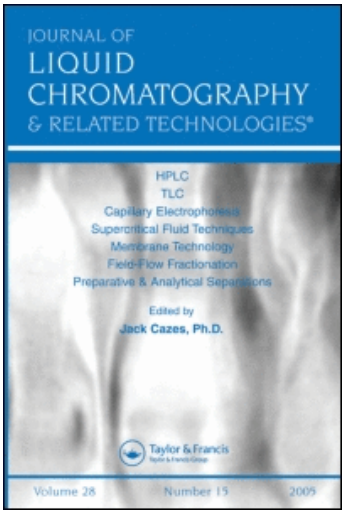

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High Performance Liquid Chromatography Analysis of Sugar Cane Bagasse Hydrogenation Products. I. Group-Type Separation

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF SUGAR CANE BAGASSE HYDROGENATION PRODUCTS. I. GROUP-TYPE SEPARATION

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ABSTRACT

An HPLC Group-Type Separation was developed for the analysis of the liquefaction product of sugar cane wood fibers (bagasse). First, a liquid-liquid extraction technique was applied to separate the highly polar and polymerized aqueous fraction from the less polar organic fraction. This last fraction was then separated by HPLC into four classification groups: three hydrocarbons (saturates, olefins and aromatics) and a combination of polar compounds.

The application of these extraction and separation methods to the analysis of Brazilian sugar cane residue liquefaction products was very promising since the major group present in the extract is the aromatic hydrocarbons, suggesting its potential use as chemical feedstock, as well as a possible renewable source of energy. In addition, the method generates discrete and "clean" fractions for further detailed characterization when desired.

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INTRODUCTION

Since 1974, the world has faced a challenging problem: the energy crisis. Crude oil, a very important resource for energy as well as a petrochemical feedstock is becoming scarcer and more expensive. These facts have motivated many oil importing countries to start utilizing natural and non-fossil resources as a cheaper and more efficient way to solve their energy problem. In countries where coal is abundant, such as the U.S.A., with about one third the world' stock, a great concern has been given to the study of the conversion of whole coal or of solvent refined coal (SRC) into products similar to those obtained by crude oil processing (1). On the other hand, in countries where coal is not that abundant alternative ways are being investigated. Because of the ease with which liquids can be processed, stored and utilized, a considerable part of this research is direct towards the convertion of solid sources into liquid products that are easy to handle.

Brazil, as an example, has been successful in using in sugar cane wood for ethanol generation to be used as an alternative energy source. In this case, the fuel generated has shown excellent performance as a substitute for gas and diesel to run engines (2). Initially the ethanol was mixed with gasoline (20:80% by volume), but now pure ethanol is used to run more than 90% of the new cars (3). One advantage in using ethanol and its derivatives is the fact that this source is constantly renewed. In 1983, Brazil produced more than 8 billion liters of ethanol, by fermenting an extract of sugar cane wood. The residual fiber (bagasse) is usually either burnt for heat generation or dumped in the fields as a soil fertilizer Considering the tremendous amounts of these fibers that are generated, some millions of tons per year (4),

it is being used very inefficiently. Thus, is quite interesting to study the possibility of converting these fibers into liquid products that could be useful as fuels and more "noble" chemical products.

Schuchardt and Matos (5) have recently studied the liquefaction of sugar cane bagasse with formate and water, while Cundy et al. (6) have discussed the combustion of bagasse. No chemical characterization of the chemicals obtained is presented in either cases. A extensive literature review on these conversions has also been presented (7).

The present work is an attempt to develop an analytical procedure which permits the extraction of liquid products and their further fractionation into less complex groups similar to those obtained in coal (8), SRC (9), shale oil (10) and asphalt (11) fractionation. The fractions generated can then be characterized by chromatographic as well as other analytical methods, such as GC/MS, already extensively used in the characterization of coal derived liquids (12).

EXPERIMENTAL

Apparatus

The analytical instrument used in this study was a Varian 5020 HPLC (Varian Associates, Walnut Creek, Ca.). The detection was done using a UV detector fixed at 254 nm in series with a differential refractomerter, both from Varian. The peaks were recorded on a dual-pen recorder, Varian model 5176, while the retention times and areas were calculated by a Varian CDS 111 System. Two high pressure six-port Valco valves (up to 7000 psi) were utilized, one for injection and the other for backflush.

Chemicals

Hydrocarbon standards were obtained from Polyscience Corporation (Niles, IL). Hexane (HPLC grade) was purchased from Burdick and Jackson (Muskegon, MI), dried for at least 5 hours over molecular sieves, type 5A (Analabs, North Haven, CT), previously activated for 8 hours at 300°C. The hexane was then filtered in a 1.2 μm Millipore system. Other standards were obtained from Aldrich Chem. Co. (Milwaukee, WI) and Fisher Co. (Fairlawn, NJ).

Columns

The optimum conditions were obtained using two columns connected in series. The first column 250 mm(L) x x 4.0 mm(I.D.) contained cyanopropyl phase chemically bonded to 5 μm silica particles (Lichrosorb CN-5, E.M. Merk). The purpose of this column was to retain the polar compounds. The group-type separation took place in the second column, 300 mm(L) x 4.6 mm(I.D.), of 5 μm silica (Micropack Si-5, Varian). 10 μl of the sample were injected into the cyano propyl column, which retained the polar fraction. The hydrocarbons were then fractionated into saturates, olefins and aromatics on the silica column while the polars were eluted as a single peak by backflushing the system after the aromatics fraction eluted from the silica column. Using a highly activated silica, it is possible to efficiently separate paraffins from olefins, but naphthenes (cyclic saturated hydrocarbons) coelute with the paraffins. The saturated fraction (paraffins and naphthenes) could be further characterized by GC (12).

Sample Preparation

Figure 1 shows the scheme utilized for processing, extraction and separation of the samples. The raw sugar

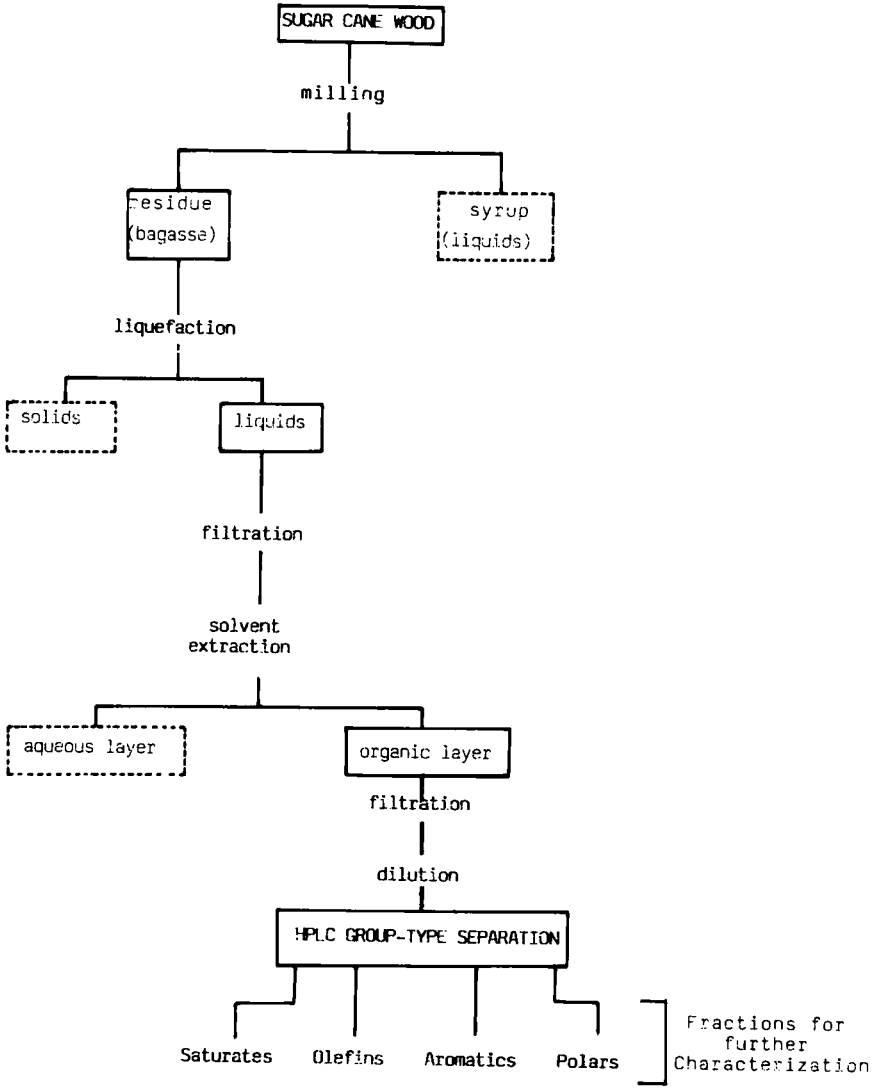

FIGURE 1. Schematics of the Analytical Method.

TABLE 1

MAJOR CHARACTERISTICS OF SUGAR CANE BAGASSE

ELEMENTAL ANALYSIS (%)*		PROXIMATE ANALYSIS (%)	
C	45,3	Fixed Carbon	36,1
H	6,8	Volatiles	48,8
S	0,3	Moisture	12,7
N	0,2	Ash	2,4
O	47,3		

*** Moisture and ash free basis.**

cane is pressed and the liquid fraction is used for the manufacture of various products including ethanol and sugar. Meanwhile, the residue, generally called bagasse, is hydrogenated in a stainless steel autoclave (14). For this purpose, the bagasse, whose major characteristics are listed in Table 1, is mixed with creosote oil (1:5 ratio w/w) and the resulting suspension is heated to 400°C under a initial hydrogen pressure of 150 atm. Further details about this conversion are described elsewhere (14). The dark viscous liquid obtained, which looks like shale oil, is filtered in a Millipore 1.2 µm system. The filterate is then extracted with a (1:1) hexane-water mixture for 12 hours under an inert atmosphere (Helium), at ambient temperature and with stirring. The aqueous layer is discarded while the organic layer is again filtered. The filtrate from the last step is diluted with hexane in a 1:10 ratio, as is then ready for the HPLC group-type separation.

RESULTS AND DISCUSSION

Although HPLC group-type separation has been extensively used in the characterization of liquid fossil fuels (15-18) its use in the analysis of "biocrudes" has not been reported. Considering the high complexity of such samples, we felt that use of group-type separation would be very important as a fractionation method provide discrete fractions for further characterization.

Figure 2 shows the separation of a standard mixture of model compounds used during the optimization of the HPLC group-type separation, whose identity can be found in Table 2.

Ten microlliters (10 µl) of the solution obtained from bagasse were injected into the HPLC system in order to generate the four fractions, displayed in Figure 3, namely: saturates, olefins, aromatics and polars.

TABLE 2

STANDARD MIXTURE FOR THE GROUP-TYPE SEPARATION

PARAFFINS	OLEFINS	NAPHTHENES	AROMATICS	POLARS
Heptane	Hexene	Methylcyclobutane	Benzene	Phenol
Nonane	Octene	Cyclopentane	Toluene	o-Chrophenol
Undecane	Undecene	Dimethylcyclopentane	Xylenes	Methyl Aniline
Tetradecane	Dodecene	Cyclohexane	Ethylbenzene	Resorcinol
Pentadecane	Tetradecene	Cycloheptane	Propylbenzene	Quinoline
Hexadecane	Heptadecene	Cyclooctane	Butylbenzene	Dimethyl Amine

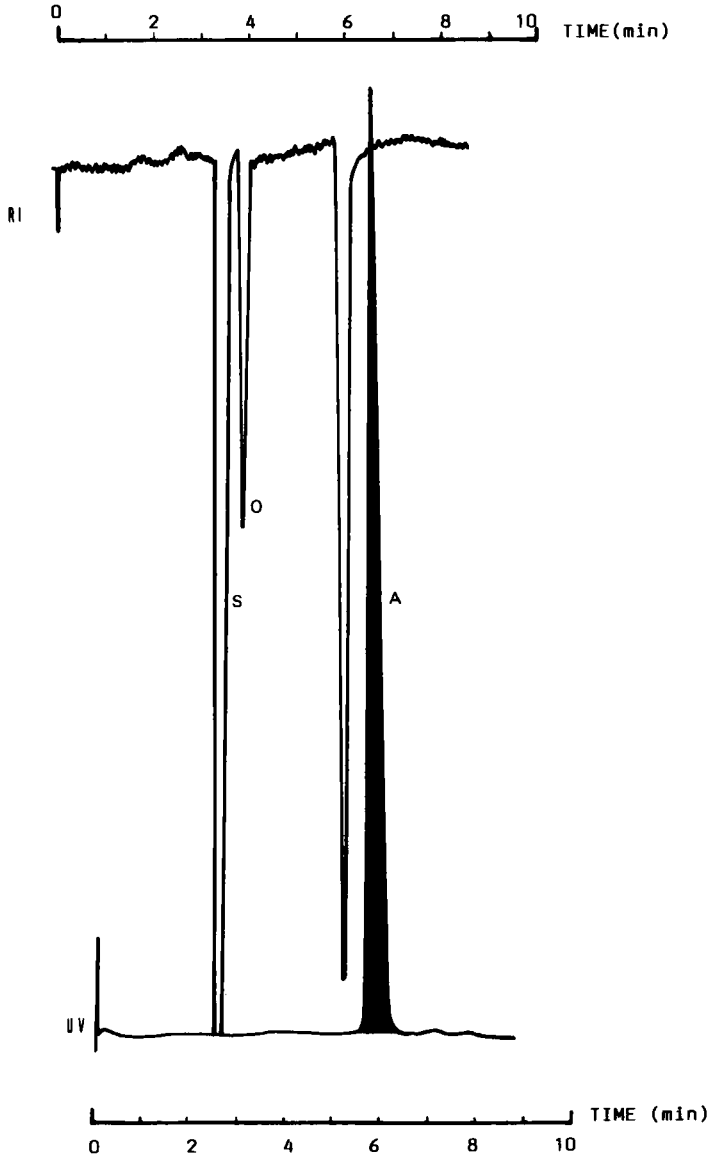

FIGURE 2. HPLC Group-Type Separation of a Standard Mixture.
Columns: Cyano Bonded Silica and Silica in Series.
Eluent: Dry Hexane. Flow Rate: 1.0 ml/min and 3.0 ml/min after Backflush Point (BF).
Detection: Refractive Index Detector (RI) and Ultra-Violet Detector (UV) fixed at 254 nm.
Injection: 1.0 μℓ. Shaded are: Aromatics. For the identity of the individual components in each group refer to Table 1.

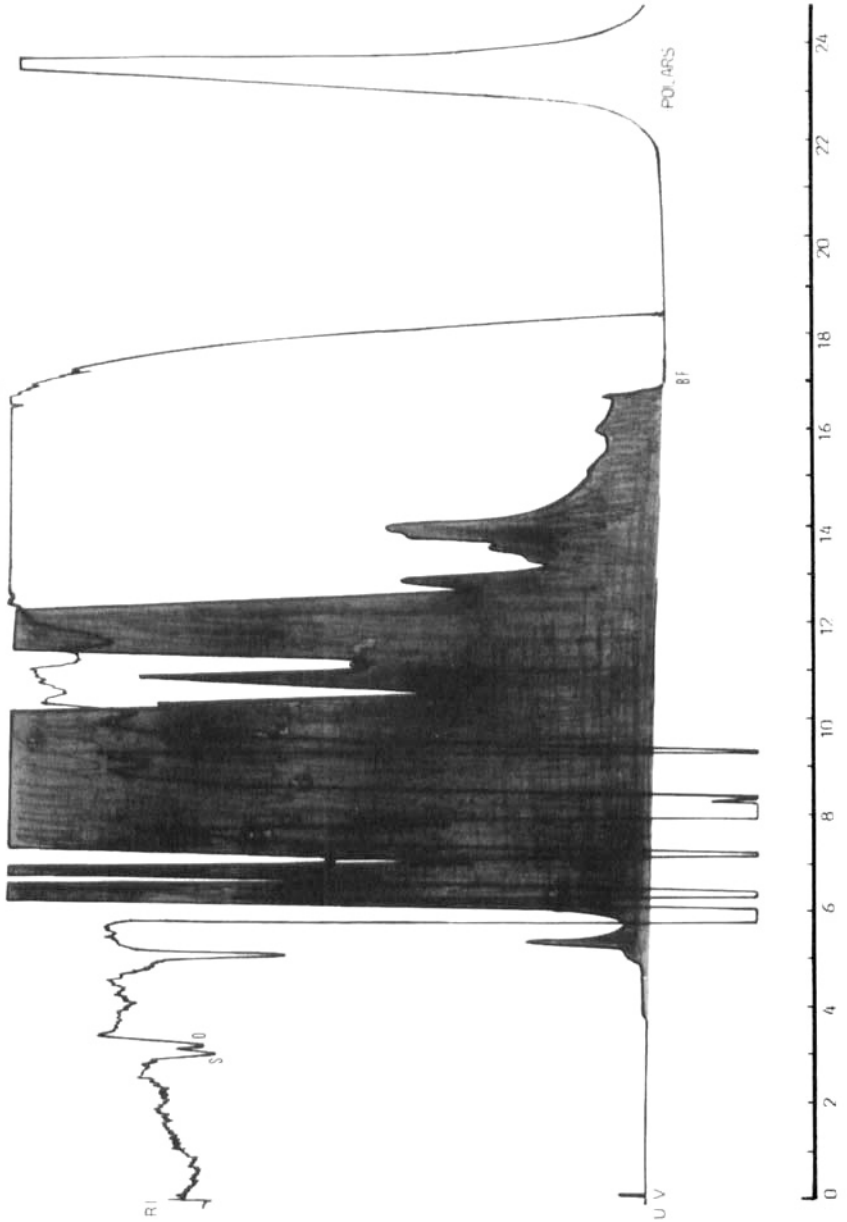

FIGURE 3. High Performance Liquid Chromatogram of "Sugar Cane Bagasse Hydrogenation Products". Conditions same as in Figure 2.

Note that the "polar fraction" is eluted as a single peak from the cyano propyl column when the system is backflushed; thus helping in its colection and characterization. The "aromatics fraction" is resolved from saturates and olefins in the silica column and elutes as several peaks. This is due to the fact that aromatic compounds are separated in the silica column according to their number of condensed rings (19). Thus, collection of compounds with varying degrees of ring number will simplify further characterization employing GC/MS (20) and/or other analytical tools. Due to the complexity with in the groups as a result of hydrogenation of sugar cane bagasse, it is extremely difficult to characterize the individuals products if the entire "dirty" sample were to be directly injected into one analytical system, such GC/MS, without fractionation.

In this work, the group-type separation proves to be quite helpfull in "cleaning" the sample of the polar compounds while providing a pre-separation that will help in the individual analysis of each group.

Detailed characterization of each group is under study at the present moment using High Resolution Gas Chromatography, Reverse-Phase High Performance Liquid Chromatography and Gas Chromatography/Mass Spectrometry (20).

CONCLUSION

The results obtained in this work show that the products of sugar cane bagasse liquefaction contain a wide spectrum of compounds, especially hydrocarbons. This suggests that the fiber residues - which at this moment are wasted and/or inadequately used - could be useful as a chemical feedstock for compounds such as aromatics hydrocarbons, or converted to liquid fuels. The results of this work encourage the development of an

in-depth procedure to improve the conversion and product analysis.

The method used for the extraction and fractionation of the sugar cane wood liquefaction products into compound classes seems to generate discrete sub-fractions which may be further characterized by chromatographic and non-chromatographic analytical techniques.

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