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QUARTERLY REPORT - April-June 1981

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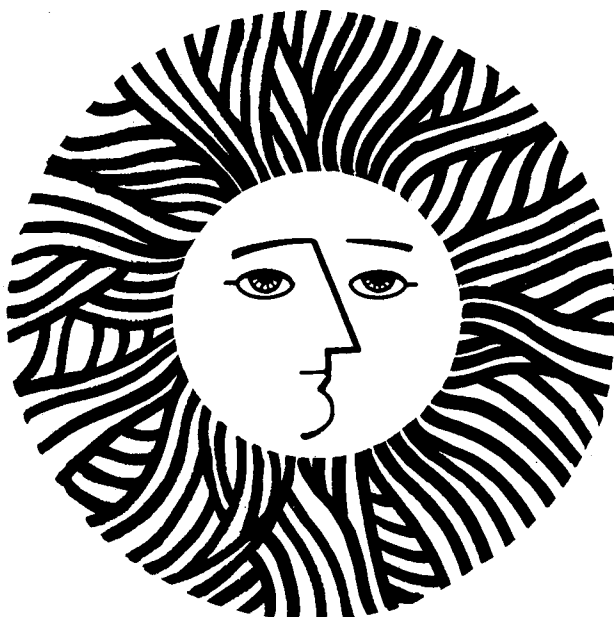
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RESEARCH AND DEVELOPMENT ACTIVITIES
ON DIRECT LIQUEFACTION TECHNOLOGY

QUARTERLY REPORT

April-June, 1981

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RESEARCH AND DEVELOPMENT ACTIVITIES
ON DIRECT LIQUEFACTION TECHNOLOGY

HIGHLIGHTS

- A second run of the continuous liquefaction unit (CLU) was again terminated by a reactor plug. However, operation for a period of 2.25 hours enabled the recovery of 173 g (24%) wood oil and the collection of preliminary operating and yield data.
- For the next runs, the tubular reactor section of the CLU has been replaced by a back-mixed reactor section. This is expected to reduce plugging problems.
- Batch autoclave experiments confirm that the amount of char/insoluble residue formed in liquefaction increases sharply with the severity of prehydrolysis.
- Mixtures of hydrolyzed wood slurry and wood oil can be pumped through a 0.25-inch i.d. tubular coil at 40°C at a water-solids-oil ratio of about 6:2:5. A 4:1 slurry-oil mixture could not be pumped. De-watering occurred during the pumping of more dilute slurry with wood oil.
- An additional 18 carboxylic acids contained in aqueous liquefaction streams have been identified by GC-MS.
- A solvent extraction procedure for isolating a high molecular weight phenolic fraction of wood oil has been developed.
- Progress is being made in the quantitation of wood oil components identified by GC-MS.
- The SESC scheme developed by Mobil for the fractionation of coal-derived fluids by chromatography has been adapted for use with wood oils. Clean separations of wood oil into six fractions plus noneluted material are achieved.
- It was shown that wood oil is an excellent solvolysis agent for Douglas fir wood chips. Complete dissolution of air-dried chips occurred when 3 parts wood oil and 1 part wood were heated together to 225°C. The phenomenon could explain some of the features of the PERC process or be the basis for an improved PERC process.

TASK 1. OPERATION OF CONTINUOUS LIQUEFACTION UNIT (CLU)

A continuous run (CLU-2) was begun May 6, 1981, using a tubular coil (100' x 0.25" I.D.) as the reactor. Plugging in the outlet line forced termination of the run after 2.25 hours of operation. Product was collected during the last 1.78 hours of the run. Operating conditions are summarized in Table I. Plugging also forced early termination of a subsequent run, reinforcing the suspicion that operation of the plug flow reactor under laminar flow conditions was not likely to prove successful. For our next run, scheduled for early July, we have replaced the tubular coil with a backmix flow reactor, i.e., a stirred 1-liter autoclave. This should achieve greatly improved mixing among gas, liquid and solid phases, and much faster heatup than is possible with the tubular coil configuration. (See discussion of slurry preparation for importance of rapid heatup).

Approximately 173 g of chloroform-soluble oil was recovered, corresponding to a 24% yield. Analytical data for the oil, residue and plug samples are given in Table II. Although the oil is fairly high in oxygen (20.3%), it is free-flowing at room temperature. The residue, which is partially soluble in acetone and almost totally soluble in methanolic KOH, appears more highly condensed (dehydrated) and less highly reduced than the oil produced. The degree of condensation and state of oxidation of the plug samples are similar to that of the residue.

Of the carbon recovered in condensed phases, 29% was found in the aqueous effluent and 71% in product oil.

TABLE I.

OPERATING CONDITIONS-RUN CLU-2

<u>INPUT</u>			
Slurry (20% total solids)		2.05	kg/hr
Gas (47.8% H ₂ , 52.2% CO)		2.05	slpm
<hr/>			
Outlet temperature		350 ^o C	(average)
Pressure	Inlet	3140	PSIG (average)
	Outlet	3000	PSIG (average)
<hr/>			
<u>OUTPUT</u>			
Oil Product Recovery		173g	
Water Phase Recovery		3060 g	
Residence Time		~ 5 min	
Total Liquefaction Run Time		2.25 hours	
Steady State Collection Time		1.78 hours	

Gas Phase -- Final Analysis (Not yet steady state)

H ₂	54%
CO	24%
CO ₂	22%

TABLE II

ULTIMATE ANALYSES OF CLU-2 PRODUCT STREAMS^a

	<u>C</u>	<u>H</u>	<u>O^b</u>
Chloroform-Soluble Oil, 173 g	72.2	7.5	20.3
Chloroform-Insoluble Residue, 7 g (4%)	75.9	5.1	19.0
Reactor Plug Sample, 14'	77.9	5.1	17.0
Reactor Plug Sample, 56'	81.6	5.0	13.4
Aqueous Effluent, Total organic carbon: 17,000 ppm			

a. Moisture, ash-free basis.

b. Oxygen by difference.

TASK 2. SUPPORT ACTIVITIES

2.1. Slurry Preparation and Characterization

2.1.1 Severity of Prehydrolysis on the Liquefaction Process

Results of batch liquefaction tests emphasize the importance of keeping the duration and the temperature of the hydrolysis pretreatment as low as possible. Table III shows the results of three tests with Douglas fir wood flour at the same batch liquefaction conditions.

At 280°C, (or during the 30 minute heat-up time to 280°C), under hydrolysis conditions, a large amount of char and/or char precursors was formed. This resulted in limiting the solubles yield on liquefaction to 15%, with an insolubles yield of 40%.

When hydrolysis was totally omitted, solubles yield was 53% and insolubles only three. After "mild" hydrolysis (roughly corresponding to the procedure used in the LBL process) solubles yield was 44% and insolubles 14.5%.

That the amount of carboxylic acid formed in prehydrolysis is a function of severity is shown by the amounts of sodium carbonate required to bring the slurry pH to 6.5-7.0 and to 9-9.8. However, acids are formed during liquefaction in any case; the final pH after liquefaction is probably more important than the slurry pH is in controlling char formation.

The results demonstrate the importance of setting prehydrolysis conditions at the lowest level of severity necessary to give a pumpable wood slurry. They also further demonstrate the bad effects of lengthy heat-up or holding times in the temperature range of ~ 180 to ~ 300°C.

TABLE III
EFFECT OF PRETREATMENT ON BATCH LIQUEFACTION RESULTS

Run No.	Pretreatment	Na ₂ CO ₃ Requirements, wt % of wood		Liquefaction Results*		Final pH of Water phase
		to pH 6.5-7	to pH 9.2-9.8	Acetone** Solubles	Acetone** Insolubles	
RA 42	No hydrolysis	0.5	2.0	53.2	3.2	4.1
RA 30	180°C, 15 min + 50 min heat- up. Initial pH = 1.8, after hydrolysis 2.5.	3.0	6.0	44.0	14.5	3.5
RA 48	280°C, 0 min + 30 min heat- up. Initial pH = 1.8, after hydrolysis 2.3.	6.0	9.0	15.4	39.8	5.2

* Conditions - Slurry pH 6.5 - 7.0; temperature 340°C; holding time 0.0 min;
heat-up time 30 min; pressurizing gas 60% CO; 40% H₂ at 800 PSIG cold pressure.

** Weight percent of wood feed.

2.1.2. Pumpability of Slurry-Oil Mixtures

Pumping tests on hydrolyzed wood slurry-wood oil mixtures were conducted in order to gain insight into the nature and flow behavior of recycle systems. The flow modelling system consisted of a stirred hold tank, a recirculating pump (Moyno 3-stage progressive cavity design), a by-pass line (1" I.D.) and tubing (0.25" I.D.) equivalent to one section of the CLU tubular reactor (ca. 30 ft). Slurry pumpability can be expressed in terms of the empirical relationship between pressure drop across the tubing, temperature of the slurry and slurry flow rate. Examination of these parameters for different mixtures at different pump settings gives an indication of the relative pumpability of these mixtures.

With the pumping apparatus described, it has proved impossible to pump a 4:1 slurry-wood oil mixture*. Heating to 200°C in an autoclave ("solvolyis" conditions) did not improve pumpability. In this and other tests on solvolysis, there was little or no dissolution of wood solids. This is in contrast to the results of solvolysis experiments with raw wood chips or wood product oil (with only small amounts of water present) where nearly complete dissolution of wood was obtained.

When higher oil/slurry ratios were tried, there was some separation of a water-rich phase. However, the partially dewatered oil-slurry mixture could be pumped, although with some difficulty. After decanting the separated water, the water-solids ratio was about 3:1 and the concentration of biomass solids was 15.5%. However, straight hydrolyzed wood slurry is readily pumped at solids concentrations in excess of 30%.

Although the extension of these preliminary pumping results to a process modification involving oil recycle is not straightforward, the present data do indicate the need for overcoming the problems of pumping high concentrations of biomass solids in a wood oil medium.

* Since the slurry is about 20% solids, the overall mixture is about 1 part solids, 4 parts water, 1 part wood oil.

2.2 Analytical Support to CLU

2.2.1. Characterization of Acids in the Aqueous Effluent

Methyl esters of acids extracted from acidic aqueous effluents and of non-extractable acids have been prepared and examined by GC-MS. Thirty major components have been observed, some of which still could not be identified. In addition to those acids reported in the *Quarterly Report April 1981*, the following have been identified with a high degree of probability:

A. Monocarboxylic Acids

Methacrylic	Hexanoic
2-Methylbutyric	4-Methylpentanoic
3-Pentenoic	3-Hexenoic
Pentanoic	Benzoic
3-Methyl-2-pentenoic	3-Pehnylpropanoic
2-Pentenoic	p-Hydroxybenzoic
3-Methylpentanoic	2,4-Dimethylpentanoic

B. Dicarboxylic Acids

2,3-Dimethylglutaric
Methylsuccinic
Adipic

C. Oxo Acids

2-Ketoglutaric
2,2-Dimethylsuccinic

2.2.2. Isolation of High Molecular Weight Phenolics

A method has been developed to determine the portion of the oils which represents high molecular phenolic material.

The oils TR-7, TR-8, and TR-10 could be totally dissolved in a mixture of methanol and sodium hydroxide. After adding a larger volume of ether, precipitates are formed. These precipitates have been isolated after extensive washing with ether; they are completely soluble in water. After adding diluted acids to the water solutions a precipitate is formed in each case; some of the material is still soluble in water after acidification and can be extracted with chloroform. Both of those fractions are phenolic, but of different molecular weight. This procedure allows an estimate of how much of the oil, formed during liquefaction of wood, is still composed of undepolymerized lignin or of higher molecular weight material which has been formed under the conditions of liquefaction by recondensation or repolymerization.

This method could be very helpful in evaluating experimental conditions and to find ways to change conditions of liquefaction in order to obtain a product free of material with molecular weight over 300.

The examined oils vary considerably in content of high molecular weight phenols:

TR-7	42%
TR-8	16%
TR-10	76%

There are distinct differences in the elemental compositions of these "high molecular weight" fractions and in the ether soluble portions of these oils; as an example TR-7-oil:

	C%	H%	O%	Formula	H/C-ratio
"high mol. weight fr."	71.85	5.38	22.77	$C_6H_{5.4}O_{1.4}$	0.9
ether soluble fr.	80.75	8.17	11.08	$C_6H_{7.3}O_{0.6}$	1.22

2.2.3. Towards Quantitative GC Analysis

Another effort has been begun to obtain a more quantitative method of characterizing the wood derived oils. So far there has been no experimental evidence on how much of an oil could be seen and examined by gas chromatography. Therefore, two oils, TR-7 and TR-12, have been distilled under vacuum up to an oil-bath temperature of 250°C, about the temperature level which has been used in the temperature program for gas chromatography.

An examination of the distilled fractions and distillation residues shows that for TR-7 at least 30% and for TR-12 at least 20% are detectable by gas chromatography. Further work is in progress for a better quantitative description of wood derived oils.

In order to deal with more stable compounds the oil TR-7 has been methylated by dimethyl sulfate reagent. Work toward a quantitative method is in progress.

2.2.4. SESC Fractionation of Albany Oils

The primary method used for characterizing biomass oils has been solvent extraction. Usually wood oil has been defined operationally as the acetone, toluene or chloroform-soluble fraction of the organic phase of the reaction product. There are, however, major difficulties with such solubility classifications. Very little chemical information is obtained and the solubility of a particular component is strongly influenced by the presence of other components acting as co-solvents. Recently, Farcasiu (1) has developed what she calls the sequential elution by specific solvents (SESC) scheme for characterizing coal-derived fluids such as SRC I. We have applied the SESC method to wood oils and find it suited for effecting gross group separations of raw biomass oils.

The SESC method involves column chromatography on silica gel. The following sequence of solvents is used to obtain the various fractions:

1. hexane
2. hexane-15% benzene
3. chloroform
4. chloroform-4% ether
5. ether-4% ethanol
6. methanol
7. chloroform-4% ethanol
8. tetrahydrofuran-4% ethanol
9. pyridine-4% ethanol
10. noneluted.

Results obtained to date for Albany oils are shown in Tables IV and V.

TABLE IV.

SESC FRACTIONATION OF TR-7 OIL

Fraction	Relative Amount	C	H	O	State
1	0	-	-	-	---
2	1	-	-	-	green-yellow oil
3	16	81.0	7.9	11.1	orange liquid
4	39	75.9	7.6	16.5	orange-brown viscous oil
5	19	72.3	6.6	21.1	dark tacky oil
6	14	71.4	6.0	22.6	dark solid
7	1	-	-	-	grey solid
8	6	-	-	-	black semi-solid
9	3	-	-	-	dark orange-brown solid

TABLE V.

SESC FRACTIONATION OF ALBANY OILS

Fraction	TR-7	TR-8B	TR-10	TR-12
1,2	1%	17%	1%	6%
3	16	21	6	12
4	39	18	17	21
5	19	-	35	34
6	14	23	19	14
7,8	7	-	6	2
9,10	4	21	16	11
	—	—	—	—
	100	100	100	100

The following conclusions can be drawn from these preliminary studies on Albany oils. Fractions 1-5 are liquid, give many peaks by capillary GC, and evidently represent distillable material. Higher fractions are solid and give no peaks by capillary GC. Each of the four oils examined is unique. TR-7 has twice the amount of fraction 4 (monophenols according to Farcasiu) as the other oils. TR-8B has an anomalously large proportion of aromatic hydrocarbons, fraction 2 (probably because the sample is from an overhead condensate). TR-10 and TR-12 are similar except that the "nondistillable" fractions (6-10) are 41 and 27%, respectively. TR-10 is a solid at room temperature while TR-12 is a heavy oil.

Characterization of biomass oil by SESC fractionation should prove useful in studying the mechanisms of liquefaction. That is, by monitoring the distributions of SESC fractions as a function of time and temperature, insight into the course of the various stages of reaction may be obtained.

The SESC technique is simple and may be completed within one day. The samples are nearly completely eluted from the column. A 2-gram sample is satisfactory.

SOLVOLYSIS OF WOOD CHIPS

Since phenol is an excellent solvolysis agent for Douglas fir wood chips, the phenolics-laden wood oil liquefaction product should also be effective. Some quantitative tests early in FY 81 indicated that this was true. A quantitative batch experiment shows that wood-oil is, in fact especially effective.

229 g air dried wood chips (200 g dry wood solids) plus 600 g TR-7 oil plus 3 g H_2SO_4 were heated to 225°C in the 1-gallon autoclave and held at temperature of 45 minutes. Examination of the product indicated complete solution of the wood chips. The product appeared homogeneous. The material is solid or gummy at low temperatures, but is a viscous liquid above about 110°C.

The results suggest that if some way of regenerating a recycle solvent can be found, a new process requiring a much lower oil recycle ratio than required for the PERC process would be available. Such a regeneration procedure might be the present CO-steam liquefaction or a light hydrogenation. It is probable that solvolysis actually occurs at some stage in the present PERC process. It may be partly responsible for the rather low yields of insolubles in some of the Albany PERC runs.

References

1. M. Farcasiu, Fuel, 56, 9 (1977)

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