LIQUID CHROMATOGRAPHIC CHEMICAL CLASS ANALYSIS OF BITUMEN AND HEAVY PETROLEUM CRUDES

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INTRODUCTION

The importance of bitumen and heavy crudes is steadily increasing as reserves of conventional crudes diminish around the world producing an increased emphasis upon the development of methods of recovery for bitumens and heavy crudes. Because of the extremely high viscosities encountered, a variety of novel in-situ recovery methods using combinations of steam, solvents, surfactants, and combustion are being investigated.

Conventional and heavy petroleum crudes consist of a large variety of organic molecules generally classified into four major groups identified as saturates, aromatics, resins and asphaltenes. Each of these classes have individual uses and their relative ratios determine the upgrading processes employed. Bitumen and heavy crudes tend to have larger proportions of resins and asphaltenes that are less economically converted to usable products. Precipitation of asphaltenes in the formation or production of asphaltenes from other compounds can occur during the recovery process necessitating some monitoring of process streams for changes in the relative ratios of these classes of compounds.

Numerous methods are used to separate petroleum hydrocarbons into their type and classes. The most common method utilizes pentane precipitation of the asphaltenes in a procedure similar to ASTM D 893-69. A variety of procedures (1-6) are employed for the subsequent fractionation of the remaining oil. Many of the procedures for the separation of the aromatics and saturates using silica and/or alumina columns are modifications of ASTM D 2549-75. Some of the methods achieve separations into subgroupings such as monoaromatics, diaromatics, polyaromatics and polar compounds.

Each of the procedures however has the disadvantage that a total class analysis requires several steps and to obtain the data regarding the distribution of the fractions requires several days.

The procedure discussed here enables the separation of the bitumen or heavy petroleum crude into three groupings namely asphaltenes, resins and a mixture of aromatics and saturates with no prior separation of the polar constituents or of backflushing of the columns. Using a 254 nm UV detector it is possible to quantify each of the fractions in the bitumen.

EXPERIMENTAL

The liquid chromatograph used in this study was a Varian Model 8500 dual syringe pump instrument equipped with a Varian Aerograph 254 nm UV detector connected to a Varian CDS 111 Data System. The columns used were a 25 cm Varian Aerograph Micropak CH-10 connected in series with a 25 cm Varian Aerograph Micropak CN-10.

Two mobile phase systems can be used to achieve the separation. One system employed 99% methanol-1% isopropanol for 4 minutes, 40% of the 99% methanol-1% isopropanol mixture-60% tetrahydrofuran for 10 minutes and finally 100% THF for 10 minutes. The second system used 90% acetonitrile-10% water for 5 minutes followed by 50% acetonitrile mixture-50% methylene chloride for 10 minutes followed finally by 100% methylene chloride for 10 minutes. Separation achieved by the two methods is comparable and is accomplished in 25-30 minutes using a flow rate of 60 cc/hr.

The bitumen/heavy crude samples are dissolved in methylene chloride at a concentration of 10-20 mg/ml with 2-5 µl of sample being injected on the columns.

DISCUSSION AND RESULTS

Figure 1 shows a typical chromatogram of the separation of saturates and aromatics, resins, and asphaltenes in samples of Athabasca Bitumen. Superimposed on the chromatogram is a plot of the change in the solvent gradient during the analysis.

Chromatograms of aromatics and resins material obtained by separation on passage through attapulgus clay and silica-alumina columns successively are given in Figures 2 and 3 respectively. The chromatograms show that the aromatics produced by column chromatography contain material that we classified as resins by this procedure while the resin samples contain some aromatic material and also some asphaltene material. A chromatogram of an asphaltene sample obtained by pentane precipitation is given in Figure 4 which shows the presence of a resins peak. It is evident from these chromatograms that a very similar fractionation of the bitumen is obtained in our HPLC method as compared to the conventional column separation. Saturates material in the bitumen is eluted with the aromatics fraction however since saturates absorption at 254 nm is negligible they are not detected. By evaluation of the amount of aromatics, resins and asphaltenes the percentage of each of the four fractions in a bitumen sample can be determined.

CONCLUSIONS

The HPLC method discussed in this paper achieves a separation of bitumen into its class components i.e., asphaltenes, resins and mixture of aromatics and saturates, in proportions comparable to that obtained in classical separation by asphaltene precipitation with pentane and subsequent successive passage through attapulgus clay and silica alumina columns.

ACKNOWLEDGMENT

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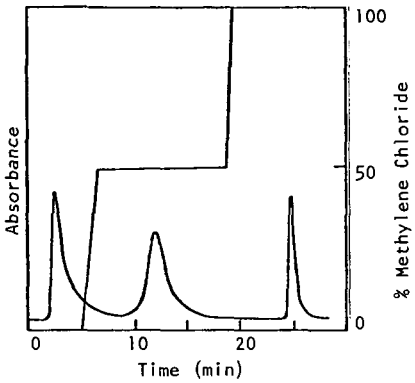

FIGURE 1 Chromatogram of Toluene Extracted Bitumen

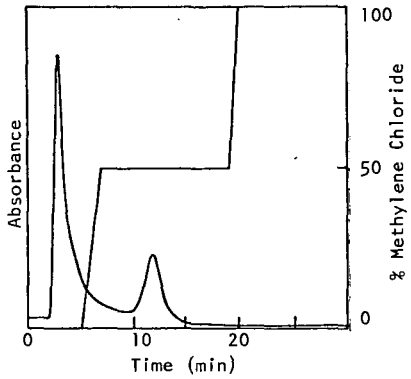

FIGURE 2 Chromatogram of an Aromatics Fraction Separated on Silica-Alumina

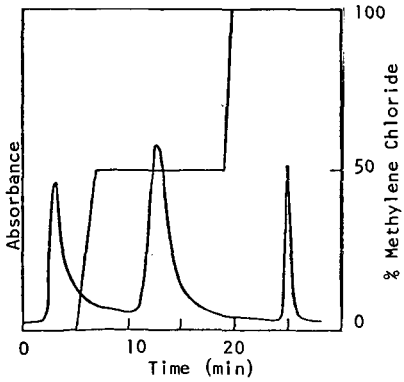

FIGURE 3 Chromatogram of a Resins Fraction Separated on Attapulgus Clay

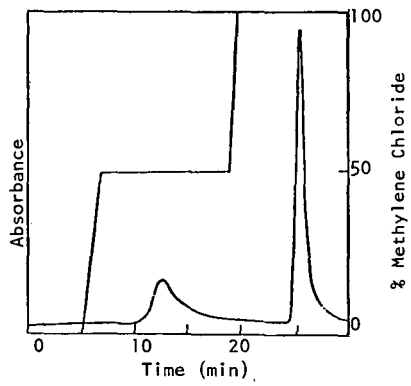

FIGURE 4 Chromatogram of an Asphaltene Fraction Precipitated by Pentane