enough and well enough dispersed to that a uniform mixture of oil and water can be withdrawn.

It is also necessary that the exit port of the reactor permit the water phase and the oil droplets to exit as rates proportional to the average oil concentration in the reactor. Failure to achieve these goals results in build-up of oil in the reactor. This is not necessarily harmful to the quality of the oil, but makes it difficult to calculate the oil residence time. It may also lead to coking.

Several observations made us realize we were not achieving a uniform oil and water dispersion in the early runs. Most importantly, very little product oil was obtained in samples collected at less than five hours after start, although reactor turnover times are estimated to be less than 1/2 hour. Also, at run termination, oil/water ratio in the reactor was greater than 1/10. A similar phenomenon was noted in LBL mode run TR-10 at Albany, in which the reactor was the PDU 120 gallon autoclave. Several changes in

FIGURE 2



BIOMASS CONTINUOUS LIQUEFACTION UNIT

the stirring were made without curing the problem. Visual observation of stirring of water-heavy oil and water-sand mixtures led to the conclusion that a single propeller, pitched to throw oil upward, gave us as good or better stirring than any of the other turbine impeller or propeller types or combinations we looked at. Starting with run CL-8, such a propeller has been used at maximum speed. The results indicate little or no excess liquid build-up in the reactor.

Results of Tubular Reactor Runs

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

- 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.
- A down-flow tubular reactor is less likely to plug rapidly than an up-flow reactor.
- Any downstream line that is below about 70°C is also likely to plug with liquid product. Product cooling should be gradual -- air cooling is safer than use of a water condenser.

Results of Back-Mixed Reactor Runs

Runs CL-2 through CL-10 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

TABLE I

CLU: SUMMARY OF RUNS WITH TUBULAR REACTOR

| Run No. | Date | Total Duration, Hours | T ^o 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. |

-10-

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

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.

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, and the real oil yield is higher than the 20% shown in Table II. A series of improvements in the let-down procedure corrected the loss problem, especially from run 8 on.

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 (Table III) 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 we have seen. 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 Moles per 100 g wood or wood hydrolysate).

CL-8

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 min and the residence time about 30 minutes) the 330°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°C. Because of the problem of vaporization, pointed out above, it is best to use 100% CO rather than

TABLE II

CLU: SUMMARY OF RUNS WITH BACK-MIXED REACTOR

| Run No. | Date | Total Duration Hours | T°C | PSIG | Reaction* time, t, min. | Slurry feed rate Kg/hr | Gas feed rate L/min | Mass Recovery wt % | Recovered oil yield wt % | Reason for Termination | Comments |
|---------|---------|----------------------|-----|------|-------------------------|------------------------|---------------------|--------------------|--------------------------|----------------------------|--|
| 2 | 6/28/81 | 1.5 | 350 | 3000 | 13 | 1.8 | 1.8 | - | - | Plug | Plugging generally in exit lines where heavy oil congealed on cooling. Better control of line temperatures helped in later runs. |
| 3 | 7/1/81 | 1 | 350 | 3000 | 13 | 1.8 | 1.8 | - | - | Plug | |
| 4 | 7/7/81 | 2 | 350 | 3000 | 17 | 1.4 | 1.6 | 80 | 24 | Plug | |
| 5 | 7/16/81 | 15 | 345 | 3000 | 18 | 1.3 | 1.6 | 92 | 20 | Plug | |
| 6 | 8/4/81 | 5 | 354 | 3000 | 29 | 0.8 | 1.6 | 100 | 15 | Gas leak | |
| 7 | 8/24/81 | 10 | 350 | 3000 | 15 | 1.6 | 2.2 | 91 | 31 | Off-gas line plugged | |
| 8 | 9/2/81 | 24 | 330 | 3000 | 26 | 0.9 | 1.6 | 100 | 32 | Voluntary | |
| 9 | 9/25/81 | 4 | 350 | 3400 | 23 | 1.0 | 1.0 | - | - | Check valves not operating | Feed gas switched from H ₂ :CO = 1 to 100% CO for runs 9 on. |
| 10 | 9/29/81 | 10 | 350 | 3400 | 21 | 1.1 | 1.0 | 95 | 27 | Feed line plugged | Outlet gas composition: H ₂ , 35%; CO, 10% CO ₂ , 55%. |

* Average residence time in CSTR assuming one liter autoclave contains 350g water + oil at reaction conditions.

Feed Slurry: Prepared 11/80 at Albany PDU; about 20% solids + wood-derived organics; pH (runs 2-8) 7-8; pH (runs 9-10) 8-9.

TABLE III

VAPORIZATION OF WATER FROM SLURRY REACTOR AT 3000 PSIA

| Temperature, °C | Vapor Pressure also, PSIA | Mols H ₂ O Vaporized per* Mol Fixed Gas | Water Vaporized and Unvaporized (6 Mols/hr fixed gas, 1 kg/hr water feed) | | |
|-----------------|------------------------------|---|--|----------------------|-----------------|
| | | | Vaporized grams | Unvaporized grams | cm ³ |
| 320 | 1540 | 1.1 - 1.8 | 157 | 843 | 1190 |
| 330 | 1860 | 1.6 - 2.7 | 232 | 768 | 1200 |
| 340 | 2120 | 2.4 - 4.3 | 362 | 638 | 1050 |
| 350 | 2410 | 4.1 - 8.1 | 650 | 350 | 615 |
| 360 | 2708 | 9.3 - 20.8 | 1000 | 0 | 0 |
| 370 | 3050 | ∞ | 1000 | 0 | 0 |

* Bases for approximate calculation: Partial pressure fixed gas = 3000 - V.P. (H₂O);
 Low value Mols (H₂O)/Mol (fixed gas) = V.P. (H₂O)/partial pressure (fixed gas).
 High value = Low value · Density (real water vapor)/density (H₂O, perfect gas).

synthesis gas and to raise the total pressure somewhat for temperatures above about 340°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, 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% H₂, 55% CO₂. The pressure ratio $\frac{H_2 \cdot CO_2}{(H_2O \cdot CO)}$ is estimated to be about 1, as compared to an equilibrium constant at 350°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 Mol/hour, is dissolved in the liquid phases. This is significant in the material balance but not in the shift reaction pressure ratio.

CHARACTERIZATION OF PRODUCTS FROM CLU AND PDU RUNS

We have used several characterization techniques to characterize the oil product of liquefaction, besides the usual elemental analysis. These include:

- GC-MS to identify key compounds and also compound types.
- Liquid column chromatography by the SESC ⁽⁷⁾ technique to separate crude oil product into fractions according to polarity.
- Gel permeation chromatography using HPLC instrumentation to estimate molecular weight distribution of whole crude oil and of SESC fractions.
- A specific column chromatographic technique devised ⁽⁸⁾ to separate biomass oil products by acidity and molecular weight into several phenolic and non-phenolic fractions.

Through the GC-MS technique, we have made credible identifications of all major (and many minor) gas chromatographic peaks in whole oil samples. This covers compounds boiling up to about 300-350°C, perhaps 30 to 40% of the whole oil. Details of the procedure and identification are currently being worked up and will be presented in a later report.

The SESC technique, originally developed by Farcasiu (7) and others at Mobil for coal-derived liquids, has been especially useful in showing up differences among the various wood oil samples. The method as we have adapted it, employs a specially prepared silica gel column. A sample (~ 2g) of oil, suspended with silica gel in hexane and or benzene, is added to the top of the column. Sequential washings with nine solvents remove portions of the oil according to increasing polarity. After evaporation of solvent, the recovered fractions are weighed and a reasonably good material balance can be obtained. Generally, the recovery is 85 wt % plus, and recoveries of less than about 80% indicate the presence of fractions of extremely high polarity and/or of molecular weight above about 1500-2000. Some properties of typical eluted fractions are shown in Table V.

Table IV shows data collected for a number of oil samples made in the CLU or PDU. Also included are average molecular weight results obtained by the gel permeation technique (HPSEC). There is considerable information in this short table, for example:

- The two runs with the lowest proportion of F1-F5 are CL-8 and TR-10. These also had the lowest total recovery and probably the highest molecular weight (CL-8 not completed at this writing). The highest severity LBL run, CL-6, shows up with the highest proportion in F1-F5, 100% recovery and the lowest average molecular weight. As discussed above, we believe this sample was vaporized from the reactor, leaving heavy ends (F6-F9 and residue) behind.
- Oils from CLU runs made at 350°C begin to approximate the better quality PDU oils, TR-7 and TR-12. Differences in the F1 to F5 distribution can be attributed to the much higher residence times in the PDU, especially in PERC mode runs like TR-12 (oil recycle ratio about 19 to 1).

- Unless we approach liquefaction as a simple dewatering operation leading to a heavy bitumen and a decantable water phase, the temperature range for study should be 340°C and up. Otherwise we will make large amounts of very polar, high molecular weight material.

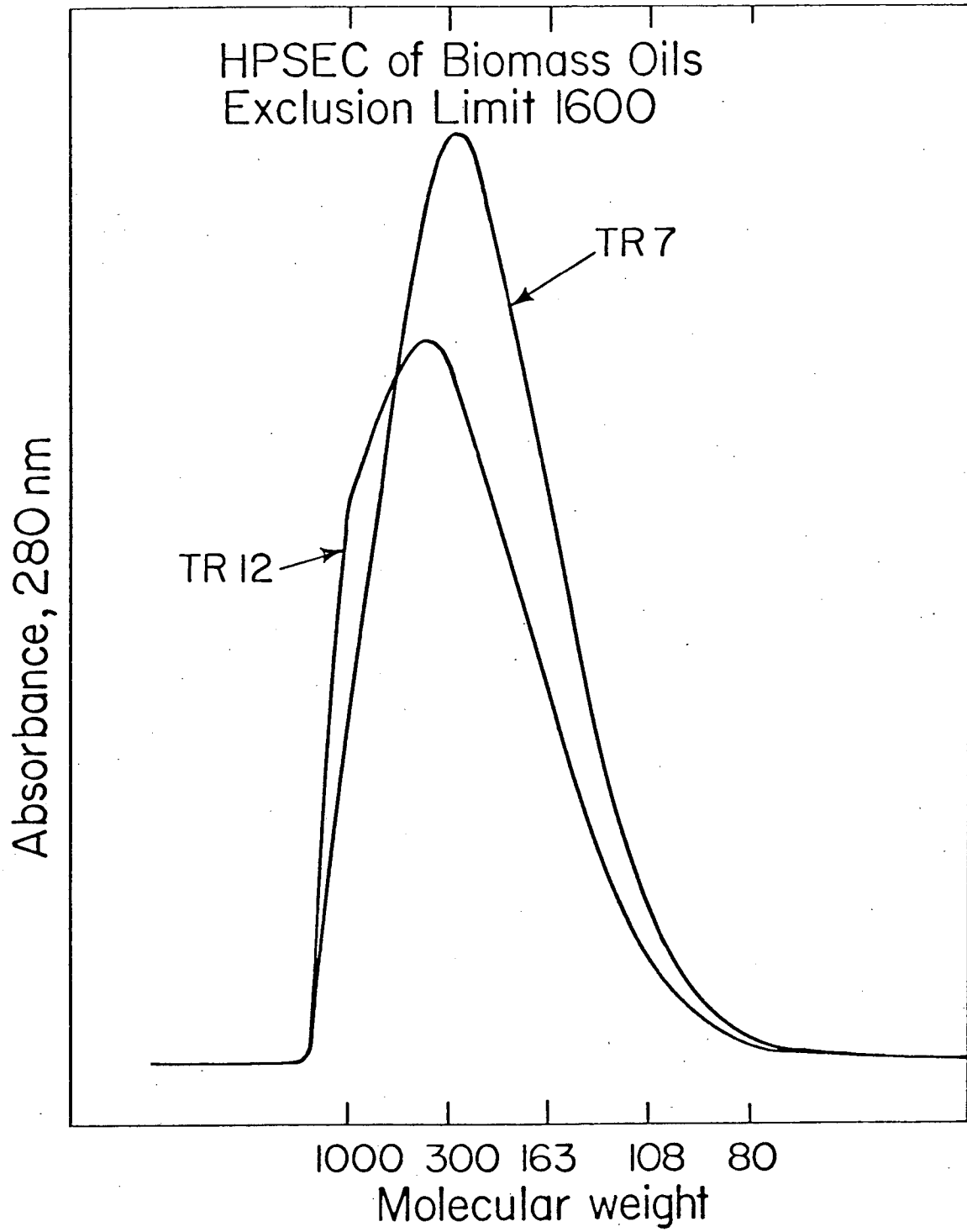
The HPSEC or gel permeation molecular weight procedure has been useful in following the SESC fractions and in comparing the average molecular weights and polydispersities of oils made in various ways. Typical results have already been shown in Tables IV and V. The technique used gives a broad distribution rather than individual peaks. However, particular samples may show bimodal distributions. This is true of samples from PDU run TR-8, where the residual start-up anthracene oil gives a definite early peak. The SESC fractions F6 and F7, 8 show a high degree of polydispersity (Table V). In F6, a shoulder on the chromatography cannot be resolved, but F7, 8, at least for the product of CL-6 is definitely bimodal. Typical HPSEC curves are shown in Figures 3, 4 and 5. Complete descriptions of the HPSEC and also of the SESC procedures are given in the LBL Quarterly Reports for July-September 1981 (in process) and for April-June.⁽⁹⁾

Process Chemistry -- Stoichiometry and Mechanisms

Observations based on PDU and CLU runs and in a series of batch autoclave runs have brought us a much clearer picture of the chemistry of the CO-steam process. As of the summer of 1980, there still remained doubt as to the need for either CO or alkaline catalysts in the process. Researchers themselves were convinced of the importance of CO and alkali, but definitive data under practicable process conditions were scarce or missing. Formate ion and/or formic acid were suggested to be a necessary intermediate in reduction by CO, and had been identified as present in products, but again some skepticism prevailed.

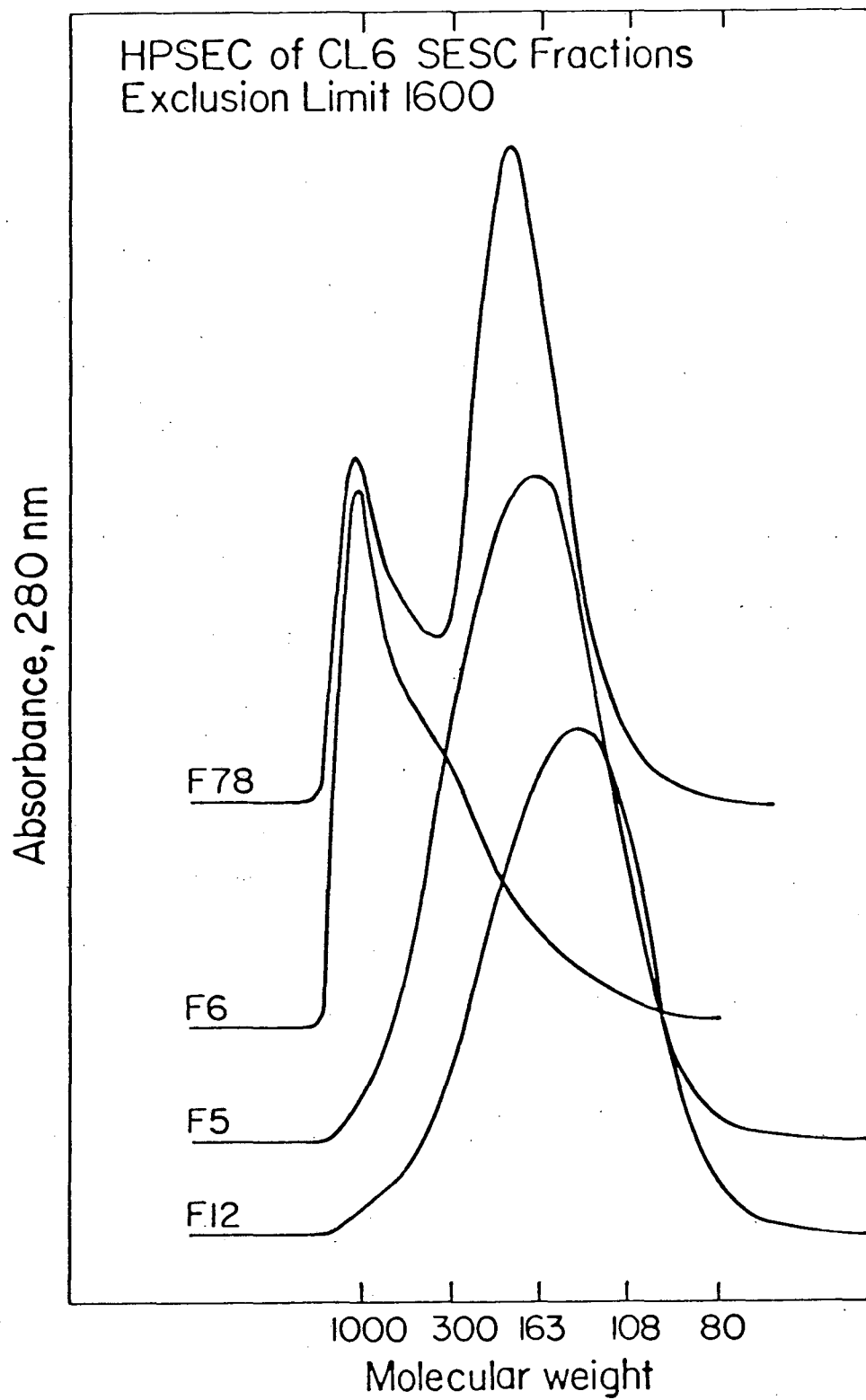
Through analysis of the material balance data obtained in PDU runs TR-8 and especially TR-12, we established that CO definitely reacts as a reducing agent,^(8, 10) at least in the PERC or oil slurry process. Preliminary analysis of material balance data from run CL-10 indicates some usage of CO in the water slurry process also, though probably to a much lesser extent than in the PERC process.

FIGURE 3



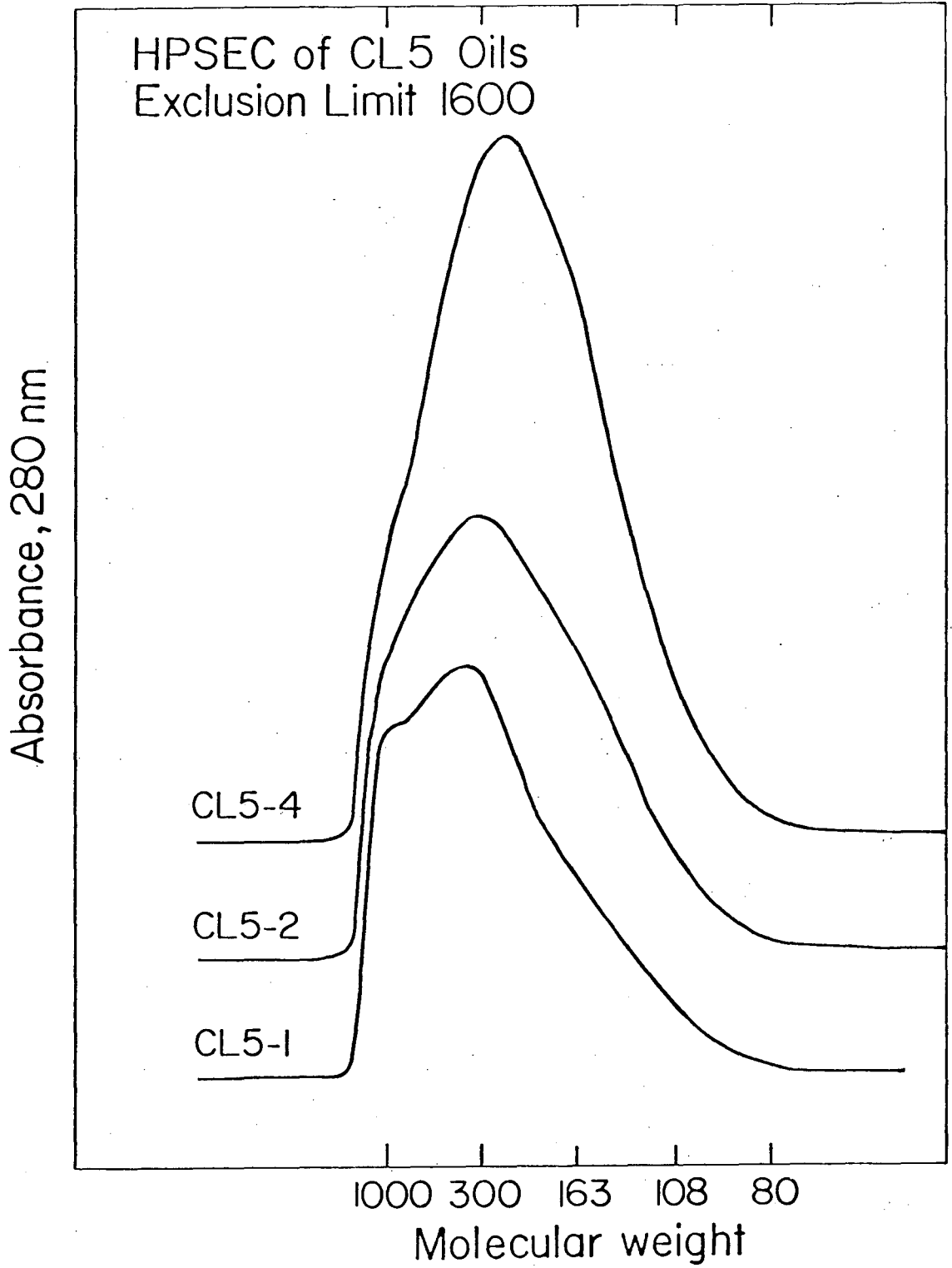
XBL 8110-1422

FIGURE 4



XBL 8110-1421

FIGURE 5



XBL 8110-1420

TABLE IV
SESC FRACTIONATION OF BIOMASS OILS

| Fraction Reactor Temperature | Sample | | | | | | | |
|------------------------------------|---------------------------|---------------------------|--------------------------|---------------------------|---------------------------|--------------------------|---------------------------|---------------------------|
| | CL4-3 ^a 345 | CL5-3 ^a 350 | CL-6 ^a 354 | CL7-3 ^a 350 | CL8-4 ^b 330 | TR7 ^b ~330 | TR10 ^b ~330 | TR12 ^b >350 |
| F1 | - | - | - | - | - | - | - | - |
| F2 | 3% | 1 | 6 | 1 | 1 | 1 | 1 | 6 |
| F3 | 2 | 5 | 9 | 2 | 2 | 16 | 6 | 12 |
| F4 | 13 | 21 | 28 | 19 | 5 | 39 | 17 | 21 |
| F5 | 47 | 46 | 41 | 50 | 37 | 19 | 35 | 34 |
| F6 | 13 | 10 | 3 | 15 | 26 | 14 | 19 | 14 |
| F7 | - | - | - | 2 | 2 | 1 | - | - |
| F8 | 11 | 16 | 13 | 5 | 10 | 6 | 6 | 2 |
| F9 | - | - | - | - | - | 3 | 4 | - |
| % F1 - F5 | 65 | 73 | 84 | 72 | 45 | 75 | 59 | 73 |
| % TOTAL | 89 | 99 | 100 | 94 | 83 | 99 | 88 | 89 |
| \bar{M}_n | 271 | 213 | 176 | 242 | - | 215 | 286 | 240 |
| \bar{M}_w | 483 | 319 | 232 | 384 | - | 306 | 467 | 370 |

^a Methanol-chloroform extract. ^b Raw oil. Note: Oil samples are generally about 98-99% soluble in the methanol-chloroform mixture.

TABLE V
MOLECULAR WEIGHTS OF CLU-6 SESC FRACTIONS BY HPSEC^a

| | <u>F1, 2</u> | <u>F3</u> | <u>F4</u> | <u>F5</u> | <u>F6</u> | <u>F7, 8</u> | |
|---------------------|--------------|-----------|-----------|-----------|-----------|--------------|------------|
| | | | | | | <u>LMW</u> | <u>HMW</u> |
| \bar{M}_n^b : | 143 | 172 | 173 | 210 | 350 | 181 | 687 |
| \bar{M}_w^c : | 158 | 210 | 211 | 286 | 604 | 195 | 892 |
| P.D. ^d : | 1.10 | 1.22 | 1.22 | 1.36 | 1.73 | 1.08 | 1.30 |

a. Each number represents the average of 2-4 determinations made at two different wavelengths, 254 and 280 nm, and on different days. ^b. Number average molecular weight. ^c. Weight average molecular weight. ^d. Polydispersity ($= \bar{M}_w / \bar{M}_n$).

Putting these observations together we can write a stoichiometric formula for TR-12 as follows:

| | |
|---------------------------|---|
| Wood, 100 lbs | Oil, 52 lbs |
| C - 51.0 | C - 41.0 |
| H - 5.8 | H - 4.3 |
| O - 43.0 | O - 6.4 |
| + CO, 16.8 lbs (0.60 Mol) | + Water solubles, 8 lbs |
| C - 7.2 | C - 4.0 |
| O - 9.6 | H - 0.6 |
| | O - 3.4 |
| Total Input: | + H ₂ O, 8.4 lbs (.47 Mol) |
| C - 58.2 lbs | H - 0.9 |
| H - 5.8 | O - 7.5 |
| O - 52.6 | + CO ₂ , 48.4 lbs (1.10 Mol) |
| | C - 13.2 |
| Total | O - 35.2 |
| 116.6 | |

For the water slurry process the product distribution is significantly different. Differences may arise because of the effects of prehydrolysis and perhaps also the effects of deterioration of stored slurry. The lack of a water effluent recycle, as used in the PDU PERC process has a definite effect (see below).

Preliminary calculations indicate oil yields in the 30's or less, water soluble yields in the 20's, with water and carbon dioxide yields by decomposition similar to the TR-12 case, but with less reduction by CO.

Several batch autoclave runs were carried out to (1) show the effect of water recycle, (2) estimate the relative contributions of unhydrolyzed solids and water solubles in the slurry feeds and (3) demonstrate the formation, decomposition and catalytic effects of formate ion under liquefaction reaction conditions.

The water recycle experiments were carried out in the first and second quarters of FY 81.⁽¹¹⁾ They appeared to show that the acids and anions generated during prehydrolysis and liquefaction were stable and greatly increased in concentration on recycle through the process as additional acids, were generated from fresh wood.

Examination of effluent water from PDU run TR-12 showed that the concentration of anions builds up also in the PERC process. The water was found to have about 27 wt % content of carboxylic anions.^(5, 8, 12) Water recycle is economically possible in the PERC process because of the absence of acid prehydrolysis and therefore of the burdensome acidification, alkalization cycle.

Contribution of Soluble Organics and Solids in Slurry

Water phase separated by filtration from wood slurry was pressurized with synthesis gas to 800 PSIG and reacted at 340°C in a 300 ml autoclave (heat-up time 40 minutes, holding time at 340°C 0 min). Small amounts of oil product, 1.4% of feed weight, and of insolubles, 0.2%, were obtained. However, the feed sample is calculated to be less than 7% wood-derived organics, so that the calculated yield based on wood organics is 20% oil + 3% insolubles. Analyses of product gas at these reaction conditions indicate that the 340°C, zero holding time used is much less severe than conditions we find necessary in the CLU or PDU. This experiment should therefore be repeated at higher severity. Nevertheless, the experiment suggests that a significant part of the oil yield from prehydrolyzed wood is obtained from the soluble hydrolysate.

Titration of the water phase after reaction showed a concentration of free acids and anions nearly as high as obtained with complete slurry, 0.40 equiv/kilogram. If the equivalent weight of product acids is 80, the water is 3.2% acid + anion and about 45% of the soluble organics wind up as carboxylate. About 60% of this had already been formed in the prehydrolysis. The balance of the yield is water-soluble organics plus a little carbon dioxide.

A similar experiment in which the substrate was an alkalized effluent water from run CL-7 showed that recycle of water to the reactor will yield very little oil (estimate about 2% of the original wood) and decompose very little of the water solubles. The number of equivalents of acid plus anions per kilogram in the water actually rose from 0.44 to 0.57. Much of this apparent increase is formate ion formed by reaction of CO with alkali, but non-acids may also have been converted to carboxylic acids or anions. Again, this experiment should be repeated at more severe conditions.

Washed solids from the original slurry were reslurried in dilute sodium carbonate (pH of reconstituted slurry = 8.5) and reacted in the autoclave. As with the runs with aqueous phases only, the indications are that the severity was much too low. Tentatively, however, we can say that the solids are the source of over 80% of the oil and less than one third of the water soluble product formed from the whole water slurry.

Mechanism of CO reaction

Several autoclave runs bearing directly on the mechanisms of reduction of biomass by CO were carried out.

- A one molar aqueous solution of sodium formate was held at 350°C for 30 minutes under pressure of CO and steam (CO cold pressure 800 PSIG). The water gas shift was catalyzed so that the final gas analysis was 43% H₂, 30% CO₂, 29% CO and there was a net conversion of 30% of the formate to carbonate.
- After similar treatment of 0.2M sodium carbonate solution the product mixture was found to be 75% formate, 25% bicarbonate. Again the gas analysis was much changed from the initial 100% CO to 39% H₂, 33% CO₂ and 28% CO, showing that the water gas shift had been catalyzed.
- Two slurry liquefaction runs were made under much less severe conditions (50% H₂, 50% CO, 340°C, zero reaction time). In one, 10% sodium formate by weight of the slurry was added. Analysis of products showed that a fraction -- probably about one-third -- of the formate reacted. The final gas analyses were H₂ 46.8, CO₂ 12.5, and CO 40.7% and H₂ 51.2, CO₂ 20.1, and CO 28.7% in the runs without and with formate, respectively. The lower percentage of carbon monoxide in the second case shows increased catalysis of the shift reaction.

The rapid interconversion of bicarbonate and formate under reaction conditions allows interpretation of the differences between runs CL-7 and CL-10, both at 350°C. Between runs 7 and 10, additional sodium carbonate, about 0.08 Mol/kg water phase, was added to the slurry, and the reaction gas was changed from 50:50 H₂/CO to 100% CO. Outlet gas analyses in runs 7 and 10 were 54% and 35% H₂, 31% and 55% CO₂ and 16% and 10% CO, respectively.

Clearly, the shift reaction was strongly catalyzed during run 10. Preliminary analysis of the data also indicates that the desired CO reduction reaction occurred to at least some degree. The excess carbonate was largely converted to formate ion.

PRETREATMENT OF BIOMASS - THE ROLE OF SOLVOLYSIS

Studies of the dissolution of Douglas fir wood by acidified alcoholic or phenolic organic solvents, termed "solvolysis," were carried out here in FY 80 and FY 81. They are covered in detail in a forthcoming Ph.D. dissertation.⁽¹³⁾ An article in the 1980 Annual Report of the LBL Energy and Environment Division⁽¹⁴⁾ summarized the effort. As is discussed in these references, solvolysis is pertinent to the biomass conversion effort as a possible front-end to a liquefaction process. It was suggested^(9, 14) that wood liquefaction product oil, because of its phenolic nature, would make a suitable solvolytic agent. If this is true, solvolysis with fresh wood and a recycle oil could be followed by a suitable solvent recovery and final product formation step -- either CO-steam liquefaction or catalytic hydrogenation.

Experiments in FY 81 have verified that wood oil is indeed a suitable solvolytic agent. Raw Douglas fir wood chips can be totally "dissolved"⁽⁹⁾ in about two to four times their weight of wood oil. The presence of some water and a small amount of mineral acid appears to be necessary, but the conditions have not as yet been optimized.

For several reasons the time to further explore this phenomenon seems to have arrived;

- Some form of solvolysis probably occurs during the early stages of the PERC-oil recycle-process. Preliminary comparison of the early CLU runs, such as CL-7 and CL-10, with the best PDU PERC runs, such as TR-12, indicates that the water slurry process produces less oil and more water solubles than the oil slurry process. Hence a process involving some recycle (but much less than the uncommercial amounts required for PERC) may be desirable.
- A solvolysis plus liquefaction process may result in limited yields of water-soluble organics, or at least permit their recycle.

- We are reaching the conclusion that effective CO liquefaction is always accompanied by the water gas shift reaction, making the unreacted feed gas a poor candidate for recycle. Thus the alternate of using hydrogen for reduction may be desirable. Hydrogenation can be effective with water slurries, but a process using a solvolysis feed, which appears to be a true solution, may be more effective.

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