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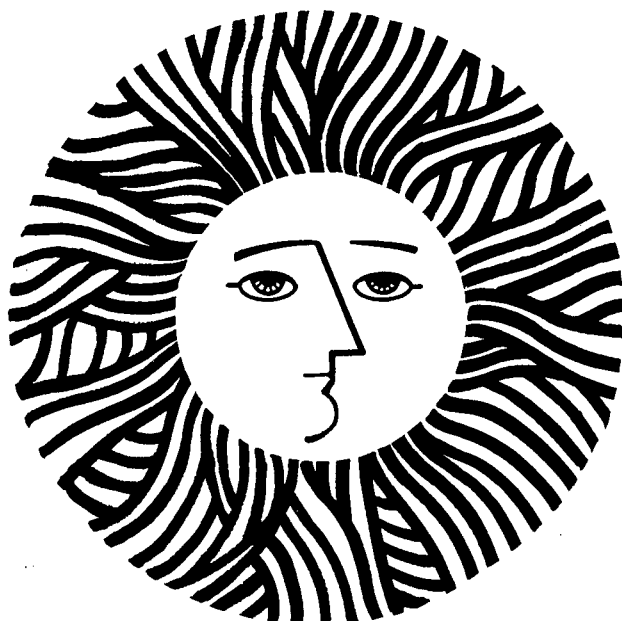
H. Davis, S. Ergun, C. Figueroa, C. Karatas,
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CATALYTIC BIOMASS LIQUEFACTION
QUARTERLY REPORT
October-December 1980

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D. Kloden, L. Schaleger, and N. Yaghoubzadeh

HIGHLIGHTS

- Revisions of the Process Evaluation Unit (PEU) are complete and the operation is on current schedule.
- A PEU product work-up procedure is presented. This is based on screening experiments on product characterization
- Results of screening tests with solvents and mixtures useful for liquid product characterization are given. A report is being written.
- Determination of acidity in aqueous product by titration is reported. Carboxylic acids and anions constitute a major part of the liquefaction product (as much as 20% of dry wood at low severities).
- Results of autoclave runs covering the severity region employed by Rust Engineering in PDU runs TR-10 and 11 (LBL process) are discussed briefly. A report will be written.

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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.

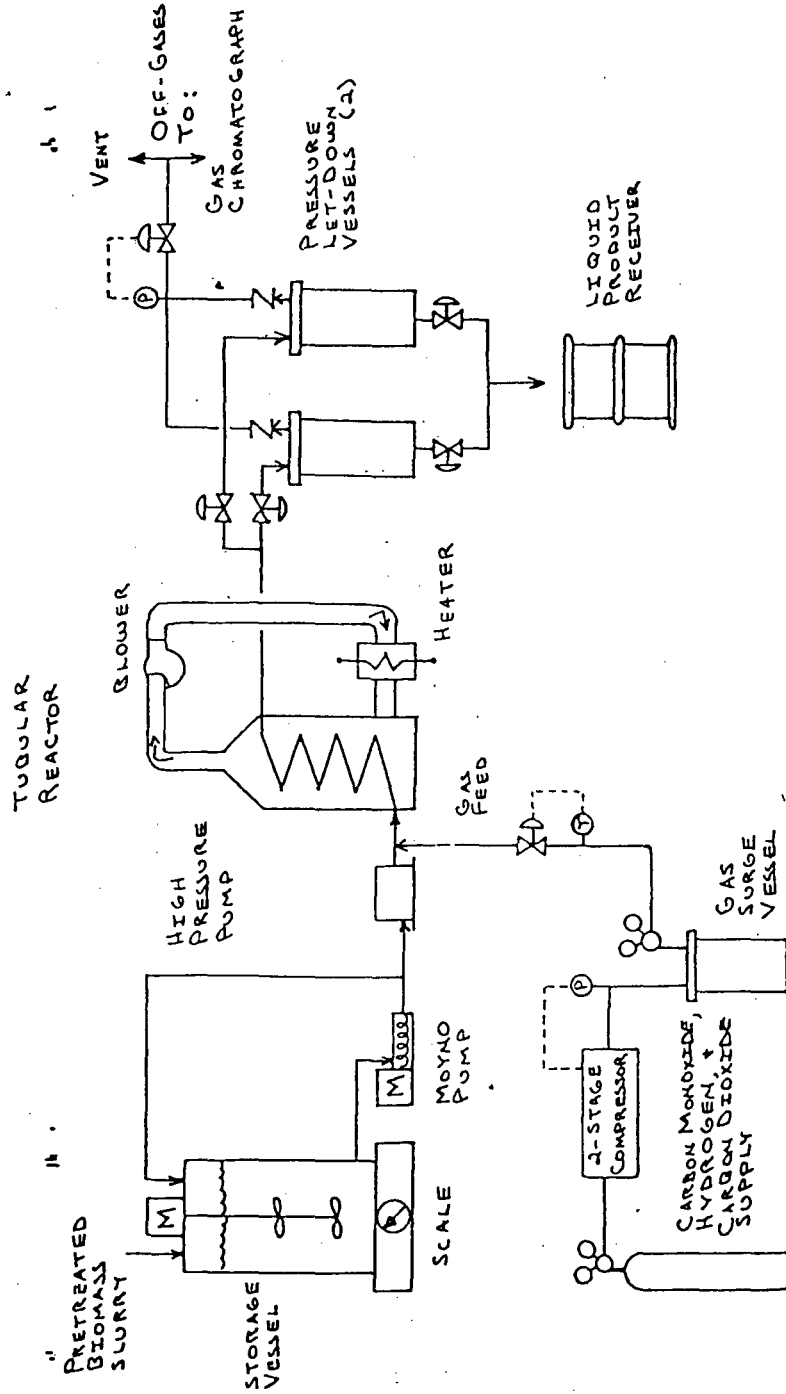
Critiques of the TR-11 operation and recommendations for future operation were written by both Sabri Ergun and Carlos Figueroa.

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.

SUBJECT

FIG 1

NAME
CARLOS FIGUEROA
 DATE
8-15-80



LBL PROCESS EVALUATION UNIT (PEU)

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