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# THE PRODUCTS OF DIRECT LIQUEFACTION OF BIOMASS

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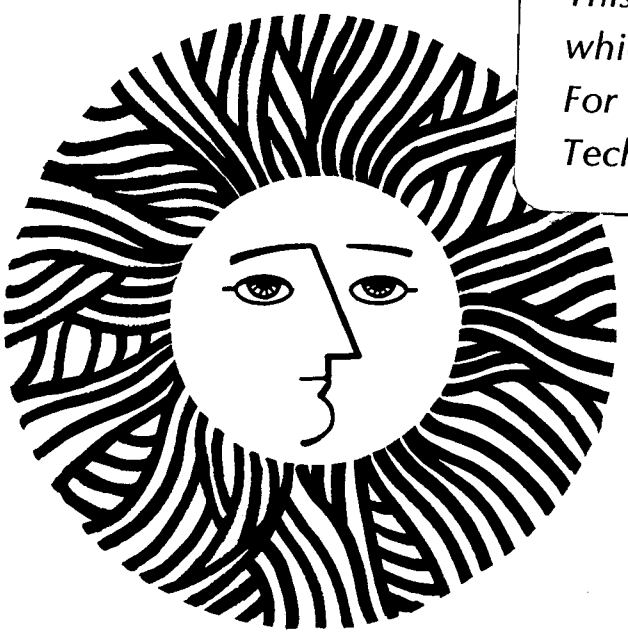

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# THE PRODUCTS OF DIRECT LIQUEFACTION OF BIOMASS


## ABSTRACT

In direct liquefaction of biomass a chemically complex mixture of aqueous and oil phases is produced. Many of the volatile constituents of these products have been identified by GC-MS in studies reported elsewhere. We have used GC-MS to further extend this list, but have also developed column chromatographic and HPLC separation techniques to provide a comprehensive means of characterizing the whole oil product. The major water-soluble carboxylic acids have been separated and quantified and molecular weight distributions for a large number of oil samples have been obtained by high performance size exclusion chromatography (HPSEC).

We have found the SESC column chromatography technique to be particularly useful for characterizing whole product oils and assessing the effects of process or of feedstock changes. Our procedure has followed, with only minor modifications, one originally applied to coal-derived liquids. We divide an oil sample into eight sequentially eluted fractions of increasing polarity. The fractions include hydrocarbons; non-acidic oxygenated organics plus highly hindered phenols; simple phenols; more polar phenols including diphenols, ketophenols, dimeric phenolics, and naphthols; polyphenols; and even more polar (or higher molecular weight) fractions. Helpful process or feedstock changes are those which reduce the amounts in the last five fractions and increase those in the first three. Helpful changes are shown to include increased temperature of liquefaction, catalytic hydrogenation and replacement of Douglas fir with aspen as feedstock.

For several reasons the existing CO-steam liquefaction processes are less than ideal. Concerns include low fresh feedstock concentration and the production of large amouts of water-dissolved organics, plus other problems peculiar to the particular process. Our current efforts to develop a new superior process are briefly reported on. The analytical and characterization techniques discussed are major tools in guiding the way toward a better process.

# THE PRODUCTS OF DIRECT LIQUEFACTION OF BIOMASS

## 1. INTRODUCTION

Wood is converted to a dense liquid fuel by thermal treatment at 300-360°C under a pressure of water and reducing gas in the presence of aqueous alkali. The product includes both an oil phase and an aqueous phase rich in dissolved organics. Previous work [1] showed that the oil phase has little in common with petroleum fuels, and the standard methods of petroleum chemistry are therefore largely inapplicable. Thus there existed a need for new methods for the fractionation of biomass oils into constituent chemical classes for the purpose of assessing comparative product quality and evaluating the best end uses and upgrading options.

Three general approaches to the problem of the chemistry of wood oil include solvent extraction, gas chromatography-mass spectroscopy (GC-MS), and adsorption chromatography. Solvent extraction schemes are in common use in the characterization of synfuels including those derived from biomass. The "oil" fraction of coal fluids is typically defined, for example, as that portion extractable into pentane [2]. By this definition, there is no "oil" in wood oil since the solubility of wood-derived fuels in pentane is virtually nil. Thus wood oil is more commonly taken as the acetone, chloroform or benzene-soluble product, and would, in the parlance of coal fluid chemistry, be classified as a mixture of asphaltenes and preasphaltenes.

An approach based on a combination of both solubility and acid-base properties of biomass oils is somewhat more useful. For example, a major part of wood oil can be extracted from chloroform into aqueous sodium hydroxide but not bicarbonate,

revealing the predominantly phenolic character of these materials. In practice, however, extraction techniques have proved to be of limited utility. They are time consuming and irreproducible owing to opacity of the two phases, difficulties with emulsions and incompleteness of extractability of high molecular weight phenolics into aqueous caustic.

A good deal of information regarding the structural characteristics has been obtained by GC-MS [3,4]. The major components include methoxyphenols, cyclopentenones, cycloalkanones, alkylphenols, dihydroxybenzenes and methylnaphthols [3]. Many of these types of compounds are also found in the aqueous phase along with C1-C6 carboxylic and dicarboxylic acids [4,5]. However, these identifications pertain only to the 20% or so of the constituents of wood oil that have yielded to GC-MS analysis. Further progress along these lines will be difficult for two reasons. First, even with the high resolution afforded by capillary GC, there is the general problem of overlapping peaks that plagues analysis of extremely complex mixtures. Elliott has observed as many as 360 distinct peaks in a typical wood oil sample [3]. The second limitation is that 30% or more of wood oil is usually too involatile to be detectable by GC. Although pyrolysis GC might find application in this connection [6], this technique has as yet not yielded significant information about wood oils.

There seemed to be a need, therefore, for an approach that would fill the gaps left by GC-MS for the characterization of whole biomass oils. The ideal method would be fairly simple, rapid, reproducible, and capable of separating these materials into classes according to chemical functionality. Adsorption chromatography, although widely used in other branches of fuel chemistry, had

not been applied to this problem and so seemed a logical starting point. Farcasiu [7] had already developed SESC (Sequential Elution by Solvents-Chromatography) for separating coal fluids into distinct chemical classes. The method seemed even better suited for the separation of biomass oils which, unlike coal products have no nitrogenous fraction to deal with. We therefore chose SESC as the basis for the development of such a method.

## 2. RESULTS AND DISCUSSION

### 2.1 Method Development

The original SESC technique required only slight modification for the purpose at hand. Since wood oil is virtually devoid of aliphatic hydrocarbons, the first step, elution with hexane, was omitted. Whatever amount of this fraction, F1, does exist is eluted along with the aromatic hydrocarbons by 15% benzene-hexane in the present technique. This hydrocarbon fraction is designated F1,2. Also, we have found acetic acid to be superior to pyridine for removing the last wood oil residues from the column. The complete sequence of solvents is shown in Table 1.

A further improvement was the use of the low pressure preparative liquid or "flash" chromatographic technique [8,9], which employs small, irregularly-shaped particles of silica gel (40 μm) and low positive pressures (20 psig) to afford speedier analysis and improved resolution with reduced consumption of solvent.

One sample of wood oil, TR-7, produced from Douglas fir at DOE's Albany, Oregon liquefaction test facility by LBL's water-based process, was fractionated four times including once with an anhydrous sample, in order to check repeatability

and the effect of water. The presence of 8% of water in the sample did not alter the results (Table 1).

Table 1.

SESC FRACTIONATION OF TR-7 OIL

| Fraction | Solvent | Amount (%) | Std. Dev. |
|---|---|---|---|
| F1,2 | 15% Benzene-Hexanes | 3.5 | ± 0.4 |
| F3 | Chloroform | 16.8 | ± 2.3 |
| F4 | 6% Ether-Chloroform | 44.1 | ± 3.7 |
| F5 | 4% Ethanol-Ether | 21.1 | ± 3.0 |
| F6 | Methanol | 6.5 | ± 1.3 |
| F7 | 4% Ethanol-$CHCl_3$ | 1.0 | ± 0.4 |
| F8 | 4% EtOH-THF | 2.5 | ± 1.7 |
| F9 | HOAc | 4.2 | ± 0.6 |

## 2.2 Characterization of SESC Fractions

Several dozen biomass-derived oil samples have now been subjected to SESC as modified for wood oil. Information regarding the chemistry of various fractions has been provided by gel permeation chromatography (GPC) for molecular weight distributions, GC-MS for specific compound identification, infrared spectroscopy, elemental analysis and solubility classification.

In Table 2 we show the ranges of the percentages found in each fraction of the oils tested, typical average molecular weights, the typical percentage of oxygen in the fraction and an average molecular formula.

TABLE 2.

CHARACTERIZATION OF WOOD OIL SESC FRACTIONS

| Fraction | Wt % | $\bar{M}_n$ [a] | $\bar{M}_w$ [b] | % O | Average Molecular Formula |
|---|---|---|---|---|---|
| 1,2 | 0-6 | 140 | 160 | 5 | $C_{11}H_{14}O_{0.5}$ |
| 3 | 1-20 | 170 | 210 | 11 | $C_{13}H_{15}O_{1.3}$ |
| 4 | 5-45 | 170 | 210 | 16 | $C_{12}H_{14}O_2$ |
| 5 | 5-55 | 210 | 290 | 21 | $C_{15}H_{16.5}O_{3.3}$ |
| 6 | 5-35 | 350 | 600 | 23 | $C_{30}H_{30}O_7$ |
| 7 | 1-3 | 180 | 210 | 46 | -- |
| 8 | 2-20 | 690 | 900 | -- | -- |
| 9 | 0-10 | -- | -- | -- | -- |

[a] Number-average molecular weight. [b] Weight-average molecular weight.

Molecular weight distributions of fractions and whole oil samples were obtained by gel permeation chromatography. The predominant band in the infrared spectra of most fractions was that due to hydroxyl stretching, except that this band is absent in F1,2 and weak in F3. Other bands included the carbonyl stretching band (F3-F6 and F8) and those characteristic of the aromatic ring.

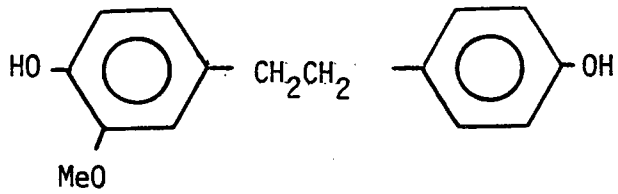
Fractions 1-5 are liquid while 6,8 and 9 are solid. Fraction 7, always minor, is usually solid. Capillary gas chromatography indicates that the distillable components reside exclusively in fractions 1-5 with the suggestion that F5 also contains less volatile matter. Fractions 4-6 dissolve rapidly and almost completely in 5% aqueous sodium hydroxide.

Fraction 1,2 contains aromatic hydrocarbons. GC-MS analysis of one F1,2 sample gave the following tentative identifications: alkylated benzene derivatives ($C_8H_{10}$, $C_9H_{12}$, $C_{10}H_{14}$, and $C_{11}H_{16}$ species); substituted indanes or alkenylbenzenes ($C_9H_{10}$, $C_{10}H_{12}$ and $C_{11}H_{14}$); 2-methylnaphthalene, biphenyl and a tetramethylphenanthrene isomer.

According to Farcasiu [7], the constituents of F3 include nonhydroxylic polar aromatics and oxygen heterocycles. Anisole, a variety of cycloalkanones, a butyrophenone (1-(p-methoxyphenyl)-1-butanone) and a hindered phenol (2,4,6-trimethylphenol) were found by GC-MS in this study. Standards were used to show that anisole, guaiacol and eugenol also elute with F3.

The present work reinforces the conclusion that F4 consists largely of monophenols [7]. Phenol and 5-indanol elute cleanly with 6% ether-chloroform. Further studies with model compounds are in progress.

Fractions 5 and 6 are also phenolic in nature as evidenced by solubility in aqueous caustic, infrared spectra and elemental analyses. It appears from TLC data [7] that 1-naphthol, 2,3-naphthalenediol, salicylic acid and chrysin, $C_{15}H_8O_2(OH)_2$, would be found in F5. We find that 3,4-bis( p-hydroxyphenyl)-3,4-hexanediol appears in F5. The average molecular formula can be fairly represented by the structure,




a fragment conceivably derivable from softwood lignin. Although there is probably considerable overlap between F4 and F5, it can be inferred that monophenols prevail in the former and phenolic dimers (e.g., bis-phenols) in the latter.

Methanol marks the approximate line between asphaltenes (benzene-soluble pentane insolubles) and preasphaltenes in SESC. The sixth fraction elutes sharply as a dark brown band with little or no contamination by the tail end of F5. This material is involatile, highly polar and phenolic in nature. The major components of SRC-derived F6 have been termed "highly functional molecules" having greater than 10 wt % heteroatoms. In the case of wood oil, F6 would seem to be polyphenolic material, perhaps partially degraded lignin.

## 2.3 SESC Profiles of Wood Oils

SESC profiles of eight biomass oils are shown in Table 3. These runs are described in Table 4, along with additional product information. The oils identified as TR-7, TR-10 and TR-12 were produced at the U.S. Department of Energy's (DOE) process development unit at Albany, Oregon. TR-7 and TR-10 were made by a process developed at LBL in which wood chips are prehydolyzed under mildly acidic conditions, neutralized, mechanically refined and introduced into a one-pass reactor system as a 15-25% slurry of soluble and insoluble wood solids in water [10, 11]. TR-12 oil was the product of a process developed from the original work at the Bureau of Mines' Pittsburgh Energy Research Center in the late 1960s — early 1970s [12]. This is a recycle process which introduces a slurry of wood flour in anthracene oil in the presence of aqueous sodium carbonate. Over a number of cycles the anthracene oil used for start-up is replaced by wood oil. The TR-12 used in the present study was judged to be 99% wood-derived [13].

TABLE 3.

SESC PROFILES OF SELECTED WOOD OILS

| Fraction | Oil: | TR-7 | TR-10 | TR-12 | CL-8 | CL-10 | CL-11B | CL-12B | CL-21[a] |
|---|---|---|---|---|---|---|---|---|---|
| 1,2 | | 4 | 1 | 4 | 1 | 3 | 4 | 3 | 5 |
| 3 | | 17 | 7 | 14 | 3 | 18 | 16 | 15 | 15 |
| 4 | | 44 | 19 | 14 | 6 | 8 | 20 | 25 | 40 |
| 5 | | 21 | 40 | 38 | 44 | 50 | 41 | 39 | 20 |
| 6 | | 6 | 21 | 18 | 31 | 14 | 12 | 12 | 13 |
| 7,8,9 | | 8 | 11 | 12 | 15 | 6 | 7 | 5 | 7 |
| 1-4 | | 65 | 27 | 32 | 10 | 29 | 40 | 43 | 60 |
| 4-6 | | 71 | 80 | 70 | 81 | 72 | 73 | 76 | 73 |

[a] From aspen. All others were from Douglas fir.

TABLE 4.

OPERATING CONDITIONS AND ANALYTICAL RESULTS FOR SELECTED RUNS[a]

| | TR-7 | TR-10 | TR-12[b] | CL-8 | CL-10 | CL-11B | CL-12B | CL-21 |
|---|---|---|---|---|---|---|---|---|
| Temperature°C | ∿350 | ∿350 | 330 | 330 | 350 | 360 | 360 | 350 |
| Steady-state yield, % | ∿25 | ∿26 | 53 | 40 | 39 | 41 | 32 | 43 |
| Reducing gas | H/CO | H/CO | H/CO | H/CO | CO | CO | H | H |
| Residence time, hrs. | 5 | -- | 0.3 | 0.4 | 0.35 | 0.3 | 0.3 | 0.3 |
| % Oxygen | 14 | 17 | 13 | 18.5 | 16 | 16 | 16 | 13.5 |
| $\overline{M}_n$ | 220 | 290 | 240 | 280 | 270 | 250 | 250 | 180 |
| $\overline{M}_w$ | 310 | 470 | 370 | 360 | 340 | 340 | 340 | 270 |

[a] Data for TR runs taken from ref. 13.

[b] PERC mode. All other runs were done by the LBL process.

The CL oils were produced in a 2 kg $hr^{-1}$ continuous liquefaction unit (CLU) designed, built and operated at LBL [14]. They were made by the LBL process using 18% to 20% aqueous slurries of prehydrolyzed wood. Except for CL-21 fro aspen (Populus tremuloides), all of the oils of Table 3 were derived from Douglas fir.

## 2.4 Quality of Wood Oils

Desirable process goals for biomass liquefaction can now be cast in terms of these SESC profiles of oil quality. From the standpoint of fuel quality the ideal wood oil would consist entirely of fractions 1-3. However, from the results shown in Table 4 (4 to 21% in F1-F3) this appears to be unrealistic

within the context of the current generation of liquefaction processes. A more practical process goal would be to maximize phenolic monomers (F4) at the expense of F5 and F6. Although a reliable index of reaction severity is not available, this does appear to be the most significant factor affecting the proportion of F1-4 in the case of Douglas fir. The effect of reaction severity is most evident in comparisons of TR-7 (65%) with TR-10 (27%), and of CL-8 (10%) with CL-10, 11B or 12B (29-43%). In general it appears that the CLU oils are somewhat underreacted. This is probably due to the fact that residence times in the CLU were of the order of 20 min, a constraint imposed by the operating characteristics of the system and the lack of oil recycle.

Several additional points about oil quality may be noted. We reported previously that the nature of the reducing gas did not appear to affect the course of biomass liquefaction, at least not under the conditions employed in runs CL-10 and 11 [1]. Although work by others suggests the possibility of a unique role for carbon monoxide as a reducing agent, perhaps acting by the putative formate ion mechanism [12, 15, 16], the results of CLU operation suggest that wood liquefaction is largely thermal in nature and that whatever advantages are to be gained by using carbon monoxide over hydrogen are minor at best.

SESC also provides a very approximate measure of total phenolics in the sum of fractions 4-6. These totals vary from 70-81% for the oils listed in Table 3. If an average steady state oil yield of 40% for CLU runs 8, 10, 11 and 12 is assumed, then the yields of phenolics based on dry wood are 32, 29, 29 and 30%, respectively. These numbers compare closely with the lignin content of Douglas fir, 28%. It would be erroneous, however, to assume that

lignin is the exclusive source of phenolic material. In the first place, the liquefaction of pure cellulose also gives rise to considerable phenolic product [17]. Second, the aqueous phase of wood liquefaction by the LBL process also contains significant quantities of substances that probably originate with lignin [18]. These include dihydroxybenzenes such as 4-methylcatechol and hydroxyalkyl derivatives of guaiacol such as vanillyl alcohol. Finally, we have seen that certain hindered phenols and simple guaiacols populate F3 rather than F4.

## 2.5 Effect of Feedstock

The results of CL-21 underscore the importance of choice of feedstock. Under conditions of comparable reaction severity, aspen gives rise to a product of quality superior to that from Douglas fir and in slightly higher yield. The total phenolics amount to 31% based on dry feedstock. This compares to a lignin content of approximately 17-18%. That aspen is more reactive than coniferous woods is well established in other technologies. A variety of additional biomass feedstocks are under examination as candidates for liquefaction in these laboratories [19].

## 2.6 Product Upgrading by Catalytic Hydrogenation

Catalytic hydrogenation offers a promising option for upgrading biomass oils. In one experiment SESC was used to evaluate the effectiveness of copper chromite catalyst. Neat, anhydrous TR-7 oil slurried with finely divided catalyst (2%) was reacted for 50 min at 400°C under a hydrogen pressure of 2000 psig in a stirred autoclave. The product was subjected to SESC with the following results (dry TR-7 oil basis):

| Fraction: | F1,2 | F3 | F4 | F5 | F6 | F7-9 |
|---|---|---|---|---|---|---|
| Wt %: | 7 | 22 | 47 | 4 | 1 | 8 |

It appears that catalytic hydrogenation was very effective in the depolymerization of higher molecular weight phenols and that monophenol was converted to less polar materials. Further studies with model substances are in progress.

In the temperature range of 180-240°C or higher, biomass samples react with recycled oil product to form a homogeneous solution or mixture [20]. This is a specific form of solvolysis [21]. The crude solvolytic product must be further treated to recover the recycle oil and net product (about 50% by weight of the dry biomass feed). Experiments such as the above with TR-7 and preliminary experiments with solvolytic products indicate that catalytic hydrogenation is the most promising way to effect this.

From the average molecular weights given in Table 2 we can estimate the boiling ranges of SESC fractions 1 to 5. Very approximately these are the following:

| Fraction | Approximate boiling range, °C at 1 atm. |
|---|---|
| 1,2 | 120 - 260 |
| 3 | 120 - 300 |
| 4 | 170 - 360 |
| 5 | 260 - 430 |

When we consider that low boilers (< ~120°C) are inevitably lost in the oil sample recovery and/or the SESC work up, it is clear that oils with 20% or more in SESC fractions 1-3 and 50% or more in fractions 1-4 should be easily distillable at atmospheric pressure to give over 20% volatiles. This is all that is necessary to provide the right proportion of net product and recycle vehicle.

## 2.7 SUMMARY

Several methods of characterizing products of biomass liquefaction including GC-MS, wet analysis, infrared and various forms of liquid chromatography have been tried. Of these the SESC sequential elution technique has been particularly helpful in separating whole product oils into chemically distinguishable fractions.

Variations in the distribution of SESC fractions have been used to show effects of changing conditions and changing feedstocks in biomass liquefaction. They have also been used to follow the effects of catalytic hydrogenation.

Liquefaction of aspen results in higher yields than liquefaction of Douglas fir. The aspen oil product is richer in SESC fractions 1-4, is more fluid and has lower oxygen content.

Catalytic hydrogenation is effective in increasing the percentage of oil in the more volatile SESC fractions 1-4. It appears to be the key to successful development of an oil recycle solvolysis process.

## 3. EXPERIMENTAL

"Flash" chromatography employed commercially available "silica gel for flash chromatography", and columns and fittings. Generally the ratio of sample to adsorbent was 1:40. Sample was preadsorbed onto silica gel by rotary evaporation of a solution of wood oil in methylene chloride; the resulting semisolid was then quantitatively transferred to the top of a column packed with the aid of hexane. Solvents were reagent grade or, in the case of chloroform, ether and tetrahydrofuran, unstabilized HPLC grade.

After elution of each fraction, solvent was removed by rotary evaporation at water pump pressure and 50-60°C, and the weight of the residue was determined. Typical recoveries were in the range of 100-115%, probably owing to the impossibility of completely removing solvent. The SESC results reported in Table 3 are normalized to 100%. With a few samples from runs at low severity we had significantly less than 100% recovery.

Gel permeation chromatography employed two columns in series packed with 200-400 mesh styrene-divinylbenzene copolymer beads with 8% and 12% crosslinkage [22]. The solvent was tetrahydrofuran. Molecular weight calibration curves were constructed using a series of 12 polystyrene and phenolic standards. The high molecular weight exclusion limit was 700-800 daltons. The calibration was checked frequently with nordihydroguaiaretic acid (mass 302) or phenolphthalein (318). The solvent, tetrahydrofuran, was pumped at 1.2 ml $min^{-1}$ with UV detection at 254 or 280 nm. Generally little or no elutable material having molecular weights above the exclusion limit of the system was observed. Molecular weight calculations were performed with the aid of commercially available computer software.

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