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LIQUID FUELS BY DIRECT LIQUEFACTION OF BIOMASS

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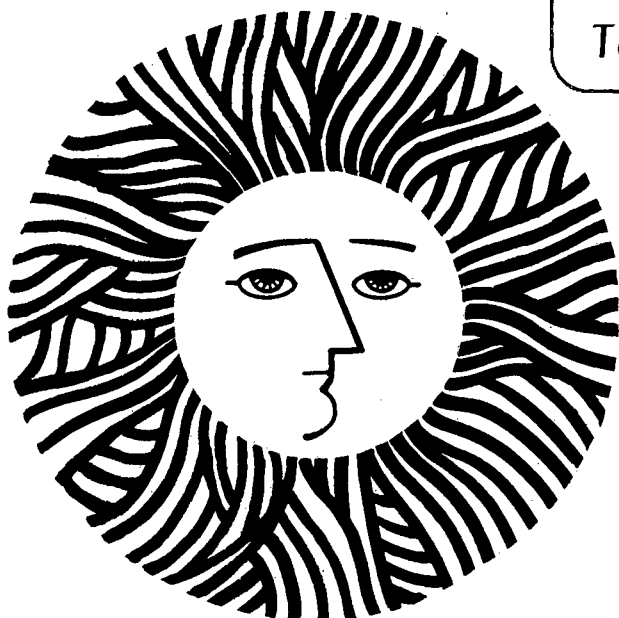
Hubert G. Davis, Carlos Figueroa,
and Larry L. Schaleger

March 1982

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LIQUID FUELS BY DIRECT LIQUEFACTION OF BIOMASS

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To be
Presented at the KTI Fifth Annual High Temperature
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SUMMARY

Domestic and international reserves of conventional fossil fuels will inevitably dwindle. The renewable fuel and raw material, biomass--wood, agricultural and municipal wastes, and energy plants--must be considered. Direct liquefaction under pressure of steam and a reducing gas is a promising method for making combustible liquids from various biomass forms.

Conversion of Douglas fir wood chips to a crude fuel oil, under an atmosphere of carbon monoxide, hydrogen and steam has been accomplished by at least two processes. An oil-wood-flour slurry (oil recycle) process has been operated smoothly at DOE's process development unit (PDU) in Albany, Oregon (Rust Engineering Co., contractor). Operability was achieved at the cost of extremely high recycle ratio of product oil (about 19/1) and of effluent water. A single pass, water-slurry process, originally developed at the Lawrence Berkeley Laboratory (LBL), has also been tested at Albany. However, while the first substantial quantities of product oil were made by this process, yields were relatively low and there were operating difficulties. An improved single-pass process or a modified process with a low recycle ratio appears to offer the best chance of commercial success.

LBL is currently operating a bench-scale continuous liquefaction unit. The feedstock has been an aqueous slurry of prehydrolyzed Douglas fir wood chips. We believe, however, that other biomass forms capable of being slurried can also be handled. Yields of oil product are higher than was estimated from the Albany experience but are consistently lower than achieved by the recycle process. The difference is real, and is caused by a greater formation of water-soluble products such as carboxylic acids in the water-slurry process. In work to date at LBL, no significant difference in either oil yield or product analysis has been found when the CO-H₂ reactant gas mixture is replaced by either CO or H₂ alone. Since CO feed largely reacts to form H₂ and CO₂ by shift reaction, it is economically desirable to use a hydrogen-rich reaction gas.

The product oil is a crude material, feedable as a heavy liquid fuel oil at temperatures somewhat above ambient, very low in sulfur and nitrogen, but containing 10 to 19% oxygen, largely as phenols. The crude product has been shown to be capable of replacing number 6 fuel oil in the test boiler at the Pittsburgh

Energy Technology Center (PETC). Upgrading to higher quality distillate fuels is a subject for further study. Experiments on hydrocracking by techniques reported to be applicable to coal-derived oils, crude shale oil and tar sand oils are needed. Calculations indicate that the hydrogen requirement should be less per unit volume of product than is needed for overall coal conversion.

At this point, an operable process offers the possibility of producing a clean, dense, heavy liquid fuel from biomass forms capable of being slurried. Since product oil/effluent water phase separation is easily accomplished, it also offers the possibility of producing a dense fuel, feedable as liquid, from wet forms of biomass such as many agricultural residues or energy plants or from peat.

Process flow sheets, stoichiometry, operating problems, and methods of product characterization are discussed, as well as possibilities for an improved process.

WHY BIOMASS AND WHY LIQUEFACTION

Biomass is renewable and fossil fuel and mineral resources are limited. It is only within the past few years that we have started to face the fact that even our seemingly boundless supply of coal has a foreseeable end. Of course, such resources don't really die; they gradually fade away as the cost and effort to recover resources of poorer and poorer quality increases.

Current estimates⁽¹⁾ of the ultimate recoverable resources of conventional petroleum--including deep offshore and polar regions and enhanced recovery--are about two trillion barrels, with perhaps 100 billion in the United States. Similarly, the ultimate recoverable reserve of natural gas is estimated at 10^{19} SCF with perhaps 10^{18} in the United States. The proven recoverable reserve of coal in the United States is currently estimated variously from $134 \cdot 10^9$ tons to a little more than $200 \cdot 10^9$ tons, with the entire world at only $700 \cdot 10^9$ tons. The ultimate recoverables depend on how deep we can strip or dig for how thin or how poor a coal. It is unlikely to be higher than about $400 \cdot 10^9$ tons and two trillion tons respectively.

The numbers are huge, but far from infinite. The rapid exponential growth rates in fuel consumption we were looking at in the 60's and early 70's no longer exist and are no longer projected into the future. West Europeans are already starting to look towards U.S. coal exports to replace depleted oil reserves and imports. Given a limited resource, a reasonable pattern for projection to the future is the normal probability curve (bell curve) as pointed out by Hubbert⁽²⁾ years ago. To make a guess as to when sizable amounts of biomass energy might be essential in the U.S., we make conservative* guesses as to the ultimate remaining recoverables of oil, gas, and coal--90 billion barrels, 500 trillion cubic feet, and 200 billion tons, respectively. Recoveries beyond these will at least be very difficult, technically and economically. We have then taken us down in oil and gas production from a bell curve maximum. Part of the drop in oil and gas will be made up from unconventional sources; oil shale, tar sands, tight gas formations and the like. Coal production is assumed to rise to replace the rest, to allow modest increases in exports and to allow for a small growth in electric power. A maximum production rate of 2.5 billion tons per year is reached in 25 years. The above figures determine the curves of fig. 1.

Under this scenario, conventional oil and gas production in 2007 is down to 44% of the present rate and falling fast. Coal is peaked at about three times the present production rate and the ultimate reserve is down to 155 billion tons. The total energy production is about 80 quadrillion Btu--roughly our present use rate (it will be only 68 quad if we export 20% of the coal production. And the reserves which are easy and economical to discover and produce have, naturally, been discovered and depleted. Any gains in energy availability will have come from imports (somewhat doubtful 25 years from now), nuclear power (doubtful today) and unconventional oil and gas (barely getting started 10 years from now).

* Perhaps "prudent" would be a better word, especially for the rather low guess on coal recovery. Presumably less accessible seams of coal will be mined, allowing the production curve to tail off slowly into the future, as it is doing in western Europe. Heavy oils, shale oil and tar sands could be thought of as doing the same thing for petroleum.

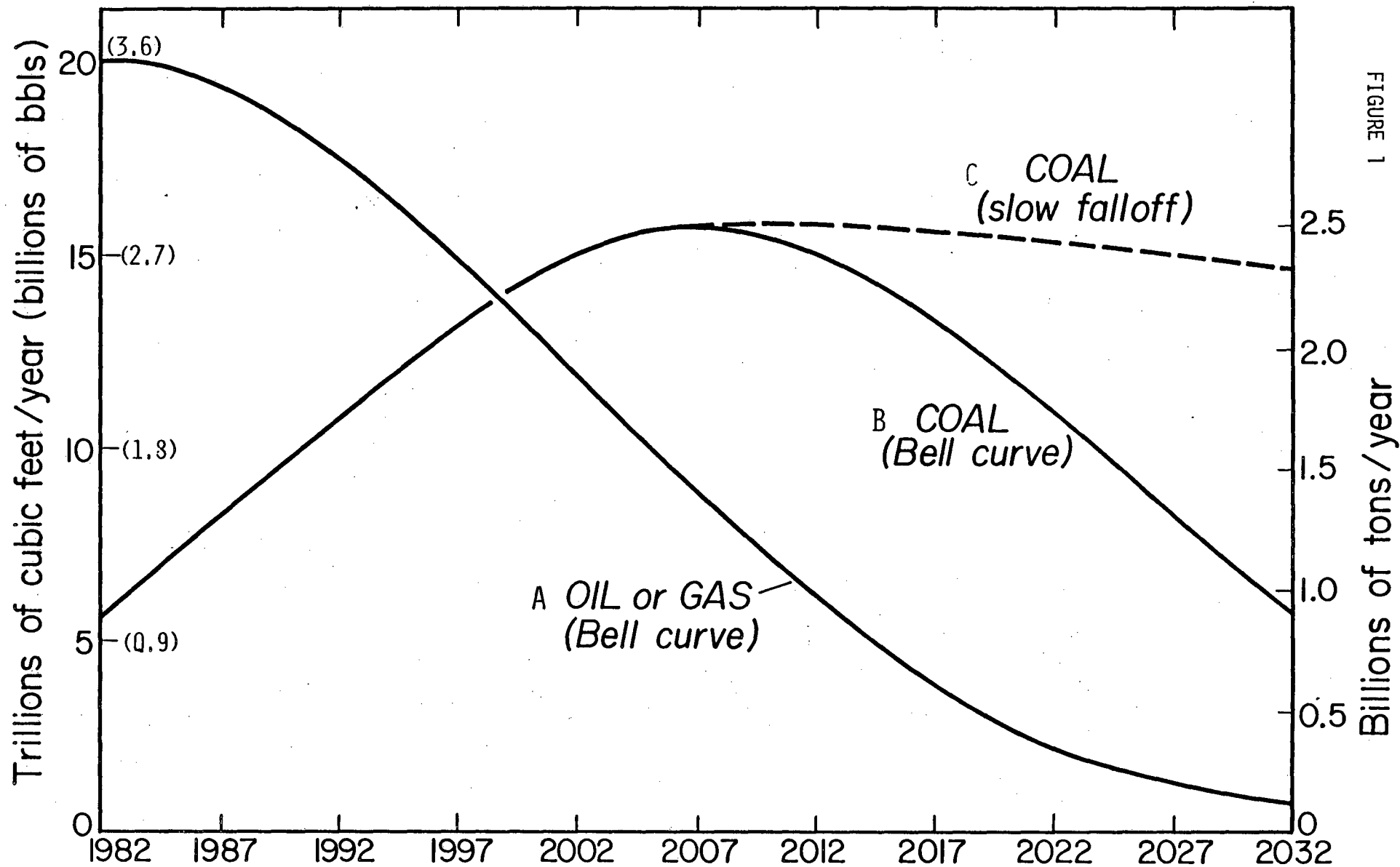


FIGURE 1

Billions of tons/year

Curve A - Oil or gas usage falling along bell curve from a 1982 peak.
 Curve B - Bell curve for coal peaking in 2007.
 Curve C - Output of coal maintained near maximum by mining poorer, less accessible deposits.

We should be ready to substitute renewable fuels long before the 25 years are up. But why liquefy? A good question to ask is one most of us who have been involved with coal liquefaction have asked: "why not just burn it?" For coal, "why not" may still be a good reply, but I don't think it is always the correct one for biomass.

Biomass typically comes associated with large quantities of water, ranging from 50 to 60% in trees to 90% or more in some of the species recommended for "energy plantations." Peat--a fossil fuel not far removed from biomass--has a similar problem. Biomass is usually fibrous. For fuel purposes it may need to be crushed, ground and torn apart, as well as dried. Then it is likely to have a low bulk density and to require compacting for uses. Shipping any distance is expensive. In any form, it is not useful for most transportation purposes and is inconvenient, at least, for power production, gasification, and home heating.

Goals for a biomass liquefaction program come from the above discussion: an economical dewatering and densification procedure; production of a crude dense product, transportable, storable, and feedable as a liquid for steam and power production; and, ultimately, production of automotive fuels.

The goal of making automotive fuels from crude biomass oil will require a lot of further experimentation. All we can say now is that it may be possible by some hydrocracking technique such as is planned for crude coal-derived oil. If it is, the overall hydrogen requirement per ton should be less than when we start with coal. The other goals can be achieved. There are process and product problems which we will discuss, but we don't believe these are insurmountable.

HISTORY

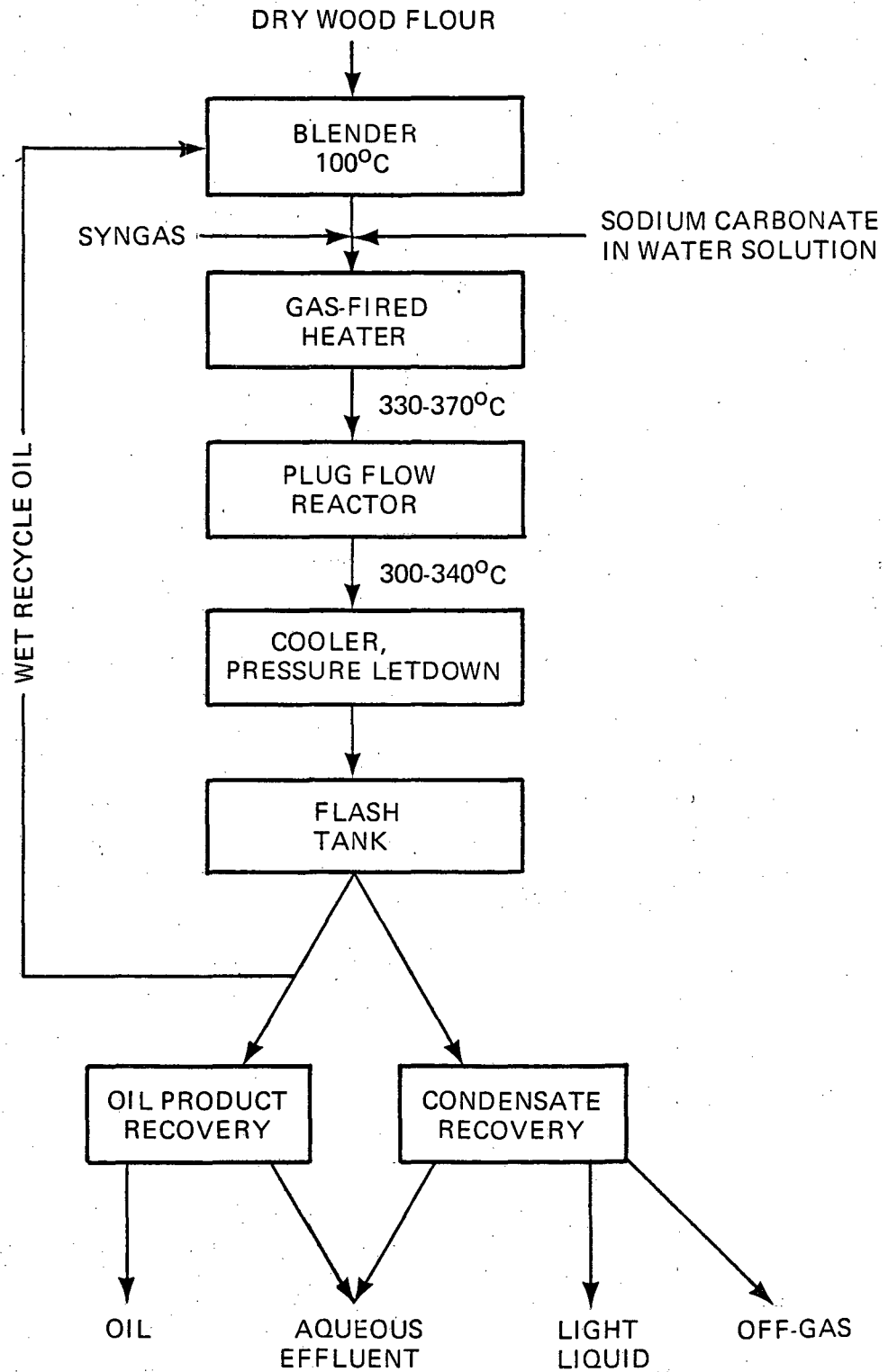
Attempts to make liquid products from biomass--mainly wood--date back at least 60 years. The current effort supported by the U.S. Department of Energy began with work⁽³⁾ at the Bruceton, Pennsylvania station of the U.S. Bureau of Mines, originally with municipal trash as the raw material and carbon monoxide as the reducing gas. In 1974, DOE's predecessor, ERDA, decided to design and construct a process development unit (PDU) at Albany, Oregon. The proposed process was

based on the work at Bruceton and termed the PERC process for the Pittsburgh Energy Research Center. The feedstock was Douglas fir wood chips. In the period 1976-1978, the original operator, Bechtel, and the later operator, Rust Engineering (1977-1981), had serious problems with the original process. A research group at Lawrence Berkeley Laboratory (LBL) recommended^(4,5) an alternative (the LBL process). This was adapted to the PDU by Rust Engineering to produce the first substantial amount of wood-derived oil. In 1980-81 Rust made two additional runs using the LBL process and were able to make three lengthy runs with a modified PERC process. The history of the Rust Engineering project was presented in some detail by Thigpen and Berry⁽⁶⁾. A brief description of the two processes, quoted from a recent LBL report⁽⁷⁾, is given here.

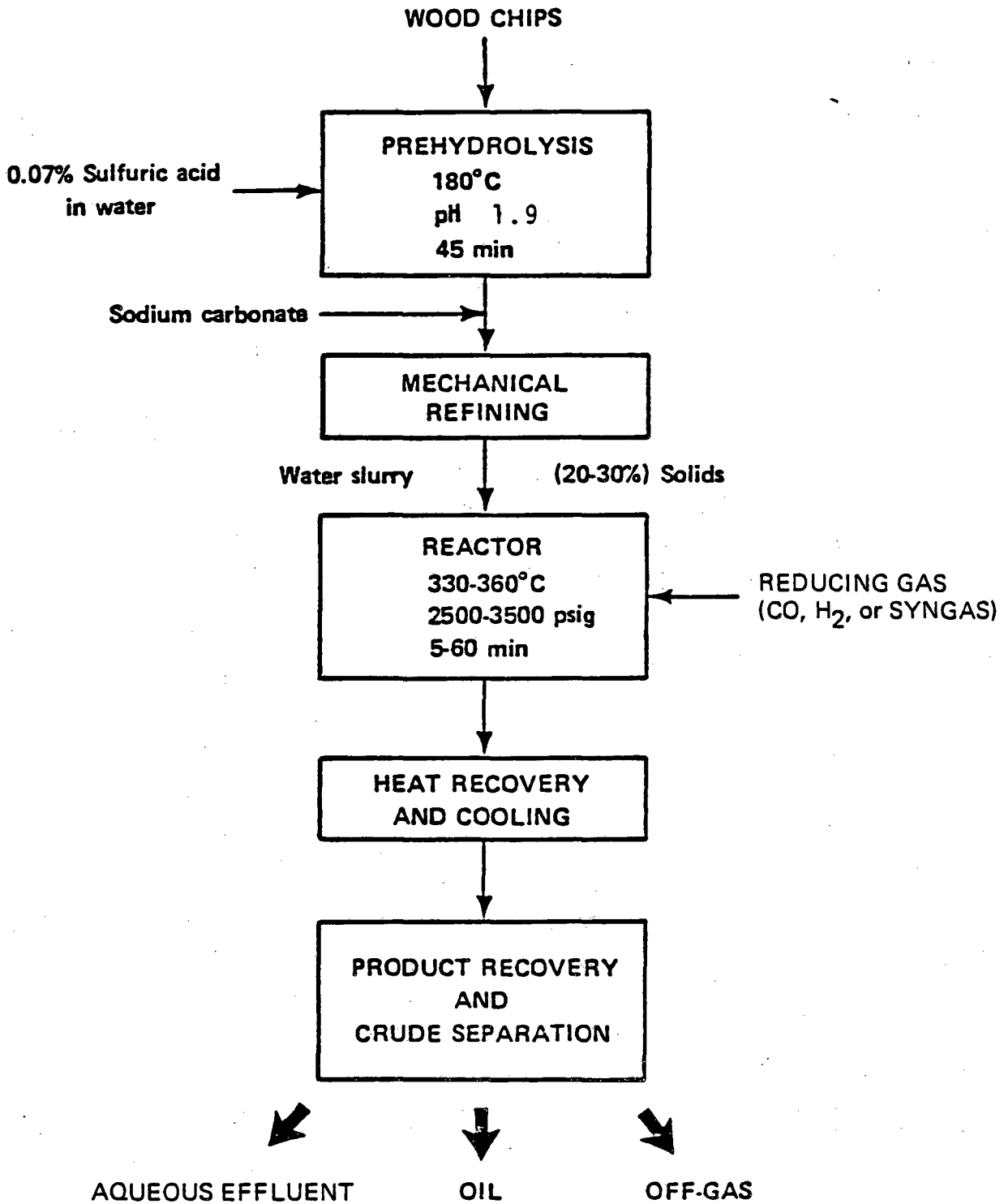
PERC (fig. 2): Wood is dried, ground to flour and slurried in a blender with a wet recycled product oil. Sodium carbonate catalyst (4 to 8% of the weight of wood) and additional water are added. The mixture is heated rapidly to a reaction temperature of 330 to 370°C in a directly fired tubular heater, with a flow of reducing gas (3 to 6 mols CO + H₂ per 100 kg wood), then passed through a tubular or standpipe reactor with volume sufficient to allow a space-time of 10 to 30 minutes. Reactor pressure is about 200 atmospheres. After cooling and pressure let-down, a portion of the existing wood oil is withdrawn as product and separated from the aqueous effluent. The remaining oil is recycled, without separation of water, to the wood-flour blender. In the absence of an existing stock of satisfactory wood oil, coal tar anthracene oil is used as the initial slurrying medium. Yields of wood oil from Douglas fir are in the range of 45 to 55%, depending on the severity of operation, i.e., on the degree of reduction of the oxygen content from the 40-45% level of wood. There are also substantial yields of water-soluble organics, largely carboxylic acids or their anions. The remainder of the wood is lost as carbon dioxide and water.

LBL (fig. 3): Wood chips with only incidental air drying, mixed with water, are brought to pH 1.9 (about 0.075% sulfuric acid). The mixture is heated at 180°C for 45 minutes to prehydrolyze the hemi-cellulose content and greatly weaken the structure of the wood. Sodium carbonate is added to bring the mixture to a

PERC LIQUEFACTION PROCESS



LBL LIQUEFACTION PROCESS

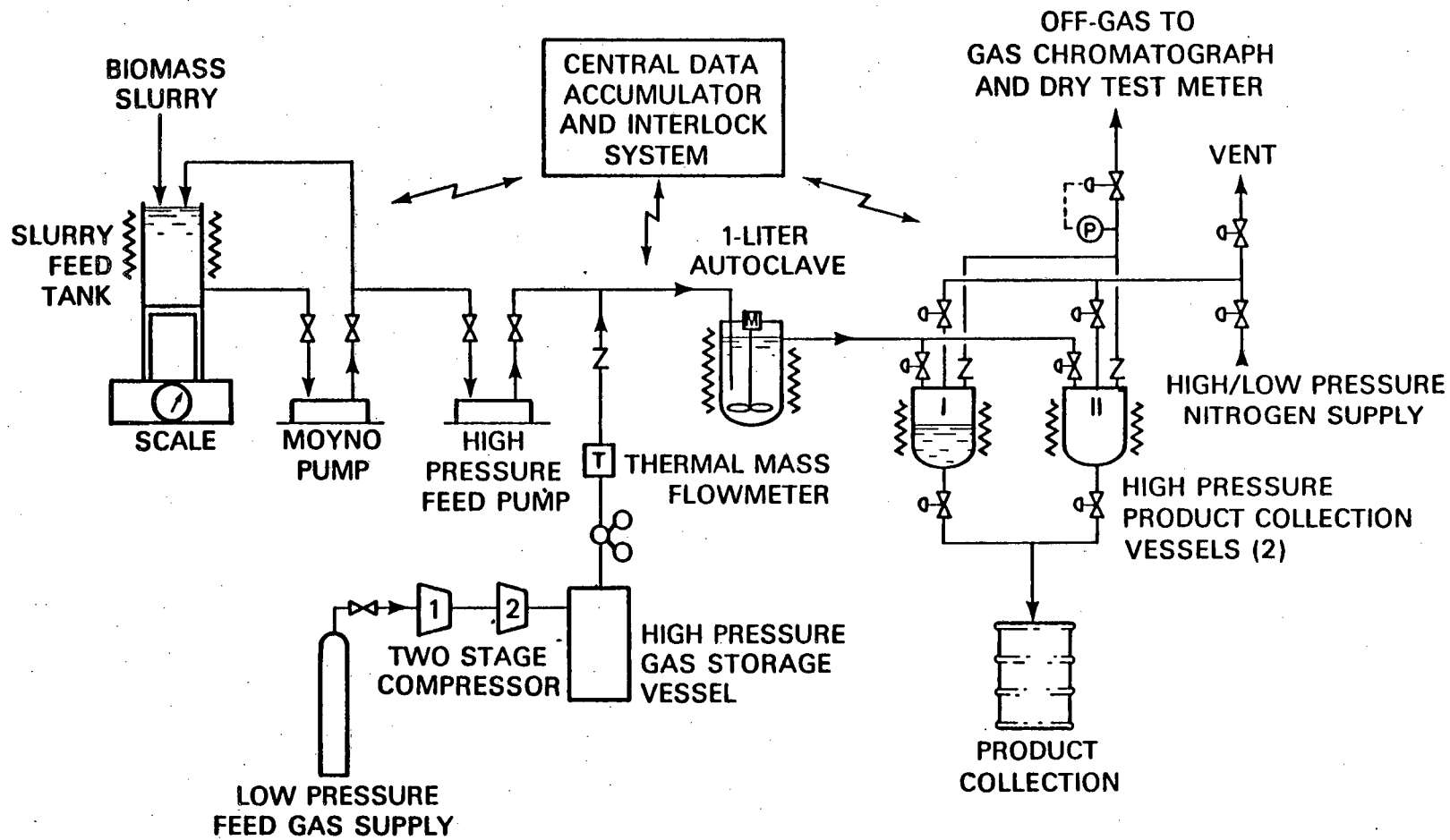


pH of about 8 and it is homogenized by passage through a refiner. Slurries of total organic content in the range 20 to 30% or higher are obtained. Slurry is heated to reaction temperature with reducing gas in a direct-fired tubular heater as in the PERC process. Additional residence time is obtained by passage through a turbulent tubular reactor or other well-stirred reactor. The effluent mixture, after cooling and pressure let down, is separated into aqueous and oil phases. Total oil plus water-soluble product is about the same as in the PERC process, but there is a higher proportion of water-solubles, at least partly because of the lack of recycle.

The major deficiency of the PERC process is the need for an extremely high oil recycle. In the PDU, wood flour contents of 10% or more have caused plugging in blenders, lines, and pumps. In the most successful run the average wood content of feed was only 7.5%⁽⁶⁾. Since the feed slurry was approximately one part wood, 2.8 parts aqueous phase and 9.5 parts recycle oil, the new oil formed was only 5% of the total oil effluent and the oil recycle ratio was 19 to 1.

As a single-pass process, the LBL process avoids the oil recycle problem totally. Since the heat capacity of water is high, it is necessary to maximize the wood content of feed slurry, preferably to 30% or more. However, some heat can probably be recovered from the process. A major economic stumbling block of the PERC process is thus spoken to. There are, however, operational problems. Also, the products produced are not identical. Efforts to improve and modify the process and to improve the product are therefore continuing.

In 1979, in order to measure process variables and further develop the LBL process, a bench-scale continuous unit was proposed⁽⁸⁾. Initially a tubular reactor was used--about 100 ft. of 1/4" I.D. tubing, with hot-air heating. At the low flow rates of bench-scale operation we were unable to operate for more than one or two hours because of coking and plugging. We finally replaced the tubular reactor with an in-line one-liter stirred autoclave. The present flow sheet is shown as fig. 4. Since June 1981, we have been able to operate successfully for periods up to 24 hours. The flow sheet is described in detail elsewhere^(9, 10). Temperatures and pressures are recorded at a small panel board which incorporates a



BIOMASS CONTINUOUS LIQUEFACTION UNIT

FIGURE 4

XBL 817-1023

microprocessor. The collection vessels are prepressurized to operating pressure with nitrogen and used alternately during sampling periods of about four hours, and liquid product and water are recovered after gas pressure let-down through electrically operated valves. We have not had trouble with plugging. There remain, however, the usual problems of leaks experienced at this scale when there are multiple fittings and valves.

One annoying problem, specific to operation with water slurries, is that of phase separation in the reactor. At reaction temperature, the specific gravity of water is about 0.58. That of the oil product is 0.9 or higher. In an autoclave or in a vertical tube, the oil tends to collect near the bottom, sometimes defying efforts to mix it with the water by violent agitation. Thus oil residence times in both CLU and PDU may be longer than average liquid residence times. This makes interpretation of data more difficult and almost certainly contributes to coking. If our understanding of this phenomenon is correct, the ideal reactor would be tubular and not far from horizontal and would be operated at high Reynolds number. This is hardly achievable at bench scale.

Since the Albany PDU was placed on standby in the spring of 1981, the LBL unit, termed CLU for continuous liquefaction unit, is currently the only equipment available for continuous flow studies of the type discussed here.

Studies of the liquefaction of biomass--again primarily wood--are being carried on in various parts of the world. The DOE-funded project includes batch experimentation on liquefaction and product beneficiation at Battelle's Pacific Northwest Laboratory (PNL). There are active groups in several parts of Canada, Sweden, Finland, Denmark, West Germany, the United Kingdom, and Brazil. Most of the effort uses batch autoclaves, although several small continuous or semi-continuous units are being built and an international pilot plant has been proposed.

RESULTS OF OPERATIONS IN PDU AND CLU

Details of the results obtained in the Albany PDU are given by Thigpen and Berry of Rust Engineering⁽⁶⁾. Both PERC and LBL processes were tested, with drum lots of product wood-oil being produced from Douglas fir wood chips in runs TR-7 through TR-12. Operationally, the most successful run was the final PERC mode

run, TR-12. Despite the high recycle ratio of product oil, (estimated above to be about 19 to 1), excellent overall material balances were obtained (gross output over input = 1.004).

The flow and analytical data are sufficiently reliable for a credible atom balance. It is clear that oxygen, of the order of 43 wt % in the dry wood, is reduced in three general ways. CO_2 is lost by a pyrolytic reaction, as is H_2O , and there is further removal of oxygen by reaction with carbon monoxide. The amount of the reaction with CO is a function of reactor temperatures, varied during the run, and parallels the reduction in percentage oxygen remaining in the liquid. In TR-12 this varied from about 19 wt % at the lowest severity to about 12% at the highest. In an earlier run, TR-8, Rust reported making wood-oil with as little as 7 to 8% oxygen.

At the middle operating severity of TR-12, with product oil having 16.4% oxygen, we estimate⁽¹⁰⁾ the following stoichiometry, compatible with measured data and the atom balance: 100 lbs dry wood plus 0.47 lb mol $\text{CO} \rightarrow$ 53 lbs oil, 8 lbs water-soluble organics, plus 0.4 mol H_2O plus 1.02 lb mol CO_2 . The higher heating value of the oil is calculated to be about 14,800 Btu/lb or 7,800 per pound of wood, so that the only heating value lost is that necessary to produce the CO . The range of HHv of oils made in the PDU is from about 16,000 Btu/lb at 7% O to about 13,000 at 19% O.

To us, the outstanding feature of the PDU has been Rust's ability to operate the equipment--not always well-designed for the process as it developed--and to obtain reproducible results with excellent material balance. Particularly encouraging is the finding that both types of feed, water and oil slurries, could be heated to reaction temperature in a direct-fired tubular preheater-reactor without serious coking or plugging problems. Also very significant is the fact that, despite the very high oil recycle of the PERC runs, build-up of solids (char) in the product oil ranges from small to negligible. In TR-12, the overall yield of "insolubles" was less than 1%. We are encouraged to believe that wood and other biomass forms can be handled--dried, ground, prehydrolyzed, blended, pumped, etc.--and the reaction and crude product recovery can be controlled without undue difficulty.

The PERC process as it stands, with its high recycle of product oil and partial recycle of water, can hardly be economically feasible. But when an improved process comes along based on the LBL or the PERC process or a new variation, it should be possible to make it operable. See the discussion of "solvolysis" below.

Although the first drum quantities of wood oil were made in the PDU by a version of the LBL process, smooth LBL-mode operation was not achieved there. Three different attempts were made to adapt the plant to water slurries in the three major runs. Initially, the reactor combination was a vertical, scraped-wall preheater plus a large stirred autoclave. The preheater had plugging and mechanical seal problems. Also, from experience with the CLU, we suspect there was a phase separation problem in the autoclave (see above). Run TR-10 used the direct-fired turbulent-flow preheater plus the autoclave. The preheater performed well but there were downstream plugging problems. TR-11 used the turbulent-flow preheater plus the scraped-wall preheater converted to a vertical non-turbulent standpipe reactor. Again, the preheater performed well, but there were plugging and coking problems in the vertical reactor and down-stream. In all three runs recovered oil yields were low--less than 29% dry wood feed vs. 40-53 in the better PERC runs. It was hoped that at least one LBL process run with only turbulent plug-flow reactors could have been made. Because of limited funding, however, the PDU was placed in stand-by condition after run TR-12. There were qualitative indications in runs TR-10 and TR-11 that liquefaction was already largely complete at the end of the direct-fired preheater, but no samples were obtained.

One aim of our Berkeley CLU experimental program has been to determine the causes of the lower yields from the water-slurry process and of the PDU plugging problems. We are also interested in the effects of such variables as gas composition, concentration and pH of feed slurry, pressure, temperature and reaction time on the yield and composition of products and on operability. Table 1 shows some typical data.

Our best yields, while somewhat higher than reported at Albany for LBL runs, are still well under 40%. From both direct data and simple stoichiometric calculations, it is clear that the sum of the water and carbon dioxide yields is about 35%. This is an inevitable consequence of the need to reduce oxygen content without consuming inordinate amounts of reducing gas. We therefore expect the remaining product--oil,

TABLE 1
 YIELDS FROM DIRECT LIQUEFACTION OF DOUGLAS FIR WOOD SLURRY

Run	Red. gas	Reac. temp. °C	Yields wt %							Off gas Mol %	% O in oil
			Crude wood oil	Water Soluble	CO ₂	H ₂ O est	Char	Oil + char from balance			
7	CO/H ₂ 1:1	350	31	25	25	9	11	41	N.A.	17	
8	CO/H ₂ 1:1	330	32	29	23	9	0.3	39	H ₂ -46 CO-38 CO ₂ -16	18.5	
10	CO	350	27	22	25	9	1.6	44	H ₂ -32 CO-9 CO ₂ -59	16	
11	CO	340- 360	33	26	25	9	4	40	H ₂ -22 CO-22 CO ₂ -56	16.5	
12	H ₂	340- 360	27	24	25	9	5	42	H ₂ -70 CO ₂ -30 CO= minor	16.8	
13	H ₂	340- 360	31	27	24	9	9	40	H ₂ -75 CO ₂ -24 CO=1	17	

Notes: H₂O and CO₂ yields are based on oxygen balance. Oil yield is recovered oil per 100 parts wood organics fed. Char is overall for run based on recovery from reactor. Water solubles are estimated from total organic carbon.

plus char, water solubles and loss--to be about 65%. There doubtless have been material losses in some of our runs, but these are fairly small. Losses of oil can occur by frothing during pressure let-down and by volatilization during work-up--perhaps as much as 3% of the total organics. A major portion of the total yield is found as organic solubles in the water effluent. This has been typically about 25% of the total weight of organics. Also, amounts of char are formed, ranging from well under 1% to 10% or more. Table 2 indicates that when overall organics recovery in our runs approaches 100%, the oil plus char yield is typically 40%. Thus to raise our yields to 40% we must control and reduce charring. To raise them above 40%, we must reduce the yield of water solubles.

Two features of the Albany PDU operation makes us believe that charring is not an inherent problem. The most convincing is Rust Engineering's ability to run the direct-fired preheater on either water or oil slurries without serious coke-up problems. The second is the ability to operate a massive recycle of whole product during PERC operation without significant build-up of solids. In our CLU runs, charring may be partly a function of temperature, feed slurry pH and reducing gas composition. Coke formation has, however, been on the whole random and unpredictable. It seems to be more a function of the need to pour all the process heat through the wall of a small reactor and of operating upsets than of basic process variables. A possible relation to phase separation and resulting excess residence time of the oil phase, has already been referred to. We hope to be able to control coking at bench scale and believe it can be eliminated as a serious problem under turbulent plug flow conditions. But there is certainly work to be done.

Too much product ends up in aqueous solution. Not only does this detract from the oil yield, but it presents a recovery or disposal problem. In Table 3, we show a list of some of the compounds and compound types we find in the water. Either recovery or disposal will be a challenge. In the PERC, oil-recycle process, yields of water solubles have been much lower than in LBL water-slurry, once-through runs. Based on our own data and Rust Engineering's⁽⁶⁾, the following distributions will be obtained at a "medium" severity (product oil about 16% O).

TABLE 2

OIL PLUS CHAR RECOVERY VS. OVERALL MATERIAL BALANCE IN CLU

Experiment	Organics Accountability Output/Input, %	Oil Plus Char, Wt % of Organic Feed
CL-7	101	42
CL-8	93	32
CL-10	85	29
CL-11	97	37
CL-12	90	32
CL-13	99	40

TABLE 3

	Water slurry, one-pass (LBL)	Oil-slurry Recycle (PERC)
Oil (+ char if any)	40	53
Water solubles	25	8
CO ₂ , H ₂ O or O removed by reduction	35	39
CO use, mols/100 lbs wood*	0.1 \pm 0.1	0.47 \pm 0.1

* Excluding water gas shift.

Since the two processes are not generically different, it should be helpful to examine why the yield of water-solubles is so much higher in the single-pass, water slurry process. Several reasons can be postulated:

- (1) Since water as well as oil is recycled in PERC (the product carboxylic acids have been through the reactor about as many times as the product oil), a high percentage of soluble organics has decomposed.
- (2) Since the ratio of oil to water is high (two or three to one) in PERC and low (about 1 to 4) in LBL, a lower percentage of potential solubles winds up in water in the former case.
- (3) The prehydrolysis in LBL creates additional routes to water solubles.
- (4) There is a qualitative difference in the product spectrum because the first step in PERC is a solvolysis by recycled oil of the wood feed.

Neither (4) nor (3) can be major influences. The oil products seem to be much the same--in compound types, molecular weight distribution, etc.--and autoclave tests with water slurries made from hydrolyzed or unhydrolyzed wood show that yields of water solubles are high in both cases. However, most of the water-solubles are formed from the soluble products of hydrolysis, so that removing these before liquefaction could greatly reduce the yield. Also see below.

Hypothesis (1) is probably important in the reduction of yields of carboxylic acids. These are retained in the recycled water at the pH maintained, about 7. It is also probably important in reducing yields of the less volatile neutrals. In the PERC process, the more volatile neutrals are recovered in a vapor condensate, thus avoiding recycle.

Hypothesis (2) probably explains low yields of the more volatile neutrals and to some extent of the less volatile neutrals. Since the carboxylic acids generally exist as anions in the aqueous phase it seems unlikely to apply to them.

A forced recycle of water through the prehydrolysis step is not possible, since inordinate amounts of mineral acid and sodium carbonate would be required to acidify for hydrolysis and reneutralize for liquefaction. Presumably, some neutrals could be extracted by washing the aqueous effluent with product oil or a solvent. Since the concentration is only of the order of two percent this does not seem very practicable. Thus solving the water-solubles problem probably requires lowering the ratio of water to oil. This means maximizing the feed slurry concentration, at perhaps a little above 30%, or modifying the process in the direction of a modest recycle of product oil, well under the 19/1 ratio which has so far been necessary for mechanical operation of the PDU. Efforts in these directions are in progress.

Hypothesis (4) requires more consideration. Solvolysis of wood by alcohols and phenols has been studied extensively at LBL⁽¹¹⁾. It has been found, for example, that heating at 180-250°C with phenol and a small amount of mineral acid makes Douglas fir wood chips soluble in organic solvents like acetone. Product wood oil, which is phenolic, is an excellent solvent. It has been suggested, therefore, that solvolysis occurs in the preheat stages of the PERC process. It is also suggested^(11, 12) that solvolysis by a recycle oil could be a first step in an improved process, to be followed by an appropriate solvent regeneration step. Solvolysis, whether premeditated or inadvertent, could modify the product distribution quantitatively, though so far this has not been shown.

PRODUCT

The current product is a heavy, bitumen-like material, low in sulfur and nitrogen but containing much oxygen--15 to 19 wt % in the CLU single-pass runs and 7 to 18% in the PDU high recycle runs. The crude product, like SRC-1, can be pumped as a liquid. It has been shown to be an adequate substitute for number 6 fuel oil. It is partly distillable in a vacuum still and the distillate can replace distillate petroleum fuel oils⁽⁶⁾. The molecular weights are fairly high--in the range of vacuum gas oils (cf. fig. 5).

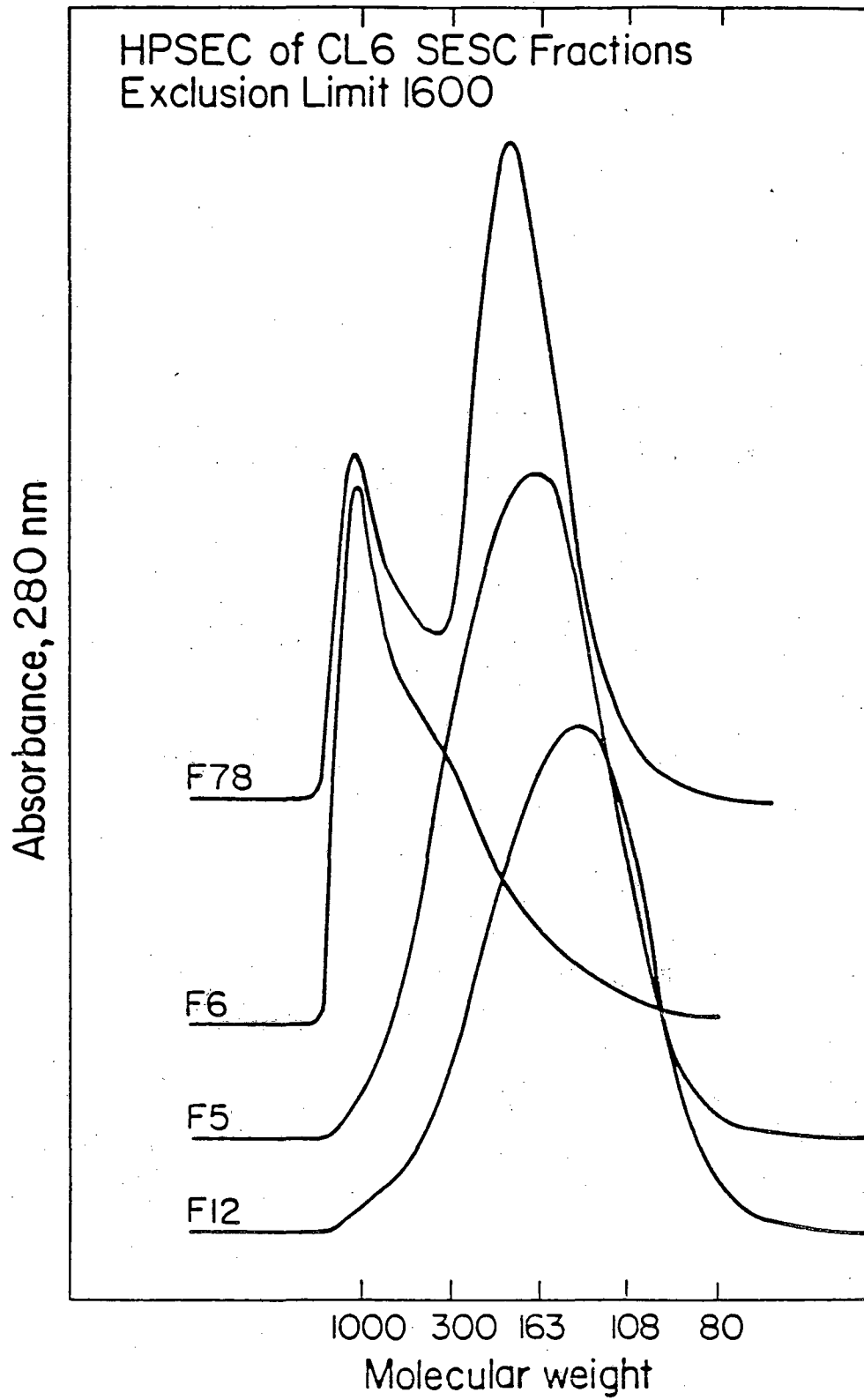
To learn something about the product, we use a variety of characterization techniques. GC-MS has been particularly useful in identifying the more volatile individual components of both oil and water-soluble fractions. The most volatile (and most abundant) carboxylic acids, formic, acetic and glycolic, have been measured most accurately by high performance liquid chromatography (HPLC) with an anion exchange column (fig. 6). Separations based on functionality and polarity have been made by solvent extraction techniques⁽¹³⁾. More recently we have used an adaptation of the column elution SESC technique of Farcasiu⁽¹⁴⁾, originally used for coal-derived oils, to fractionate the product oil. In Table 4 we summarize some of the information about components and component types which has been collected during the past year.

FUTURE WORK REQUIRED

It must be evident from the above that a lot of work remains to be done. We list here the major components of a short and long term program.

- (1) Immediate problems: reduction in the average amount of coking during runs and further demonstration that remaining coking is operational and specific; raising oil yield at the expense of water-solubles; solving operation problems related to oil and water phase separation; increasing feed slurry concentration.

FIGURE 5



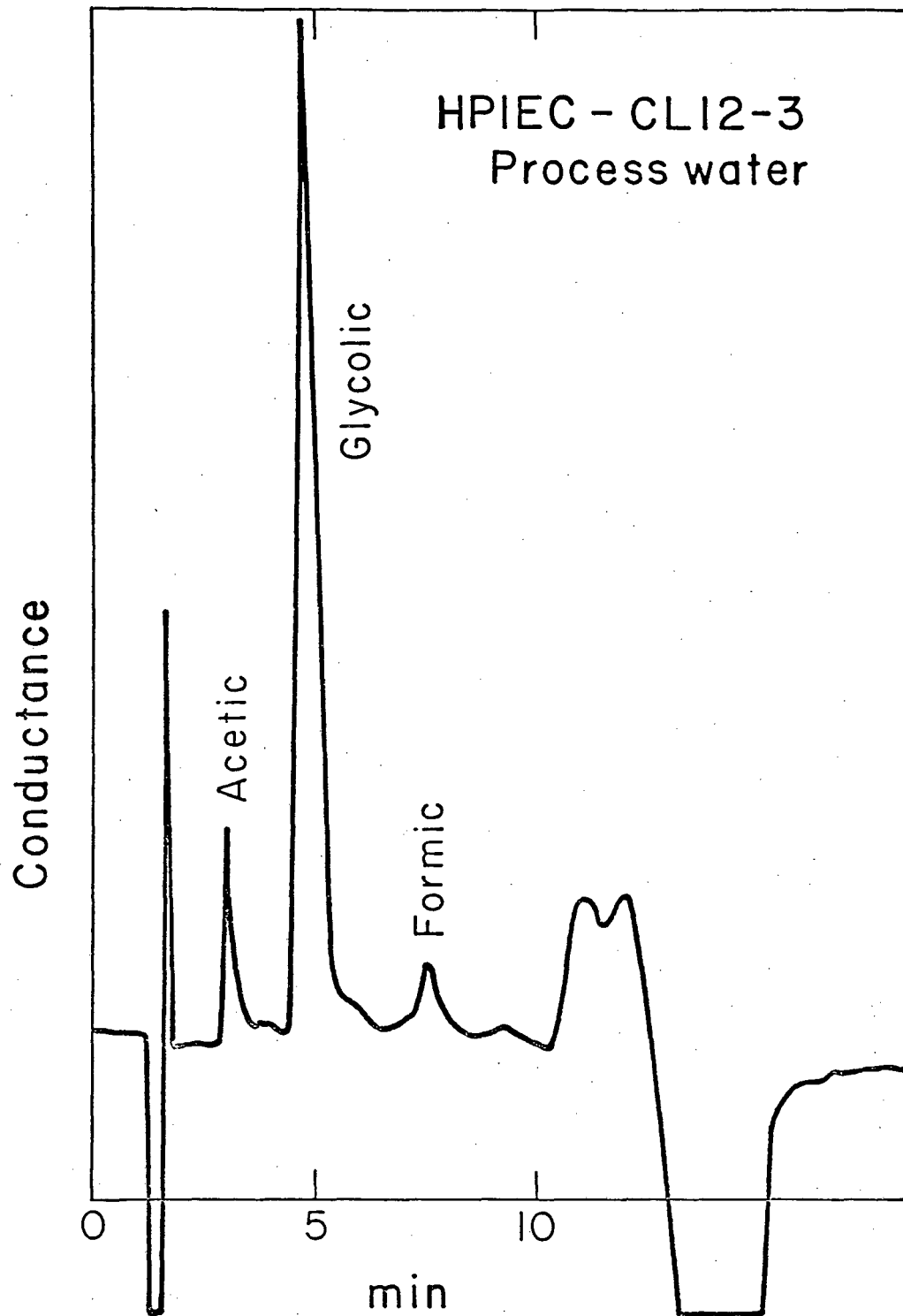


Fig. 6. High performance anion exchange chromatogram of aqueous effluent from run CL-12.

TABLE 4

COMPONENTS OF OIL AND WATER-SOLUBLE PRODUCT

A. Oil (Based on LBL Process Product from PDU, TR-7)

Component Type	Approximate Percentage in Oil	Approximate number of Components Identified
By Extraction:		
Low-molecular weight phenols (average MW about 200)	22	about 80
High molecular weight phenols (average MW about 700)	41	—
Neutrals (average weight about 250)	37	Over 20 (ketones, furans, hydrocarbons)

B. Water Solubles (Bases on LBL Process Product, CLU-11-4)

Compound or Type	Approximate Percentage of the total water soluble organics	Approximate number of Comounds Identified*
Formic acid	3	
Acetic acid	12	3
Glycolic acid	25	
C ₃ ⁺ Carboxylic acids	10	40
Neutrals and phenols	50	12 ketones 35 phenols

* Many of these compounds are polyfunctional: keto acids, diphenols, ketophenols, methoxyphenols etc.

- (2) Other feestocks: extension of effort to other fast-growing woods such as populus or eucalyptus species; to agriculture wastes such as sugar beet residues, rice straw, rye grass, coconut shells; to peats of various types; to energy plants like Jerusalem artichoke, euphorbia, etc.; to municipal wastes. Batch experimentation is currently underway.
- (3) Upgrading the product: hydrocracking the crude oil to obtain high-grade distillate fuels; recovering values from water-solubles and disposing of residues.
- (4) Modifying the process to make it more energy efficient, improve gross yield and quality. Possibilities: incorporate better features of both LBL and PERC processes; employ phenomenon of solvolysis; integrate with hydrolysis and alcohol production.

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