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DIRECT LIQUEFACTION PROCESS DEVELOPMENT ACTIVITIES AT LAWRENCE BERKELEY LABORATORY

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ENERGY & ENVIRONMENT DIVISION

Presented at the 12th Biomass Thermochemical
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March 18-19, 1981

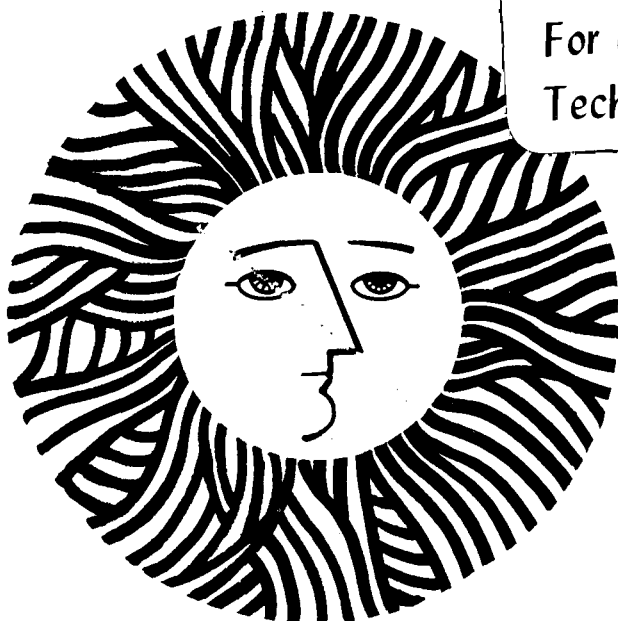
DIRECT LIQUEFACTION PROCESS DEVELOPMENT
ACTIVITIES AT LAWRENCE BERKELEY LABORATORY

Hubert Davis, Sabri Ergun, Mark Featherstone,
Carlos Figueroa, Ray Ganzley, Cihan Karatas,
Dieter Kloden, Larry Schaleger, Nasser Yaghoubzadeh,
Gary Yu, and Rafael Zamora

March 1981

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Introduction

This presentation is based on the October-December 1980 Quarterly Report of the Group, plus an update covering the period of January-February 1981. The material of the quarterly report is given as the second major section of the report.

Task 1 - Continuous Experimental Unit

During the period October 1980-February 1981, the continuous process evaluation unit (PEU or CEU) was substantially modified and brought into operating readiness. Major necessary improvements in safety, process control and sample recovery were made. In January and February dry runs on the various parts of the system were made and members of the group were trained in operation so that a shift can be set up. The operating manual was revised and issued.

Following the training seminars, initial operation of the CEU was set up for the week of March 2. However, a sizable gasket leak forced postponement to the following week. As of the date of this writing (March 5, 1981) a "dress rehearsal" is scheduled for March 6 and start-up for March 10, 1981.

Task 2 - Support Activities

2a. Slurry Preparation/Characterization

The colloid mill — small scale substitute for a refiner — has been used to reprocess the necessary quantities of slurry of CEU operation. Pumping tests on slurries have been run. From the pressure drops through tubing (equivalent to the CEU reactor section) effective viscosities can be calculated for this non-Newtonian fluid. A plot of log viscosity vs. reciprocal absolute temperature is reasonably linear, so that it is possible to extrapolate to higher temperatures (cf figure S-1). If there were no reaction, the effective viscosities at CEU reaction temperatures would be about 4 poise. With gas flow calculated to be near turbulent and effective viscosity in this range it seems reasonable to anticipate good contacting of the slurry by synthesis gas. As time permits, further data on slurry behavior with and without gas flow will be obtained, as well as data on slurries made from feedstocks other than Douglas fir.

2b. Analytical Support to CEU

At this point we have facilities and methods for the basic analyses needed for oil product analysis, with the possible exception of molecular weight distribution, which requires more work on HPLC with size exclusion columns.

The procedure given in this report still looks like an adequate framework. Chloroform seems to be a better solvent than methylene chloride for taking up the crude oil sample. Much of the trapped water of the sample is sprung and azeotropic distillation may not be necessary. On the other hand, we expect to add additional determinations such as total phenolics and similar groupings along lines being developed at LBL and/or PNL.

Since very little had previously been done to characterize the water effluent, we have spent a fair amount of time in this area. The organic and inorganic products dissolved in water are of importance for several reasons:

- The organics are at concentrations high enough to strongly influence the material balance.
- Their overall yield is large enough to make recovery desirable.
- Both organic and inorganic constituents constitute a potential serious disposal problem.
- Water-soluble organics are formed whether or not there is a wood pre-hydrolysis as in the LBL process. Thus they are important in an oil recycle process (like PERC).
- The water-soluble materials are related to the mechanism of liquefaction. At the very least, the carboxylic acids and anions formed must be intermediates in the always extensive carbon dioxide formation.

The work on water effluents has been along four lines. Simple acid-base titration of free acids, organic anions and bicarbonate ion (if present); gas chromatography on alkaline and acidic water samples or on extracts, coupled with GCMS to identify components; extraction of acids and non-acids separately followed by determination of recoverable quantities; derivatization followed by GCMS.

From the titration curves alone, it can be shown that several types of organic acid are present (figure S-II). The average pK of the carboxylic acids present is, from the titration curves, close to 4.0 (cf. 4.76 for acetic acid). The range of pK's must be from about 3 or less to 5 or more. Carboxylic acids with pK's near 5.0 are numerous (acetic acid and homologues, most dicarboxylic acids, such as adipic, some hydroxy and keto-acids). For pK's below 4 we must look for compounds like α -hydroxy or α -keto-acids such as glycolic or pyruvic and their homologues, or for polyfunctional acids (e.g. citric). A list of acids which are clearly identifiable is shown as Table S-I.

Acetic acid is the most abundant carboxylic acid — apparently up to 25% or more of some samples. In fact, acetic acid may well be the single largest individual product. It is formed both in the hydrolysis step and in liquefaction.

A tentative scheme for following the effect of process variables on the water-soluble product is shown as S-3.

Exhaustive extraction of non-acids (from alkaline aqueous product) followed by acids (from the acidified raffinate) has been tried with several samples — notably the water from PDU run TR-10. Some 25% or so of the acids are very resistant to extraction. These are largely compounds which do not give peaks in the gas chromatograph as we have been running it and are perhaps polyfunctional acids which are highly hydrophilic. By concentration and weighing of recovered extracts, we estimate the neutrals in the aqueous layer to be very approximately 40% of the weight of the acids. Also, the amounts of acid recovered are consistent with an earlier estimate of about 90 for their equivalent weight.

Task 3 - Related Experimental Activities

Batch autoclave tests have been run to determine effects of severity and prehydrolysis on the aqueous layer and to investigate the possibility of recycling the water layer.

The effect of severity on total acid/anion content is shown in Table S-II. There is a trend in content downward from the least severe (330°C - 0 min at temp) to the most (360°C, 30 min at temp), although little difference can be seen among the 3 middle-severity runs (330°C at 30 and 60 min and 360°C at 0 min). A run without prehydrolysis at 340°C, 0 minutes fits at about the expected place on the table, i.e. roughly the same quantity of acids is formed whether or not prehydrolysis is used.

Two series of recycle tests were made. In each, water from a liquefaction run was used in hydrolysis of fresh wood flour. Since the anions from the prior hydrolysis and liquefaction had to be acidified for the hydrolysis step and the acids then neutralized before liquefaction, increased amounts of sulfuric acid and sodium carbonate were required.

In the first series of runs, the amount of sodium carbonate was limited to 3% of the weight of dry wood hydrolyzed. The slurry pH before liquefaction was 3.2 - 3.4 and after liquefaction the aqueous phase was scarcely changed (3.3-3.6). The total acidity (free acid plus anion) was 0.7 equiv./kg in the water from the inal phase. Yields of acetone insolubles were high (~ 25% of dry wood).

In the second series, the sodium carbonate necessary to bring the slurry to a pH of about 7.0 was added. In a typical run, with 70% of the product aqueous phase recycled (30% made-up water), the sulfuric acid required was about 8% of the weight of dry wood and the sodium carbonate about 18%. Final pH's of product water were about 5.0-5.3 and the total content of carboxylic acid plus anion was about 0.8 equivalents per liter (if the equivalent weight is 90, this corresponds to 7.2 wt% of the water)

It is easy enough to calculate the necessary usage of sulfuric acid and sodium carbonate from the anion and acid content of the aqueous phase. For example, assume a process in which 1000 kg dry wood, 1000 kg fresh water (as content of wet wood chips or of sodium carbonate solution) and 2500 kg recycle water, containing 0.7N anions and 0.15N free acids, are mixed before hydrolysis. Assume also, based on experience, organic acids equivalent to 0.12 eq/kg H_2O are generated in the hydrolysis stage. Calculations indicate that 88 kg H_2SO_4 is needed and 172 kg Na_2CO_3 to bring the slurry to pH = 8.0. This is 8.8% and 17.2% of the weight of dry wood, respectively, and is in the range found in the experiments. It appears to be a heavy load for the economics to bear.

One reason so much sodium carbonate is required is the fact that sodium bicarbonate is such a weak base. Figure S-4 shows typical curves for the titration of prehydrolyzed slurry with 0.2N NaOH and 0.1 M (0.2N) Na_2CO_3 . Beyond about pH = 5.1, sodium carbonate no longer contributes two equivalent per mol. If we go to pH = 8.0 with sodium carbonate, 0.1M Na_2CO_3 contributes effectively about 0.16 equivalents per liter.

An aqueous product sample with pH > 5.1 can be expected to have an appreciable content of bicarbonate ion. The amount can be estimated by titrating to pH ~ 8 with NaOH, back titrating to low pH with HCL, then retitrating with NaOH after the carbon dioxide formed has evolved.

Task 4 - Evaluation of Process Improvements

There was good news and bad news from the two recent LBL mode runs at the PDU (S-1). The fact that the direct-fired tubular reactor operated well is extremely encouraging since the evidence points towards a plug flow tubular reactor as chemically most promising as well as most economic. The actual residence time in the PDU reactor, well under one minute over the whole span of temperature, appears to be too short. The efforts to increase the reaction time at the PDU by using either the original preheater or the stirred autoclave for reaction space were not very successful, however. The one final experiment at the PDU which we would like to have seen — a run with the tubular reactor alone followed by direct cooling — will obviously not be carried out.

(S-1) Operations of the Biomass Liquefaction Facility, Albany, Oregon.
Quarterly Report October-December 1980. Rust Engineering Co.
January 29, 1981.

General

The recent work with the aqueous product throws some light on the sequence of events during liquefaction.

In the LBL process during hydrolysis, a substantial amount of carboxylic acid is formed. This is about 0.12 equivalents per kilogram of slurry. Thus to bring the slurry to pH > 7 requires an amount of sodium carbonate equal to over 3% of the weight of dry wood. At this point the slurry contains sodium salts of carboxylic acids, a little sodium sulfate and considerable sodium bicarbonate.

In the liquefaction step more carboxylic acids are formed, as well as quantities of carbon dioxide, presumably from decomposition of some of the acids. The acids react with bicarbonate or excess carbonate to form sodium salts. At the high temperature of reaction it is possible that hydrolysis plus instability of sodium bicarbonate keeps the aqueous phase alkaline or nearly alkaline. But when the temperature cools carbon dioxide will react with sodium carbonate not otherwise neutralized by carboxylic acids, forming sodium bicarbonate or a carbon dioxide -- bicarbonate buffer. Thus, even with considerable excess of sodium carbonate present, the final pH is likely to be less than 8. At the usual end pH's (~ 4) the water contains anions (sodium salts of carboxylic acids) and free carboxylic acids. It also contains considerable other material: alcohols, ketones, phenols etc.

At very low severities of operation the total organic content of the water can be 7 wt % or more, but this is reduced at increased temperatures or times of reaction. In any case the largest single entity is acetic acid, but this is only one of many acids and non-acids.

In spite of some difficulty in collecting hard evidence, it still seems probable that an alkaline or nearly alkaline condition during liquefaction is desirable and that excess sodium carbonate is needed.

In the PERC process, a primary difference is the absence of prehydrolysis. Basically the same total amount of acid is, however, generated. Since the aqueous product is recycled with the oil, larger amounts of sodium carbonate are required. However, the high recycle ratio tends to concentrate the organic salts to a high level in the final aqueous effluent. As in the LBL process, other water-soluble organic compounds -- alcohols, polyols, phenols, ketones, etc. -- are present in the aqueous phase.

TABLE S-1

SOME ACIDIC COMPONENTS OF AQUEOUS PRODUCT

A. Monocarboxylic Acids

Acetic	CH_3COOH	
Propionic	$\text{C}_2\text{H}_5\text{COOH}$	
Butyric	$\text{C}_3\text{H}_7\text{COOH}$	
Isobutyric	$\text{C}_3\text{H}_7\text{COOH}$	
$\text{C}_5\text{-C}_8$ Straight Chain + Isos		} Probable

B. Dicarboxylic Acids

Succinic	$(\text{CH}_2)_2(\text{COOH})_2$
Glutaric	$(\text{CH}_2)_3(\text{COOH})_2$
Methyl Succinic	
Adipic	$(\text{CH}_2)_4(\text{COOH})_2$
2-Methylglutaric	

C. Oxo - or Hydroxy-Acids

Levulinic	$\text{C}_5\text{H}_8\text{O}_3$
2,3, Dihydroxybenzoic	$\text{C}_7\text{H}_6\text{O}_4$
4-Oxohexanoic	$\text{C}_6\text{H}_{10}\text{O}_3$
5-Oxohexanoic	$\text{C}_6\text{H}_{10}\text{O}_3$
γ -Valerolactone	$\text{C}_5\text{H}_8\text{O}_2$
($\overset{\sim}{=}$ 4-Oxyvaleric)	$\text{C}_5\text{H}_{10}\text{O}_3$

TABLE S-II

EFFECT OF PROCESS SEVERITY AND PREHYDROLYSIS ON CARBOXYLIC ACID FORMATION

<u>Reaction</u>	<u>Conditions</u>	Total Carboxylic acid plus anion, equivalents/kg in process water
Temperature °C	Time at * Temperature, Minutes	
330	0	0.58
340	0	0.52 **
330	30	0.44
360	0	0.43
330	30	0.41
360	60	0.36

* Excluding heat-up time (~ 25 min to 330^o, ~ 35 min to 360^o) and cooling time.

** Prehydrolysis omitted for this run.

FIGURE S-1
EFFECTIVE VISCOSITY OF ALBANY SLURRY

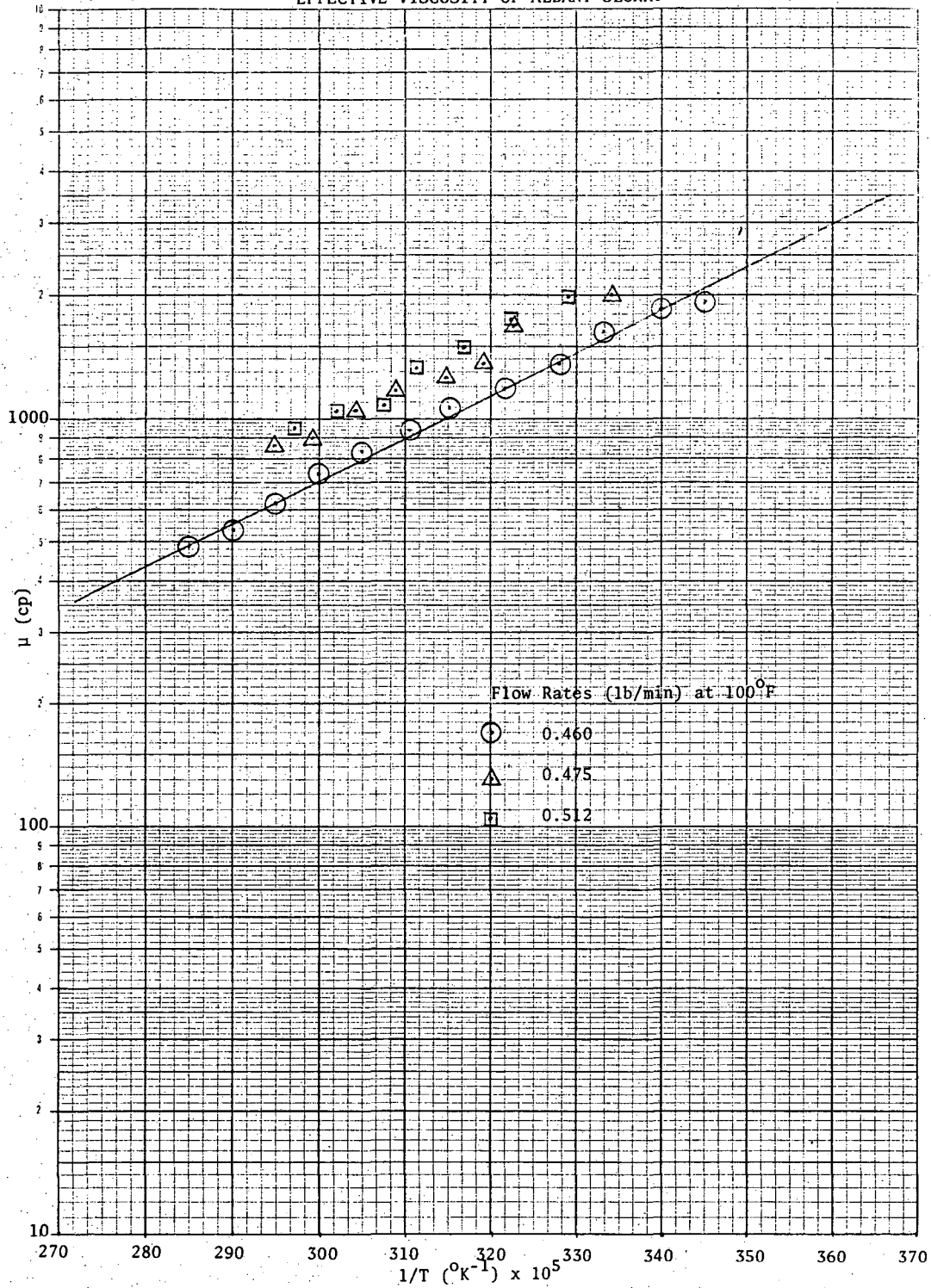


FIGURE S-2
TITRATION OF PROCESS WATER

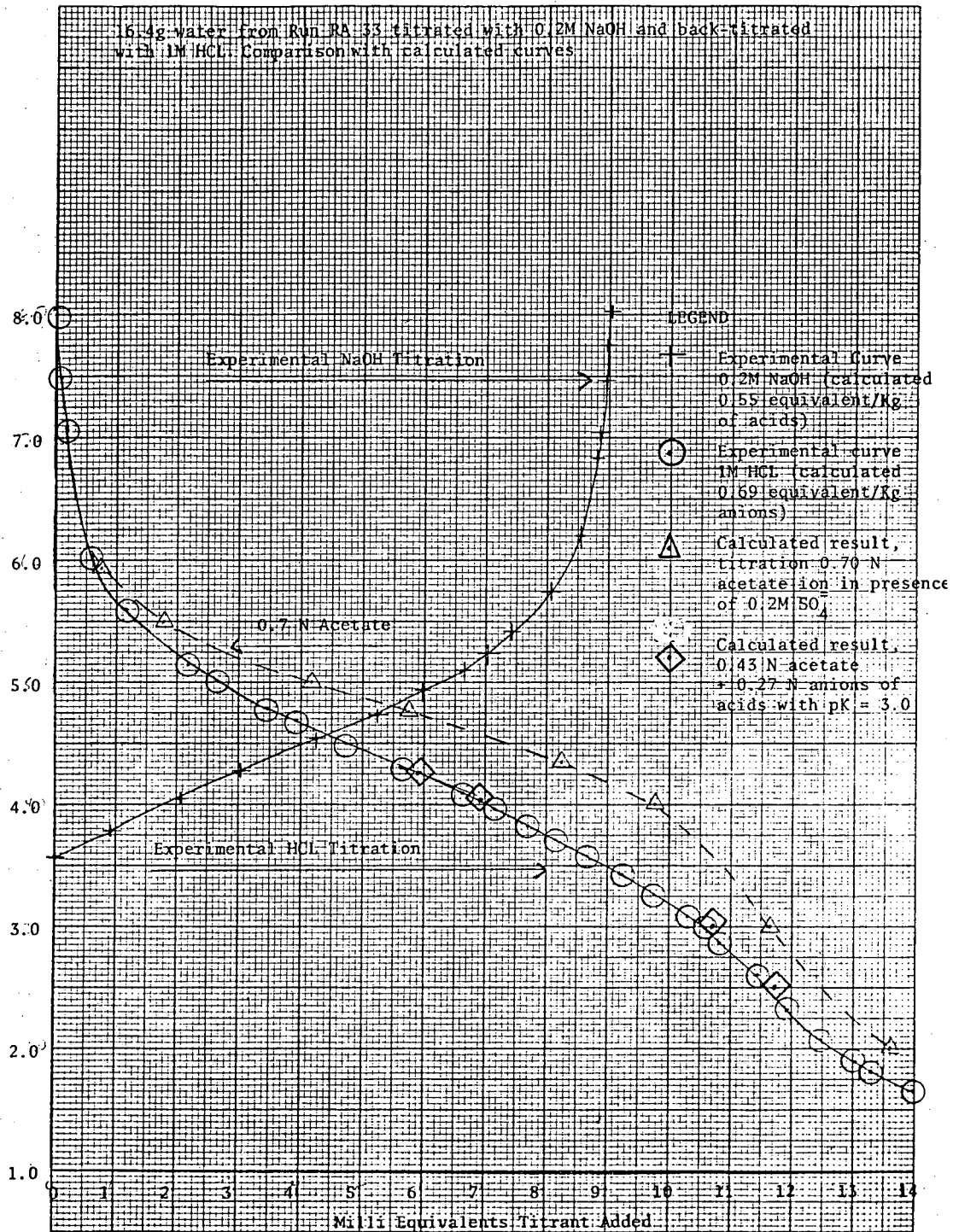
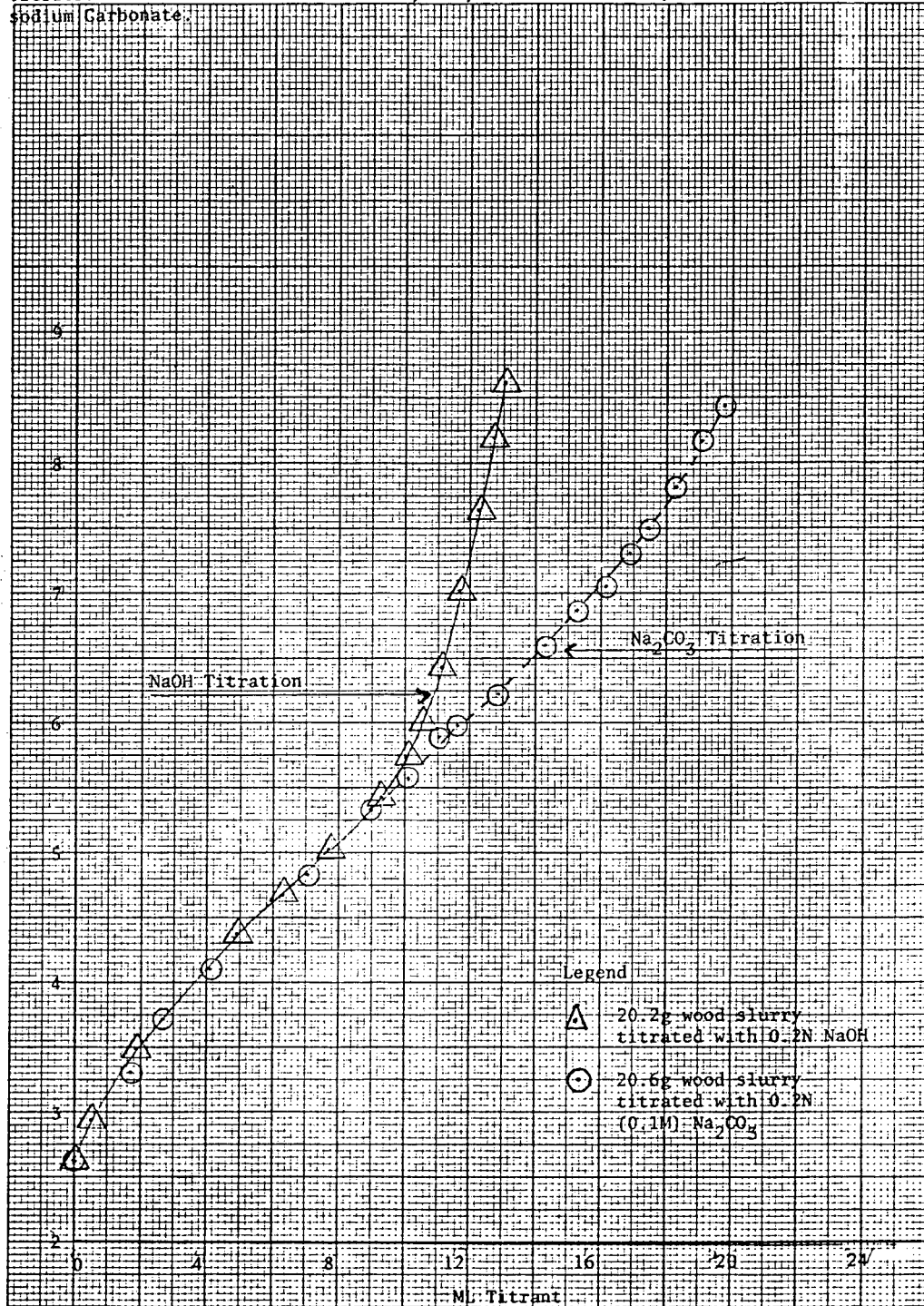


FIGURE S-3

Tentative Scheme for Analyzing Process Waters

1. Titrate 20 g sample with 1.0N NaOH to pH \sim 8.0 (free acid).
2. GC on alkaline solution. Then extract neutrals with chloroform or hotter solvent (GC on extract).
3. Titrate raffinate with 1N HCL to pH \sim 1.7. Correct for excess HCL and sulfate. Total carboxylic acid + anion (+ bicarbonate if present). GC on acid solution.
4. If bicarbonate was initially present, back titrate with 1N NaOH to determine net carboxylic acid + anion.

FIGURE 5-4
 Titration of Wood Slurries after Prehydrolysis with Sodium Hydroxide and with
 Sodium Carbonate.



INTRODUCTION

The end of the first quarter finds the process evaluation unit (PEU) finally complete. At this point it becomes possible to achieve the objective of building our program around the PEU operations. The report is structured as follows:

A. PEU Operating, Maintenance, and Direct Support

The revised PEU is described in some detail, along with calibration techniques, safety features, initial program and direct support requirements. The possible effects of small scale are discussed.

B. Analytical and Chemical Support

The status of our effort to provide methods of product characterization which can be used to better follow the effects of variables in the PEU on the products is covered. A preliminary work-up procedure for PEU product is given.

C. Batch Experimental Back-up

Autoclave studies in the first quarter throw considerable light on the behavior of the Albany PDU in recent runs. The future program will be aimed at studying variables, like recycle, not easily studied in the PEU and screening ideas or alternate feedstocks for testing in the PEU.

D. Slurry Preparation and Characterization

Slurry characteristics constitute an important variable in the PEU operation. A program to prepare slurries for study in the PEU is described.

E. Support for PDU Experiments

Two runs in the LBL mode were carried out at Albany in this quarter. LBL advised on those and helped set up strategy for operations. Recommendations for future efforts are discussed.

A. Construction and Operation of the Process Evaluation Unit (PEU)

I. Status of Revision

As of the end of the quarter the construction of the revised process evaluation unit was complete. A flow diagram of the PEU as it now exists is attached as Figure 1. Many revisions are in the direction of improved safety and operability and do not show as changes in the basic flow diagram. A high percentage of the original fittings were replaced, lengths of pressure tubing were placed in channels or otherwise tied down, the original gas feed manifold was disassembled and the gas cylinders removed from the laboratory, better metering devices and a small microprocessor were installed and so forth. Calibration, pressure testing and the like began in November. Some specific items are detailed below.

- The thermal gas flowmeter was calibrated with nitrogen at one atmosphere and 3000 PSIG, with a small deviation with pressure noted.
- Ambient alarmed air monitors for CO and combustibles are on order for March delivery. Meanwhile operation with a portable CO detector should provide adequate personnel protection.
- Installation of an outside gas cylinder storage shed was completed.
- A tubular reactor cool-down system was installed and tested. Reactor temperatures can be brought down from 350°C to 200°C within ten minutes (average rate 15°C/minute).
- The microprocessor was installed and programmed to print out system pressures, temperatures, and flow rates.
- The operating manual is being revised to fit the new system.

It should be pointed out that scale-down to bench-scale of this process -- as with other chemical processes -- requires certain compromises. These can be seen from a comparison of conditions in the PEU and the tubular reactor recently installed in Rust Engineering's Albany PDU. The Albany tubular reactor is, of course, really only a preheater and additional residence time is necessary for high severity reaction. The comparison is shown in Table I. The purpose in describing these differences is to lay the basis for eventual comparison and interpretation of results. Of the differences shown in the table, the velocity region (laminar in PEU) is most likely to cause operating problems,

while the reactor type (plug flow in the PEU) is most likely to cause differences in kinetics. Plug flow results are generally the easier to interpret and a plug-flow reactor is believed to be the ultimate goal for the process. However, the PEU can be operated as a back-mixed reactor by substitution of a continuous autoclave for the tubular reactor now installed.

II. Planned Activities, January - March 1981

A minimum of three runs is planned, each lasting up to five days. All LBL personnel will be available so that 24-hour operation can be achieved. Tentative conditions for the first three runs are as follows:

1. Conditions approximating LBL mode runs at Albany; i.e. $\sim 340^{\circ}\text{C}$ temperature, 50:50 CO/H_2 , initial slurry pH ~ 7 to 8.
2. As above, but with CO_2 replacing CO in feed gas, to check indications from batch work that this is effective.
3. Duplication of run 1. or run 2.

Products will be collected for analysis and mass balance calculations during 4-hour periods of steady state operation. Between runs all personnel will be available as needed to do follow-up analyses and calculations and to assist with preparation for the next run.

B. Analytical Back-up and Product Characterization

I. Preliminary Program for Following PEU

The total product resulting from steady-state operation will be discharged at 4 hour intervals. At a slurry feed concentration of 20% solids, the product will consist of approximately 0.5 liters of oil and 5.5 liters of aqueous phase. The analytical scheme which follows is designed to provide a basis for determining the mass balance and to furnish preliminary information concerning oil quality and characteristics. It is descriptive only and does not go into the details of sample-taking, the use of aliquots, or the preparation of samples for combustion analysis.

TABLE I

Comparison of Conditions in the Albany Tubular Reactor and the PEU

	LBL PEU	RUST Tubular Reactor
Typical Flow rate	0.4 gallons/hour	60 gallons/hour
Velocity Regime	laminar	turbulent
Flow Direction	upward	downward
Heat Transfer	convective	radiant
Residence Times	> 2 minutes	< 1 minute (+ additional space)
Additional Reactor Space	none	standpipe reactor, stirred autoclave
Reactor Type	plug flow	plug flow, plus back-mixed

1. Aqueous Phase (by decantation)
 - 1.1. pH
 - 1.2. Neutralization curve by titration against standard base.
 - 1.3. Volatiles
 - 1.3.1. Recover by steam distillation, extraction into ether (or methylene chloride) and careful solvent removal. Determine C, H, O, ash, (HHV if necessary).
 - 1.3.2. Quantitatively determine acetic, other non-extractable, volatile acids by direct gas chromatography.
 - 1.4. Nonvolatiles
 - 1.4.1 Carefully evaporate remaining water, removing last traces azeotropically if necessary. Determine C, H, O, ash, HHV.
2. Oil Phase/Solid Residue
 - 2.1. Take up in methylene chloride or better solvent (to be determined).
 - 2.2. Isolate solid residue by filtration and extraction. Determine C, H, O, ash.
 - 2.3. Remove solvent from filtrate by fractional distillation at atmospheric pressure to obtain wood oil.
 - 2.3.1. Determine water by azeotropic distillation.
 - 2.3.2. Determine distillation characteristics (ASTM D-1160 or D-2887-70T (simulated)).
 - 2.3.3. Determine C, H, O, ash, HHV, viscosity, molecular weight distribution by GPC.
3. Gas Phase -- Samples consisting mainly of hydrogen, carbon monoxide, carbon dioxide, methane and other fixed gases will be analyzed by gas-solid chromatography at 15 minute intervals by means of a Carle Series 0158 automatic gas chromatograph.

II. Solvent Extraction, Chromatography Effort

In the initial effort to find better methods of characterizing both the oil and aqueous products of liquefaction, a number of exploratory experiments have been performed. The conclusions to date may be summarized as follows:

- The oil product can be separated into fractions of differing polarity by extraction methods or column chromatography. Appropriate solvents have been identified. Thin layer chromatography (TLC) was used to follow the separations and 100/5 chloroform/methanol is an especially useful solvent for this.
- Even PDU sample TR 8-C (PERC process) has larger amounts of alkaline soluble materials (probably phenols) -- 33.5 wt % by one test.
- "Old" samples of oil from the PDU contain some acetone-insoluble residue but are essentially totally soluble in methylene chloride. The low boiling point of methylene chloride is an asset.
- Methylene chloride can also be used to extract organics from the aqueous phase. For example, 2.7g was extracted by four batch extractions of 100 ml water from an autoclave run. TLC tests showed the extract to contain materials ranging from quite polar to very highly polar. However, emulsion problems are frequently serious when methylene chloride is the solvent -- ether may be better.
- Either acetylation or nitration of TR-7 oil (LBL process) gave product with no highly polar material. Derivatization, in general, can be a useful analytical tool, especially as a prelude to gas chromatography.
- GCMS analyses of many of the samples obtained in the extraction work have been obtained.

The total quantity of data obtained in this initial effort is considerable. A report is being written.

III. Organic Acids in Aqueous Effluent.

Conventional wet analytical methods can be used to follow this portion of the liquefaction product. Even when feed materials are made definitely alkaline, the aqueous effluent is acidic, with pH's typically in the 3 to 5 range. This is from the formation of a substantial yield of organic acids. The amount of acid -- equivalents per liter -- can be measured by titration with standardized alkali. In addition to acids, the product contains anions (sodium salts of the organic acids). These can be measured by titration with standardized hydrochloric acids. A program to follow the acids and anions and their dependence on process variables was initiated in December.

Samples of the main effluent water stream and of the overhead water condensate from PDU run TR-10 were received from Miles Porter of Rust Engineering. Unfortunately, the samples were stored in metal cans and had increased in pH slightly by reaction with the metal. However, they were titrated with 0.2N NaOH, with the results shown in Table II. The main effluent titrated as a buffered weak acid solution -- the buffering effect being expected from the presence of anions corresponding to the sodium added in neutralizing the slurry. The condensate stream titrated as a simple weak acid of pK slightly below 5 (e.g. acetic acid, pK = 4.8). Concentrations of acid are surprisingly high.

If both condensate and main effluent were solutions of acetic acid only, we would expect the two concentrations to be related through the relative volatility of water and acetic acid for separation of acetic acid from dilute aqueous solution at temperatures near 100°C. This is 0.75 (= Mol % HAC in vapor/Mol % HAC in liquid). The condensate proved to be .058 N acid. $0.058/0.75 = 0.077$, compared to 0.21 N found. The major effluent thus clearly contains a large amount of acid of molecular weight higher than that of acetic acid (60). If the average equivalent weight is 90 and we add anion corresponding to the sodium carbonate added in slurry manufacture (estimated at 0.18N) the total acid and anion content is about 3.5 wt %. On the average the ratio of aqueous effluent to wood feed in TR-10 was perhaps 6/1, so that the acid plus anion content may well have corresponded to a yield of 20% organics. Further, if the organic acids are (as would be expected) about 50% C, the organic C content from acids is 1.8%. This compares with 2.0 to 2.2 found by Porter for total organic carbon and indicates the major part of the water soluble organic material is acids.

While there is much guesswork in the above, it is clear that aqueous acids are a major product and their formation and fate during the process is of major importance. Therefore, a program was set up to determine these and follow their behavior on recycle, etc. This is ongoing in the second quarter. Preliminary results in December show:

- The anions can be titrated with 1NHCL. Their amount corresponds reasonably well to the sodium ion added in slurry neutralization.
- Aqueous products from autoclave batch runs have acid contents similar to those from the PDU.
- The acid content falls with increasing severity of processing.

The future effort includes use of titration to follow effects of process conditions in the PEU, identification of some of the acids, probably by ion-exchange chromatography, and determination of average molecular and/or equivalent weight. The behavior of these acids on recycle is of particular interest. We also plan to extract both acidic and neutralized samples of aqueous product to get a better handle on the amount of non-acidic aqueous product.

TABLE II.

TITRATION OF SAMPLES RECEIVED FROM RUST ENGINEERING - PDU

SAMPLE	INITIAL pH	EQUIVALENT ACIDITY PER LITER (NORMALITY)	ESTIMATED WT % ACID
Aqueous Condensate (TR-10-105 Drum 502)	3.50	0.058	0.35*
Aqueous Effluent (Tr-10-104 Drum 441)	4.28	0.21N	1.9**

* Assumes equivalent weight = 60 (acetic acid)

** Assumes equivalent weight = 90

C. Batch Experimental Back-Up Experiments

It is intended that work under this task will be used primarily for screening experiments for the PEU, or for carrying out experiments not easily run in the PEU. During the first quarter several runs were made to get the 1-liter autoclave system set up for such use.

- The quick-heating silicone oil system was rebuilt so that time from ambient to 330-360°C is 20-30 minutes.
- A series of runs at 330°C and 360°C with holding times zero to 60 minutes was made. 60 minutes at 330°C was roughly equivalent to 0 minutes at 360°C. Even at the lowest severity acetone insolubles were disturbingly high (15% of dry wood feed).
- Oxygen contents of recovered acetone solubles and insolubles were essentially the same, but hydrogen is higher in the solubles. (See Table III.) The range of oxygen content includes the percentages found in PDU test TR-10 and TR-11 and indicates the severities of operation were comparable.
- A study of agitation showed that with an improved impeller acetone insolubles could be reduced (to 12% from 18% at 360°C, zero time). Extremely good gas/liquid contacting appears necessary to insure low insolubles.

Work continuing in January is on recycle of the aqueous product as the slurring water. Successful recycle of this phase could appreciably help process economics by

- greatly reducing the amount of water which must be evaporated or otherwise disposed of
- Concentrating the organics (see section B-III), making them easier to recover.

However, if alkaline pH's are required during liquefaction, the amount of alkali must be enough to neutralize all the organic acids formed in the successive steps of prehydrolysis and liquefaction. Also the amount of sulfuric acid added for prehydrolysis must be more than equivalent to all the alkali added in previous cycles. Thus the overall problem is not a simple one.

The autoclave work will be documented in a short technical report.

TABLE III

ELEMENTAL ANALYSES OF BATCH PRODUCTS

Run	Temperature °C	Time at Temp., Min	% Acetone Solubles*	% Insolubles	Elemental Analysis				Ash-Free			
					Solubles				Insolubles			
					C	H	O	Ash	C	H	O	Ash
17	360	0	31	18	75.7	7.0	17.3	1.7	77.2	5.1	17.7	4.3
20	360	30	27	18	79.0	7.3	13.7	0.5	79.5	4.7	15.8	3.8
21	360	60	10	30	80.8	7.7	11.5	0.4	84.0	4.7	11.3	11.9
22	330	60	37	15	76.3	7.2	16.5	0.1	76.4	5.3	18.3	7.7
23	330	30	38	18	76.0	7.0	17.0	0.4	77.9	5.4	16.7	3.4
24	330	0	32	17	72.6	6.4	21.0	0.1	74.7	5.7	19.6	3.5

* Recovered by extraction of total oil sample followed by vacuum evaporation and oven drying. Because of loss of volatiles this number must be multiplied by a factor, probably ~1.1 to 1.2. Improved methods of recovery have been suggested for PEU product (see Section B-I).

D. Slurry Preparation

As of the beginning of January 1981, the colloid mill which we plan to use as a refiner has been put in operating condition. It is in use to rerefine all slurries scheduled to be fed to the PEU. A Moyno pump, previously out of service, has been repaired and is available for pumping tests to be used for slurry characterization. A 10-gallon autoclave, suitable for prehydrolysis of wood chips is currently not scheduled for delivery until April 1981 (it has been on order for nearly a year). Therefore, slurry preparation work is limited to small batches run in 1-liter or 1-gallon autoclaves. Slurry testing will thus mainly be limited to the large batches prepared at Albany and presently available here. Drums of the slurry fed successfully to the tubular reactor in Albany in Runs TR-10 and TR-11 will be shipped to LBL.

The experimental program is a very limited one involving the effort to characterize slurries by checking the flow of pressure drop through reactor coils and visual (microscopic) examination plus viscosity measurements. The prime purpose is slurry preparation for PEU operation.

E. Assistance with PDU Operation

The Albany PDU was operated by Rust Engineering in the LBL mode during two runs, TR-10 and TR-11. Success was somewhat variable, but the results were understandable in view of the process compromises which had to be made. LBL took part in all planning sessions. Run TR-10 was very short and very near the Thanksgiving weekend when travel arrangements were difficult. Larry Schaleger assisted in straightening out problems in prehydrolysis, but no LBL personnel were present during the actual run. During TR-11 either Sabri Ergun or Carlos Figueroa was at the PDU for all but the final day.

Recommendations for the near-term operation of the PDU are difficult to make. The large stirred autoclave will not be available during the January-March operating period. The scraped-wall preheater converted to a standpipe reactor had very limited success. The most successful piece of equipment was the new direct-fired tubular reactor, operated essentially as a preheater since the residence time in it was somewhere between 20 seconds and a minute. We agree that this reactor should be used as the sole reactor in one run. From our laboratory experience this will give a rather high conversion to acetone-soluble products. However, the oxygen content of this product will be high and there will be a large co-product of water-soluble organic acids and other polar products. Using the standpipe reactor downflow without a level controller should add very little to the liquid residence times. Drums of product can be produced either by the LBL process with the tubular reactor alone or by the PERC process using tubular reactor and standpipe -- or by both processes.

Critiques of the TR-11 operation and recommendations for future operation were written by both Sabri Ergun and Carlos Figueroa.

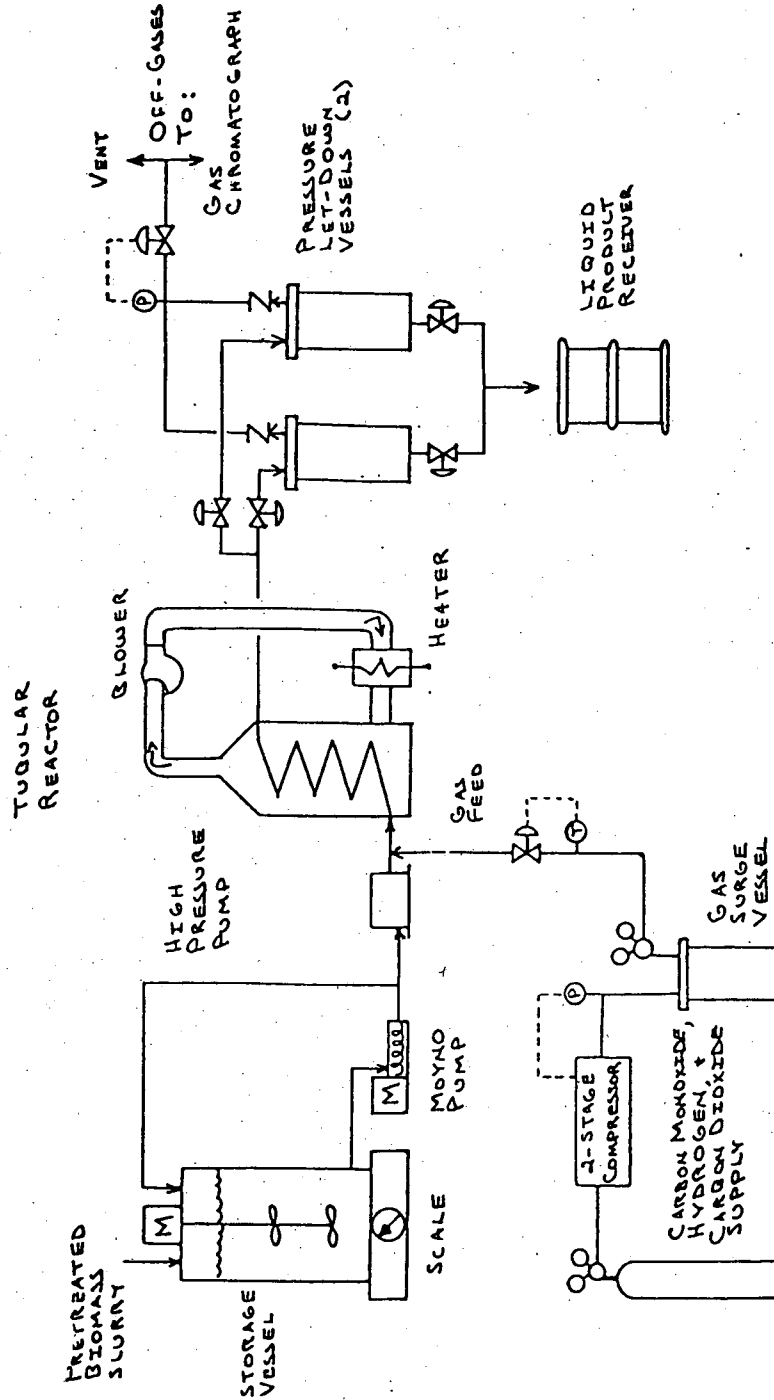
During the remainder of FY 81, the LBL program is to help plan any further operation of the PDU, to assist in PDU runs as necessary and to help plan for future development.

ENGINEERING NOTE

SUBJECT

FIG 1

NAME
CARLOS FIGUEROA
DATE
8-15-80



LBL PROCESS EVALUATION UNIT (PEU)

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