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RESEARCH AND DEVELOPMENT ACTIVITIES
ON DIRECT LIQUEFACTION TECHNOLOGY
QUARTERLY REPORT
July-September 1981

H. Davis, C. Figueroa, C. Karatas, D. Kloden,
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October 1981

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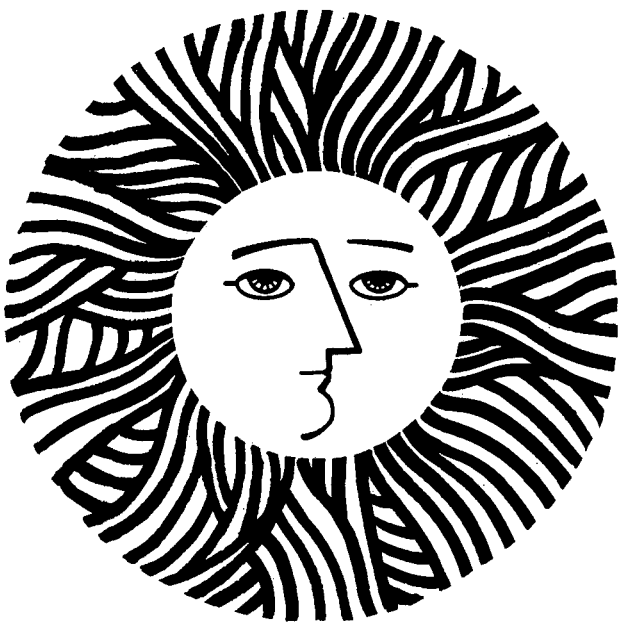

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RESEARCH AND DEVELOPMENT ACTIVITIES ON DIRECT LIQUEFACTION TECHNOLOGY

QUARTERLY REPORT
July-September, 1981

H. Davis, C. Figueroa, C. Karatas,
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HIGHLIGHTS

- The continuous liquefaction unit (CLU) reached full operation during the quarter.
- Run lengths of up to 24 hours (voluntary shutdown) were achieved, and the ranges of operating variables for study have been defined.
- The liquid chromatograph "SESC" procedure, originally developed for coal liquefaction product, has been shown to be a useful method of following effects of changes of variables on the oil product.
- In CLU runs at high feed slurry pH there is a great deal of water gas shift reaction, but only a little (possible zero) net synthesis gas usage.

TASK 1

Operation of Continuous Liquefaction Unit (CLU)

Following the very limited success with small-bore tubular reactors, as reported in the previous Quarterly Report[1], the reactor section of the CLU was replaced with a stirred one-liter autoclave. This converts the plug-flow reactor to a CSTR (continuous stirred tank reactor), effectively a 400 to 1 scaledown from the Albany PDU (cf Fig. 1). As operating problems other than reactor tube plugging have proved to be solvable, acceptable operation has been achieved, starting with run CL-5, July 16, 1981. Minor improvements in stirring, slurry injection, pressure let-down, and reactor hardware have been made during the summer, and run CL-6 turned up a special problem which is discussed below. Runs from CL-7 on are based on our overall plan for an overall study of operating variables to be completed in FY 82.

The operating conditions of the runs made are summarized in Table I. The results of individual runs were instructive enough so that we will discuss them individually or in groups.

CL-2 to CL-4

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

CL-5

The overall run time was about 16 hours. Good samples were obtained and the overall material balance was fair (about 92%). It was found that over-rapid let-down of pressure from the product recovery vessels leads to a loss of oil product by a foaming mechanism. Hence, in CL-5, a disproportionate amount of oil was contained in the 8% overall loss, and the real oil yield is higher than the 20% shown in Table I. 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 II) 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 Mols 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 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.

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* Equivalent to 640 g or 36 Mols H_2O/hr and about 6 Mols/hr of synthesis gas plus generated CO_2.

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 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 line out, shortly after start-up, at 10% CO, 35% H_2, 55% CO_2. The pressure ratio $H_2 \cdot CO_2$ ($H_2O \cdot CO$) 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. The potential for feed line plugging was reduced by shortening the inlet line into the CSTR. Through run CL-10, this brought the feed almost to the bottom of the reactor. Starting with CL-11 (10/15-10/16/81), the line ends just below the expected level of the liquid during operation.

TASK 2 - Support Activities

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[2] 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 [1, 3] 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[2] 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 (~ 2 g) 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 III.

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 molecular weight. As discussed above, we believe this sample was vaporized from the reactor, leaving heavy ends (F6 and 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 a 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 III and IV. 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 III). 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 Figs. 3, 4, and 5. The HPSEC and SESC procedures have been further described in the Quarterly Report for April-June[1].

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[5], we established that CO definitely reacts as a reducing agent,[3, 4] 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. Zero usage is, however, not yet excluded, and it is possible that the small usage corresponds only to a net formation of formate.

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_2O, 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 116.6	O - 35.2

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.

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 prehydolysis. 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.

The experiment with effluent water is indicative of one of the differences between the PERC and LBL processes. The oil recycled in the PDU is actually a very wet mixture containing perhaps 30% water. The water-soluble products as well as the oil are therefore recycled. Concentrations of water-solubles build-up to a high level and a small contribution to the total oil yield comes from the decomposition of water solubles. Re-use of water effluent for prehydrolysis in the LBL case[6] is not promising economically because of a burdensome and costly acidification, neutralization cycle.

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% H_2, 30% CO_2, 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% to 39% H_2, 33% CO_2 and 28% CO, showing that the water gas shift had been catalyzed.

- Two slurry liquefaction runs were made under much less severe conditions (50% H_2, 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 H_2 46.8, CO_2 12.5, and CO 40.7% and H_2 51.2, CO_2 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 H_2/CO to 100% CO. Outlet gas analyses in runs 7 and 10 were 54% and 35% H_2, 31% and 55% CO_2 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 some degree. The excess carbonate was largely converted to formate ion, and, of course, this reaction uses some CO.

Pretreatment of Biomass - The Role of Solvolysis

Studies of the dissolution of Douglas fir wood by acidified alcoholic or phenolic organic solvents, termed "solvolyis," were carried out here in FY 80 and FY 81. They are covered in detail in a forthcoming Ph.D. dissertation.[7] An article in the 1980 Annual Report of the LBL Energy and Environment Division[8] 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[1, 8] 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 reported in the previous Quarterly Report[1] verified that wood oil is indeed a suitable solvolytic agent. Raw Douglas for wood chips can be totally "dissolved" 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.

Analytical Support: Improved Methods of Oil Product Characterization

We reported last quarter that the SESC fractionation technique for characterizing coal-derived fluids developed by Farcasiu of Mobile Oil could be used for wood oils as well. We have applied the method to all oils produced in the continuous reactor through September 20. We have also examined both individual fractions and whole oils by high-performance size exclusion chromatography (HPSEC), providing information about the distribution of molecular weights within each sample. This body of information is beginning to provide insights into the mechanism of the liquefaction reaction and the relationship between oil quality and certain operating variables, notably temperature. A more precise definition of the term, oil quality, is also being fashioned.

The columns for HPSEC were packed with "Biobeads" (BioRad Laboratories), a relatively inexpensive gel of polystyrene cross-linked with divinylbenzene to provide a range of effective pore sizes. A UV detector operating at either 254 or 280 nw was used. The solvent was THF.

The data were processed by a Perkin-Elmer Sigma 10 data station using the GPC2 program available from Perkin-Elmer. The program provides both number and weight average molecular weights as well as detailed molecular weight distribution frequency plots. A calibration curve was constructed using 18 standards varying in molecular weight from 78 to 2350. We noted considerable dependence of elution volume on molecular structure. Thus the molecular weights reported here are more significant in a relative than in an absolute sense.

Column stability was checked several times daily using a freshly prepared solution of nordihydroguaiaretic acid (NW 302) in THF. The columns gave quite reproducible results over several weeks of constant use.

Molecular weights so determined for individual SESC fractions are shown in Table I. The first four fractions (through F5) are reasonably monodisperse and seem to represent largely monomeric material. The increase in average molecular weight from F12 to F5 parallels an increase in oxygen content. However, F6, which is eluted with methanol, is of much higher molecular weight than the preceding fraction and is also more polydisperse. In fact the recorder trace of UV absorbance vs. elution volume for F6 reveals an unresolved doublet with a shoulder on the low molecular weight side of the main peak.

The molecular weight distribution for F78 is bimodal; the low molecular weight material may consist of highly polar dihydric or trihydric phenols. It appears that the fractionation scheme should be modified so as to isolate the two subfractions of both F6 and F78.

Table II summarizes the results of the SESC fractionation of eight wood oils, five produced at LBL, two at Albany, Oregon by the LBL process (TR7 and TR10) and one at Albany by the PERC process (TR12). There are few striking differences. CLU-6 was recognized immediately as an exceptionally high quality oil by its low viscosity and this is borne out by the numbers. It is characterized by a low molecular weight, as expected from the small proportion of higher fractions, namely F6 and F78, and by the absence of noneluted materials. These observations are consistent with our suspicion that somehow this oil was distilled rather than flushed out of the back-mix reactor. Furthermore a large amount of solid material was recovered from the reactor after the premature shutdown of the run. Thus this oil must be regarded as nonrepresentative. Accordingly, the data of Table I should probably be extended to include more representative samples.

Several differences among the other oils seem worth noting. The ratio of F6 to F1-F5 is much higher in the case of CLU 8-4 than in the case of any of the other oils. This is significant because CLU-8 was conducted at 330°C whereas all of the other runs, with the possible exception of TR10, were operated at 350°C or higher.

TR-7 oil differs from the others in another aspect. It has the highest proportion of F3 and it is the only oil where the amount of F4 is greater than that of F5.

An understanding of the relationship between oil quality and reaction variables remains largely beyond our grasp. However, several important steps have been taken. The SESC fractionation technique coupled with HPSEC puts the complex question of oil quality on a numerical basic. It is now clear how futile were earlier efforts to relate reaction variables to such nebulous concepts as "yield" and "conversion." Now that the CLU system has been shaken down, it appears that a meaningful evaluation of the potential of biomass liquefaction can finally be undertaken.

Future efforts in the area of analysis and characterization include the following:

1. Improve the SESC fractionation scheme so as to resolve the F6, F7, and F8 fractions into more homogeneous cuts.

2. Undertake a detailed chemical characterization of individual fractions by means of infrared spectroscopy, GC-MS of volatile fractions, nuclear magnetic resonance spectroscopy, HPSEC and HPLC.

3. Isolate certain fractions, such as F5, on a preparative scale and subject them to further liquefaction under forcing conditions or to catalytic hydrogenation in order to determine the potential of upgrading the product to transportation fuel.

TABLE I

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 helpe 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	Water completely vaporized; See text.
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 II

VAPORIZATION OF WATER FROM SLURRY REACTOR AT 3000 PSIA

Temperature, °C	Vapor Pressure also, PSIA	Mols H_2O Vaporized per* Mol Fixed Gas	Water Vaporized and Unvaporized (6 Mols/hr fixed gas, 1 kg/hr water feed)		
			Vaporized grams	Unvaporized grams	Unvaporized 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. (H_2O);
Low value Mols (H_2O)/Mol (fixed gas) = V.P. (H_2O)/partial pressure (fixed gas).
High value = Low value · Density (real water vapor)/density (H_2O, perfect gas).

TABLE III

MOLECULAR WEIGHTS OF CLU-6 SESC FRACTIONS BY HPSEC[a]

	F12	F3	F4	F5	F6	F78 LMW	F78 HMW
$\overline{M}_n^b$:	143	172	173	120	350	181	687
$\overline{M}_w^c$:	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 determination 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 (= $\overline{M}_w/\overline{M}_n$).

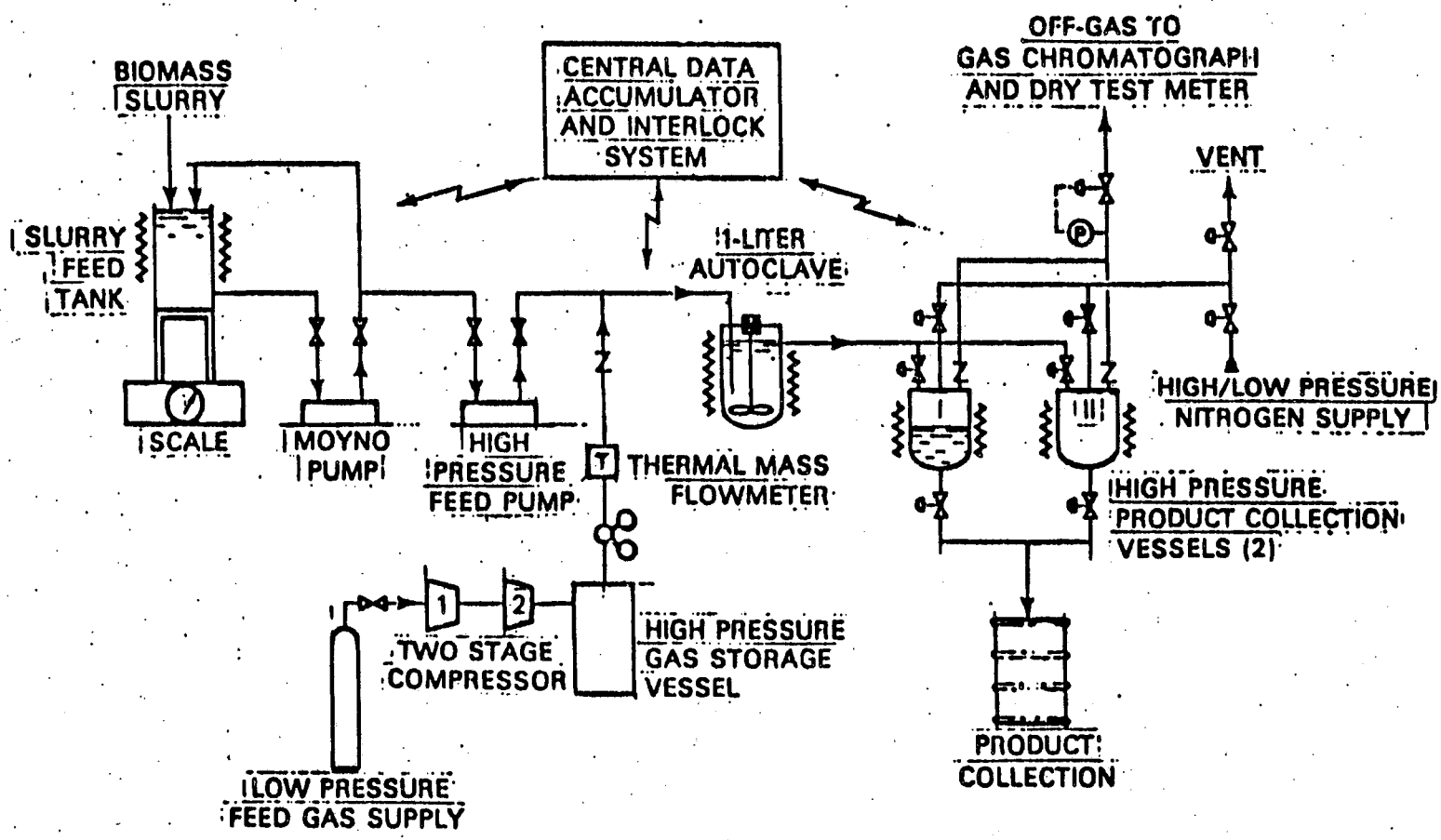
TABLE IV

SESC FRACTIONATION OF BIOMASS OILS

Fraction	Sample							
	CL4-3[a]	CL5-3[a]	CL-6[a]	CL7-3[a]	CL8-4[b]	TR7[b]	TR10[b]	TR12[b]
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	-
% Total	89	99	100	94	83	99	88	89
$\overline{M}_n$	271	213	176	242	-	215	286	240
$\overline{M}_w$	483	319	232	384	-	306	467	370

[a] Methanol-chloroform extract. [b] Raw oil.

FIGURE I



BIOMASS CONTINUOUS LIQUEFACTION UNIT

XBL 817-1023

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