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GAS CHROMOTOGRAPHIC ANALYSES OF BIOCRUDE-PRODUCING TREES

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ABSTRACT

Gas chromotographic procedures were used to compare commercial diesel fuel with cyclohexane, ether, and methanol extracts from various tree species. Standard n-paraffin hydrocarbons ranging from C-10 thru C-34 were used as standards. These analyses indicated that several extracts, notably those from *Juniper virginiana* (juniper) and *Pinus echinata* (pine) trees of Northeast Arkansas and the Brazilian tree *Copaifera langsdorffii* (copaiba), contain numerous hydrocarbon and selected chemical products which serve as potential renewable biocrude sources.

INTRODUCTION

Photosynthetic plants produce extractable chemicals called biocrude which can be used directly as petroleum-like chemicals (Buchanan et al., 1978a; Buchanan et al., 1978b; Calvin, 1977, 1979; Buchanan et al., 1980; Wang and Huffman, 1981; McLaughlin and Hoffmann, 1982; Campbell, 1983). Biocrude is the hydrocarbon and hydrocarbon-like chemical fraction of plants which may be extracted by organic solvents and upgraded to liquid fuels and chemical feedstocks (McLaughlin and Hoffmann, 1982). Feedstocks are mixtures of materials, derived from the source by physical and/or chemical means, whose composition is controlled to make specific primary chemicals or fuels (Lipinsky, 1981). Extractable biocrude may contain waxes, terpenoids, resins, phytosterols, latex, terpenes, fats, fatty acids, polyphenolics, phlobaphenes, oils, and tannins (McLaughlin and Hoffmann, 1982).

Since many of the plant extractives that could serve as potential liquid fuels have high carbon numbers and are not combustible at low temperatures, these fuel stocks could be subjected to catalytic cracking (Wang and Huffman, 1981). Major plant substances that could be catalytically converted are terpenoids, phenolics (flavonoids, phenols, and polyphenols) and long chain aliphatics (waxes, triglycerides, fatty acids) (Adams and McChesney, 1983). Weisz et al. (1979) studied the mechanism for the conversion of plant extracts rich in hydrocarbons and/or hydrocarbon-like compounds into low molecular weight fuels. They found that Mobil's zeolite catalyst could catalyze molecules such as latex and oils into products comparable to fuel gas. In all cases studies, there was a high degree of conversion into benzene (C-6), toluene (C-7), xylenes (C-8), and other aromatics. Although they could convert various plant materials into high grade liquid fuel, the economic feasibility of the process was a concern, that was yet to be determined.

Much of the current interest in biocrude research seems to be focused on identifying the best biocrude producing plants and determining economic feasibilities. Buchanan et al. (1980) and Adams (1982) suggested that agricultural production of hydrocarbons would be economically feasible only if the entire plant were harvested and processed. This concept would involve the development of multi-use crops (biocrude, fiber, food) with the final choice of multi-use plant species dependent upon survival, growth rate, ease of obtaining biocrude, productivity, and the quality and quantity of extractibles. Species should also be evaluated on the need for fertilizer, especially nitrogen.

Bassham (1977) and Calvin (1979) have suggested the development of biocrude farms or plantations. Calvin (1979) further suggested developing these farms in the arid Southwest. This would put to cultivation immense areas of unused land unsuitable for conventional crops. Johnson and Hinman (1980) recommended development of marginal lands for biocrude farming because they would not compete with food and fiber crops. Calvin (1979) identified members of the genus *Euphorbia* and the genus *Asclepias* as the best hydrocarbon crops for these and southwestern lands, especially *Euphorbia lathyris*. Here, entire plants would be harvested and processed.

This preliminary study utilized gas chromatographic analyses to identify trees having potential for biocrude production. Economic feasibility of biocrude production was not considered.

MATERIALS AND METHODS

Copaifera langsdorffii Desf. seeds were obtained from Brazil and grown in a greenhouse. All other experimental species were collected from their natural habitat in Northeast Arkansas. Samples consisting of young stems without leaves were collected from *Asimina triloba* L. Dunal (pawpaw), *C. langsdorffii* (copaiba), *Gleditsia tricanthos* L. (thorn), *Juniper virginiana* L. (juniper or eastern red cedar), *Pinus echinata* Mill. (short leaf pine), *Rhus copallina* var. Latifolia (dwarf sumac) and *Sassafras albidum* (Nutt.) Nees. (sassafras). The samples were oven dried and ground before weighing.

Tissue samples were extracted with ether overnight (Fig. 1A). Pigments and polar materials were removed with Darco G-60 activated charcoal. Internal standard was added before the extracts were dried under nitrogen. Separate stem tissue samples were extracted in a Soxhlet extractor for approximately 12 hours with 150 ml of cyclohexane (Fig. 1B). The cyclohexane extract was transferred to a rotary evaporator to remove excess cyclohexane. The ground stem tissue, which had been extracted with cyclohexane, was then extracted with methanol as previously described for the cyclohexane extraction (Fig. 1B). Internal standard was added to the cyclohexane and methanol extract before drying. The dried extracts obtained with ether, cyclohexane, and methanol solvents were stored dry at -10°C in vials covered with teflon tape. Each extract was redissolved in one ml of ether before a 4µl sample was injected into the chromatograph. A second chromatographic analysis was run with the methanol extract redissolved in 87.5% methanol.

Gas chromatography of extracts was performed using a Perkin-Elmer Model 3920 B chromatograph with dual flame ionization detectors (F.I.D.). The chromatograph was equipped with a 6 ft × 0.085 I.D. stainless steel column packed with 5% silicone SE 30 on 100/120 chromosorb WHP (Alltech Associates, Inc.), The chromatograph was programmed for an injection temperature of 190°C with an initial temperature of 125°C (8 min) changing at a rate of 8°C/min with a final temperature of 290°C (32 min) and a nitrogen flow rate of 8 ml/min. The chromatograph was attached to a Varian Vista 401 data system which collected, analyzed, and stored all data.

Standard n-paraffin hydrocarbons (Alltech Associates, Inc.) ranging from C-10 to C-34 were used for preliminary identification and quantification of extracts. N-triacontane (C-30) was the internal standard

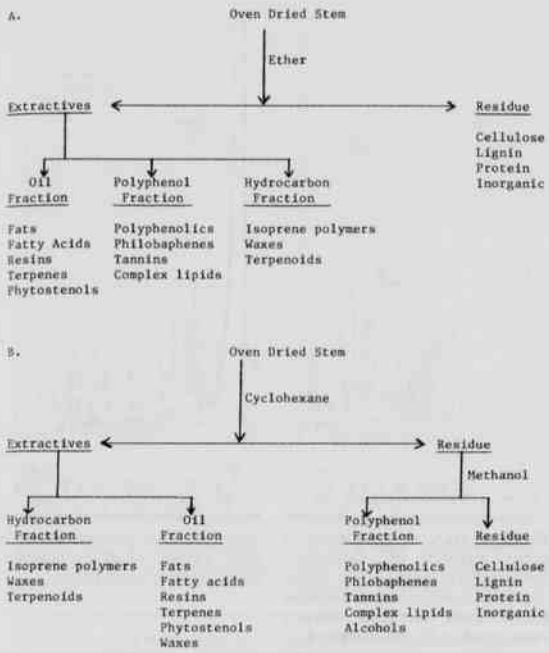

Figure 1. Scheme for extracting stem components (A. modification of the scheme presented by Buchanan et al., 1979; B. Buchanan et al., 1979).

(0.186 mg/ml) added to all extracts and was the basis for determination of correction factors for all other n-paraffins (Table 1). Final data was corrected to mg of extract detected by F.I.D. per gm dry weight of stem tissue. The chromatograph was calibrated each day to update the retention times for the n-paraffin standards. Typical retention times for the standards are shown in Fig. 2. These retention times and their corresponding n-paraffin standards were recorded as references in the chromatograms of each sample.

RESULTS

The commercial diesel fuel samples contained a wide variety of components (Fig. 3). Several components had retention times comparable to those of the small n-paraffin standards (Fig. 2). The copaiba tree ether extracts were similar to the diesel fuel in the numerous components were present. These extracts, however, had a greater proportion of larger molecules and no components were indicated with retention times less than the C-14 n-paraffin standard (Fig. 4). Ether extracts of the sumac and thorn tissues contained relatively few components, all in meager amounts (Figs. 5, 6). Additional analyses indicated that the most abundant component in the thorn extract eluted between the C-28 and C-30 n-paraffins (Fig. 7). The retention times of the components in the pawpaw and shortleaf pine ether extracts indicated the presence of medium to large molecules in relatively abundant amounts (Figs. 8, 9). In contrast, sassafras ether extracts contained small amounts of many small nonpolar molecules and conspicuously large quantities of two large components (Fig. 10). Juniper ether extracts were exceptionally abundant in a wide range of molecules as evidenced by retention times ranging from less than five min to more than 40 min (Fig. 11).

All the cyclohexane extracts of the various tree tissues were similar in that each extract contained several minor components and only one

Table 1. n-Paraffin Standards

Peak Number	Retention Time	Carbon Number	n-Paraffin	Correction Factor[a]	Amount (mg/ml)
1	2.76	*C10	Decane	2.67675	0.190
2	4.18	*C11	Hendecane	1.47443	0.230
3	6.61	*C12	Dodecane	1.45125	0.240
4	10.26	*C13	Tridecane	1.29877	0.246
5	13.02	*C14	Tetradecane	1.26864	0.254
6	15.24	*C15	Pentadecane	1.34584	0.176
7	17.01	*C16	Hexadecane	1.18011	0.192
8	18.58	*C17	Heptadecane	1.20771	0.184
9	19.97	*C18	Octadecane	1.15569	0.244
10	21.29	*C19	Nonadecane	1.04052	0.226
11	22.51	*C20	Eicosane	1.05701	0.228
12	23.65	*C21	Hereicosane	1.08329	0.384
13	24.78	*C22	Docosane	1.05617	0.204
14	25.83	*C23	Tricosane	1.08899	0.204
15	26.84	*C24	Tetracosane	1.08337	0.168
16	27.80	*C25	Pentacosane	1.04970	0.238
17	28.74	*C26	Hexacosane	0.99540	0.196
18	30.77	*C28	Octacosane	1.10684	0.250
19	33.56	*C30	Triacontane	1.00000	0.186
20	37.64	*C32	Dotriacontane	1.10721	0.268
21	43.77	*C34	Tetratriacontane	1.25787	0.202

[a]n-paraffin correction factors were calculated on the basis of C-30 which was assigned a value of 1.00.

major component. The retention time for the major component was similar to n-paraffin C-24. The shortleaf pine and sassafras extracts also contained minor components that eluted after the internal standard (Figs. 12-17).

The dried methanol extracts were gummy residues only slightly soluble in ether or methanol. However, the extracts were almost completely soluble in warm 87.5% methanol. The GLC chromatograms of extracts redissolved in ether showed internal standard (C-30) peaks whereas the chromatograms of extracts redissolved in 87.5% methanol did not. The thorn methanol extracts were low in biocrude materials (Figs. 18, 19). The methanol extracts of pawpaw, sumac, pine, sassafras, and juniper tissues contained much biocrude materials. Of these, the juniper extracts should be noted for their relatively high quantities of biocrude substances and the sassafras extracts noted for their abundance of low molecular weight biocrude components (Figs. 20-29).

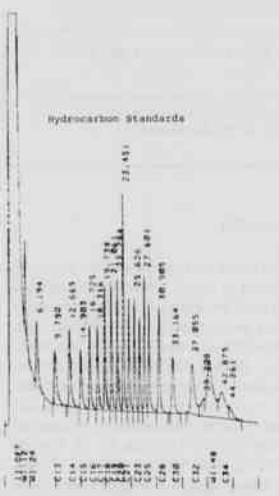

Figure 2. GLC chromatogram of n-paraffin hydrocarbon standards.

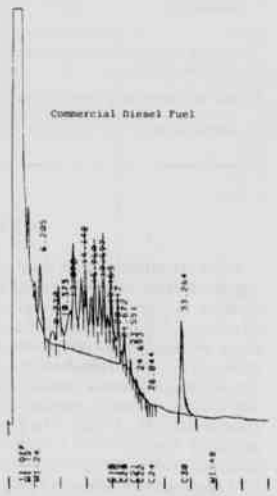

Figure 3. GLC chromatogram of commercial diesel fuel.

Solvent extraction yields for the species analyzed are given in Table 2. The highest yield by ether extraction of oven dried stem tissue was obtained from eastern red cedar. Copaiba was a distance second followed in decreasing order by pine, pawpaw, sassafras, sumac, and thorn.

Copaiba was not extracted in cyclohexane-methanol. Sassafras gave the highest yield in cyclohexane. Sumac gave unexpected high cyclohexane yields equal to red cedar followed by pawpaw. Pine, a species known to be high in resin, gave a lower cyclohexane yield than expected. Thorn, again, gave the lowest cyclohexane extraction yields.

Soxhlet extractions yielded higher extraction concentrations with methanol than cyclohexane in all species studied. This was consistent with data reported by Erdman and Erdman (1981) and McLaughlin and Hoffmann (1982). GLC chromatograms of methanol extractives redissolved in ether indicate much lower yields than when these extracts are redissolved in 87.5% methanol/water. This is probably due to the high concentration of polar compounds in this fraction with low ether solubility. Eastern red cedar (juniper) again yielded the greatest quantity of extractives followed in decreasing order by sumac, pine, pawpaw, sassafras, and thorn.

Table 2. Summary of biocrude extracts[a,b]

Species	Ether extract	Soxhlet Extraction: cyclohexane	Soxhlet Extraction: methanol: ether	Soxhlet Extraction: methanol: 87.5% methanol
Asimina triloba (pawpaw)	1.14	0.15	0.4	6.45
Copaifera langsdorffii (copaiba)	2.40	--	--	--
Gleditsia tricanthos (thorn)	0.12	0.08	0.17	0.12
Juniper virginiana (juniper, eastern red cedar)	6.33	0.18	1.25	21.42
Pinus echinata (short leaf pine	1.80	0.09	0.56	7.78
Rhus copallina (dwarf sumac)	0.31	0.18	0.42	8.25
Sassafras albidum (sassafras)	0.87	0.22	0.17	4.87

[a] Reported as mg of extract detected by F.I.D. per gram day weight of stem tissue.

[b] Ether extracts were redissolved in ether; cyclohexane soxhlet extracts were redissolved in ether; and, methanol soxhlet extracts were redissolved in ether or 87.5% methanol.

DISCUSSION

Ether extraction of oven dried stem tissue was performed by suspending dried tissue overnight (12-15 hours) at room temperature without shaking. Soxhlet extraction was not used because of the high volatility of ether. F.I.D. analyses of the ether extract gave higher values than those obtained with cyclohexane possibly due to the higher solubility parameter of ether (Buchanan et al., 1978b) which permitted extraction of the polyphenolic fraction. The cyclohexane extraction of sassafras was the only exception possibly due to the high oil content of sassafras (Buchanan et al., 1978a). The higher cyclohexane-nethanol extraction probably resulted from a high polyphenolic fraction in all species analyzed which is consistent with data reported by Adams (1982), McLaughlin and Hoffmann (1982), Adams and McChesney (1983), and others.

The total cyclohexane-methanol extract was significantly below that reported by Buchanan et al. (1978a), Erdman and Erdman (1981), McLaughlin and Hoffmann (1982) and others. Adams and McChesney (1983) reported a minimum of 20 hours of soxhlet extraction produced more than 95% extraction with both cyclohexane and methanol.

Assuming sassafras is a potential biocrude source (Buchanan et al.,

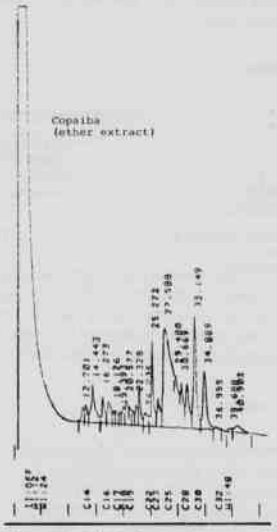

Figure 4. GLC chromatogram of ether extract of *Copaifera langsdorffii* (copaiba) stem tissue. (All extracts are redissolved in ether except those methanol extracts redissolved in 87.5% methanol.)

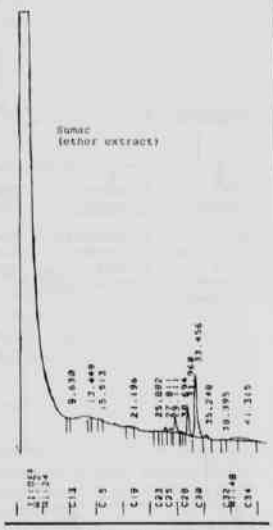

Figure 5. GLC chromatogram of ether extract of *Rhus copallina* (dwarf sumac) stem tissue.

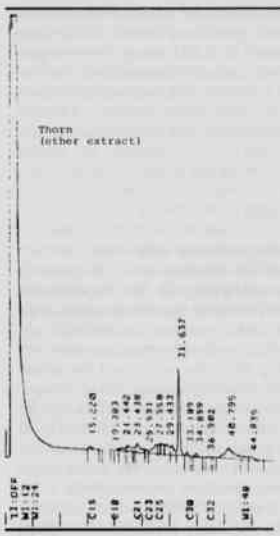

Figure 6. GLC chromatogram of ether extract of *Gleditsia tricanthos* (thorn) stem tissue.

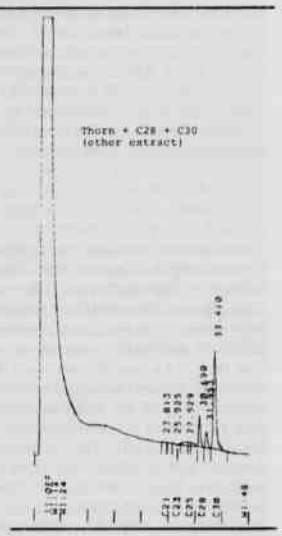

Figure 7. GLC chromatogram of ether extract of *Gleditsia tricanthos* (thorn) stem tissue plus octacosane and triacontane n-paraffin hydrocarbons.

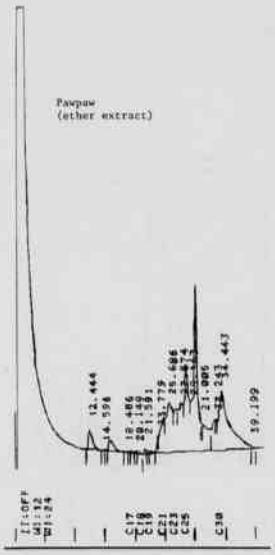

Figure 8. GLC chromatogram of ether extract of *Asimina triloba* (pawpaw) stem tissue.

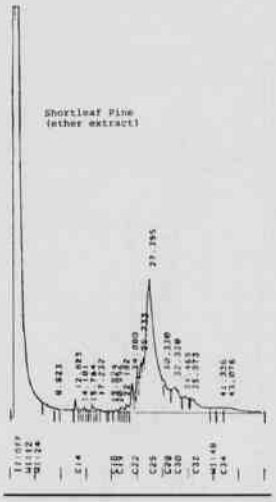

Figure 9. GLC chromatogram of ether extract of *Pinus echinata* (shortleaf pine) stem tissue.

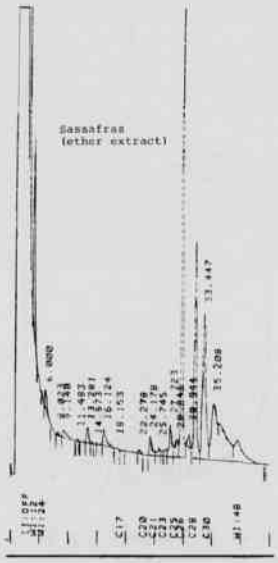

Figure 10. GLC chromatogram of ether extract of *Sassafras albidum* (sassafras) stem tissue.

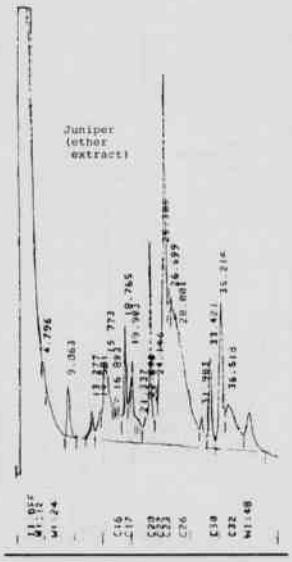

Figure 11. GLC chromatogram of ether extract of *Juniper virginiana* (eastern red cedar) stem tissue.

1978a), all species with greater total cyclohexane-methanol extract could also be considered as potential sources of biocrude (see Table 2). Pawpaw, pine, sumac, and eastern red cedar have larger total cyclohexane-methanol extract values than sassafras.

The cyclohexane extract, containing the oil and hydrocarbon fractions (Buchanan et al., 1978b), is the high energy components of plants most efficiently converted into burnable liquid fuels and feedstocks (McLaughlin and Hoffmann, 1982). Adams (1982) reported that the

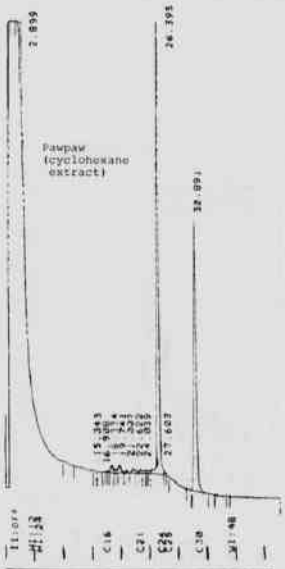

Figure 12. GLC chromatogram of cyclohexane extract of *Asimina triloba* (pawpaw) stem tissue.

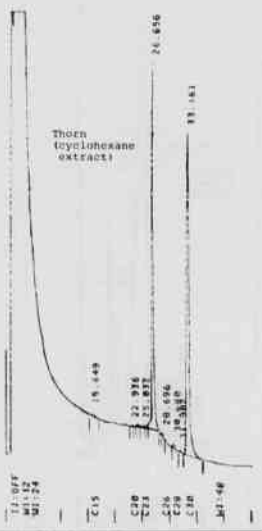

Figure 13. GLC chromatogram of cyclohexane extract of *Gleditsia tricanthos* (thorn) stem tissue.

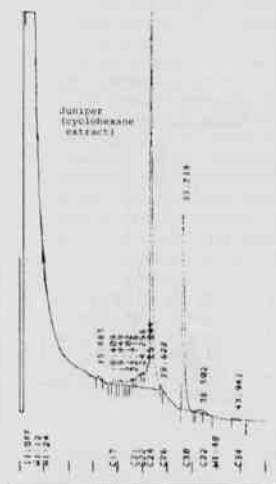

Figure 14. GLC chromatogram of cyclohexane extract of *Juniper virginiana* (eastern red cedar) stem tissue.

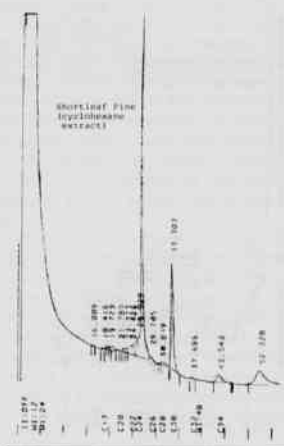

Figure 15. GLC chromatogram of cyclohexane extract of *Pinus echinata* (shortleaf pine) stem tissue.

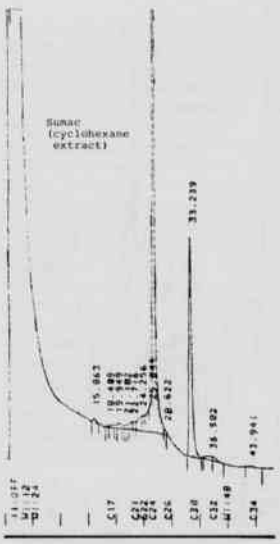

Figure 16. GLC chromatogram of cyclohexane extract of *Rhus copallina* (dwarf sumac) stem tissue.

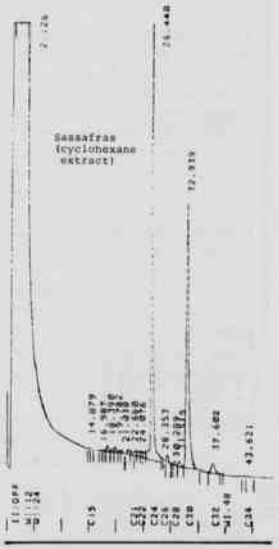

Figure 17. GLC chromatogram of cyclohexane extract of *Sassafras albidum* (sassafras) stem tissue.

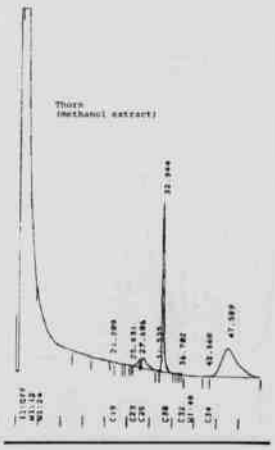

Figure 18. GLC chromatogram of methanol extract of *Gleditsia tricanthus* (thorn) stem tissue.

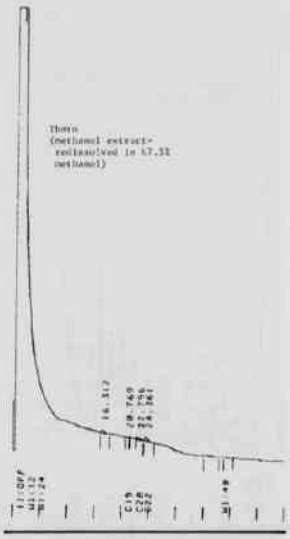

Figure 19. GLC chromatogram of methanol extract of *Gleditsia tricanthus* (thorn) stem tissue (redissolved in 87.5% methanol).

heat value of the hexane (cyclohexane) extract is comparable to crude oil. Although the cyclohexane extract has more than 2.2 times the heat value of the methanol extract (Erdman and Erdman, 1981) the high quality of methanol extract compensates for its lower heat value.

Plants producing the highest amounts of biocrude are latex and resin producers (McLaughlin and Hoffmann, 1982). Both are composed of isoprene polymers and represent promising potential fuel sources and can be readily collected by tapping. Latex has molecular weights rang-

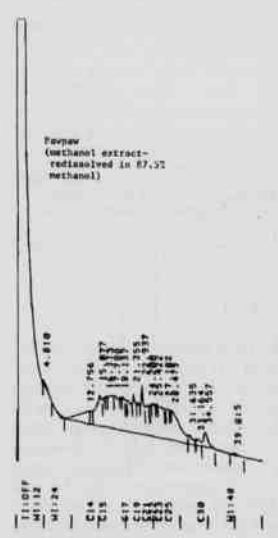

Figure 20. GLC chromatogram of methanol extract of *Asimina triloba* (pawpaw) stem tissue.

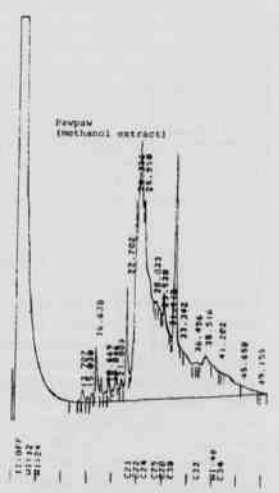

Figure 21. GLC chromatogram of methanol extract of *Asimina triloba* (pawpaw) stem tissue (redissolved in 87.5% methanol).

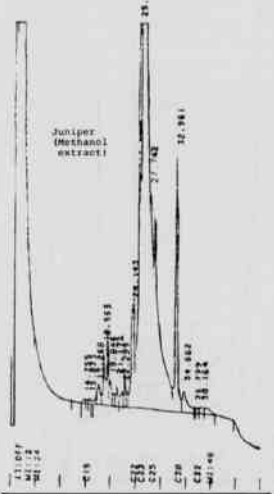

Figure 22. GLC chromatogram of methanol extract of *Juniper virginiana (eastern red cedar) stem tissue.*

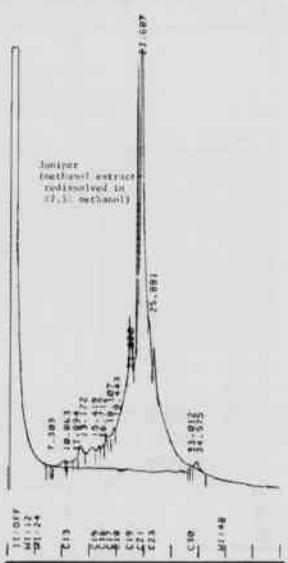

Figure 23. GLC chromatogram of methanol extract of Juniper virginiana (eastern red cedar) stem tissue (redissolved in 87.5% methanol).

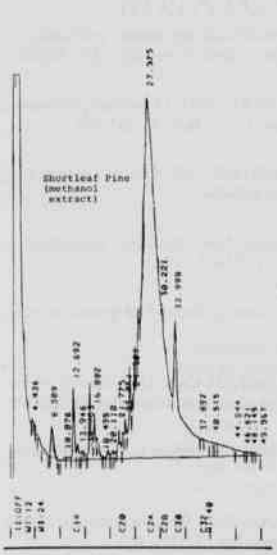

Figure 24. GLC chromatogram of methanol extract of *Pinus echinata* (shortleaf pine) stem tissue.

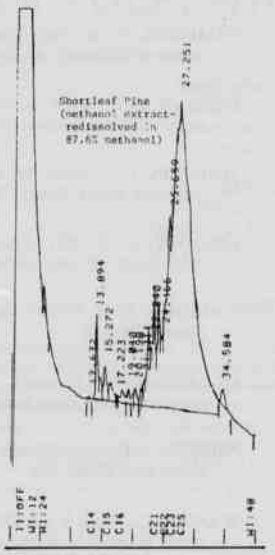

Figure 25. GLC chromatogram of methanol extract of *Pinus echinata* (shortleaf pine) stem tissue (redissolved in 87.5% methanol).

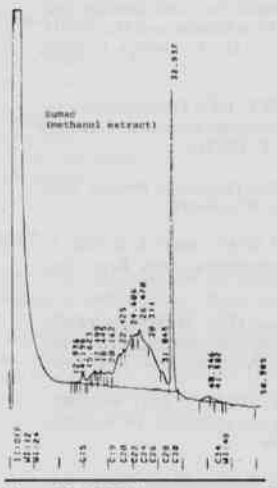

Figure 26. GLC chromatogram of methanol extract of *Rhus copallina* (dwarf sumac) stem tissue.

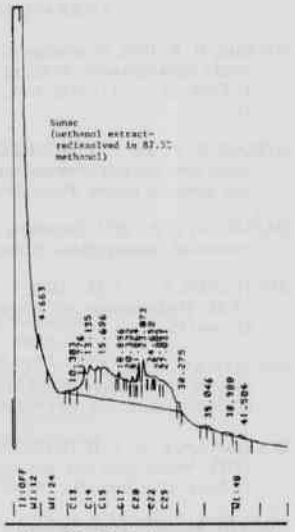

Figure 27. GLC chromatogram of methanol extract of *Rhus copallina* (dwarf sumac) stem tissue (redissolved in 87.5% methanol).

ing from 500,000-2,000,000 down to 50,000 or less. The higher molecular weight latex would be most economically used as natural rubber. The lower molecular weight range could be catalytically cracked to liquid fuel (Wang and Huffman, 1981).

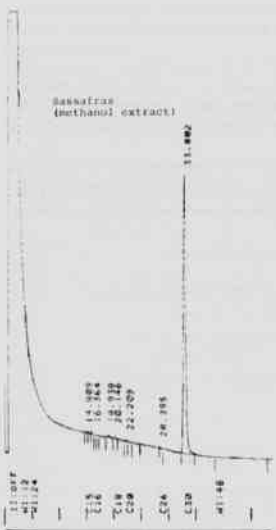

Figure 28. GLC chromatogram of methanol extract of *Sassafras albidum* (sassafras) stem tissue.

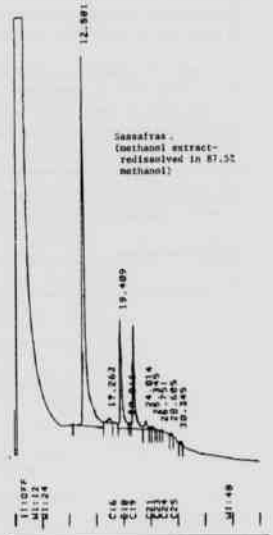

Figure 29. GLC chromatogram of methanol extract of *Sassafras albidum* (sassafras) stem tissue (redissolved in 87.5% methanol).

Pines represent a major source of resin readily collected as a volatile oil called turpentine. Turpentine is highly combustible and should be considered an important potential fuel source. Turpentine has a heat content equivalent to gasoline and butanol (40 gigajoules per metric ton) and could be used as liquid fuel or mixed with gasoline (Wang and Huffman, 1981).

Maugh (1979) identified the exudate from *Copaifera langsdorffii* Desf. trees as a source of an oil (oleoresin) sap obtained by tapping that could be used as diesel fuel. Wang and Huffman (1981) estimated that one acre of 100 *C. langsdorffii* trees could produce 25 barrels of exudate per year. This amounts to 1375 gallons (1 barrel = 55 gallons) of exudate per acre per year, enough to drive 27,500 miles per year at 20 miles per gallon. If we assign diesel fuel a cost of $1.10 per gallon, this represents a monetary value of $1,512.50 per acre per year.

This research represents a preliminary study to determine the feasibility of using trees as a source of biocrude. The development of photosynthetic plants as fuel feedstock has been hindered by the difference in production when compared with fossil fuels. However, biocrude is renewable, has flexibility afforded by crop rotation, and can be genetically altered to modify the chemical composition of extractives. These advantages may be partially offset by the high technology and market development of the petroleum industry and the seasonal dispersion of plant resources (Lipinsky, 1981).

Although current interest is focused on whole plants for biocrude (Buchanan et al., 1978a,b; Calvin, 1979; Erdman and Erdman, 1981; Adams, 1982; Campbell, 1983) we believe that biocrude-like tree exudates could be a potential alternative. Adams (1982) reported that harvesting only the exudate would result in a loss of ⅓ of the oil, ½ of the resin, and ⅓ of the latex. We believe these losses could be partially offset by the ecological benefits of trees. Farmers would see a direct economic benefit from planting trees. Trees could reduce wind erosion, improve the water table, improve wildlife habitat, provide shade for homes and livestock, and serve as a source of liquid fuel, lumber, pulp, and firewood.

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