CHAPTER VI

EXRERIMENTS

The general procedures that were employed in this study outlined as flow chart in Figure 21.

Removal of Asphaltenes

By definition, asphaltenes are insoluble in pentane or hexane but soluble in dichloromethane. Therefore, the bitumen and crude oil can be separated into asphaltenes and non-asphaltenes by precipitation with an excess of n-pentane or hexane. A 40-fold (V/V) exess of n-pentane was used with an exact weight of crude oil and the solution was stirred for around 30 minutes and left to stand for at least 8 hours to ensure total precipitation of the asphaltenes. The precipitate was removed by filtration through a sintered glass funnel (porosity 4.5 μm) and the non-asphaltene fraction was collected into a round bottom flask under vaccum. Repeated washing of the precipitate was required for that a pure asphaltene fraction was obtained. The n-pentane washings were combined with the non-asphaltene fraction and the asphaltenes were retrived by dichloromethane in another flask. Both the asphaltene and non-asphaltene fractions were evaporated to dryness by using a rotary evaporator and the final residues weighed.

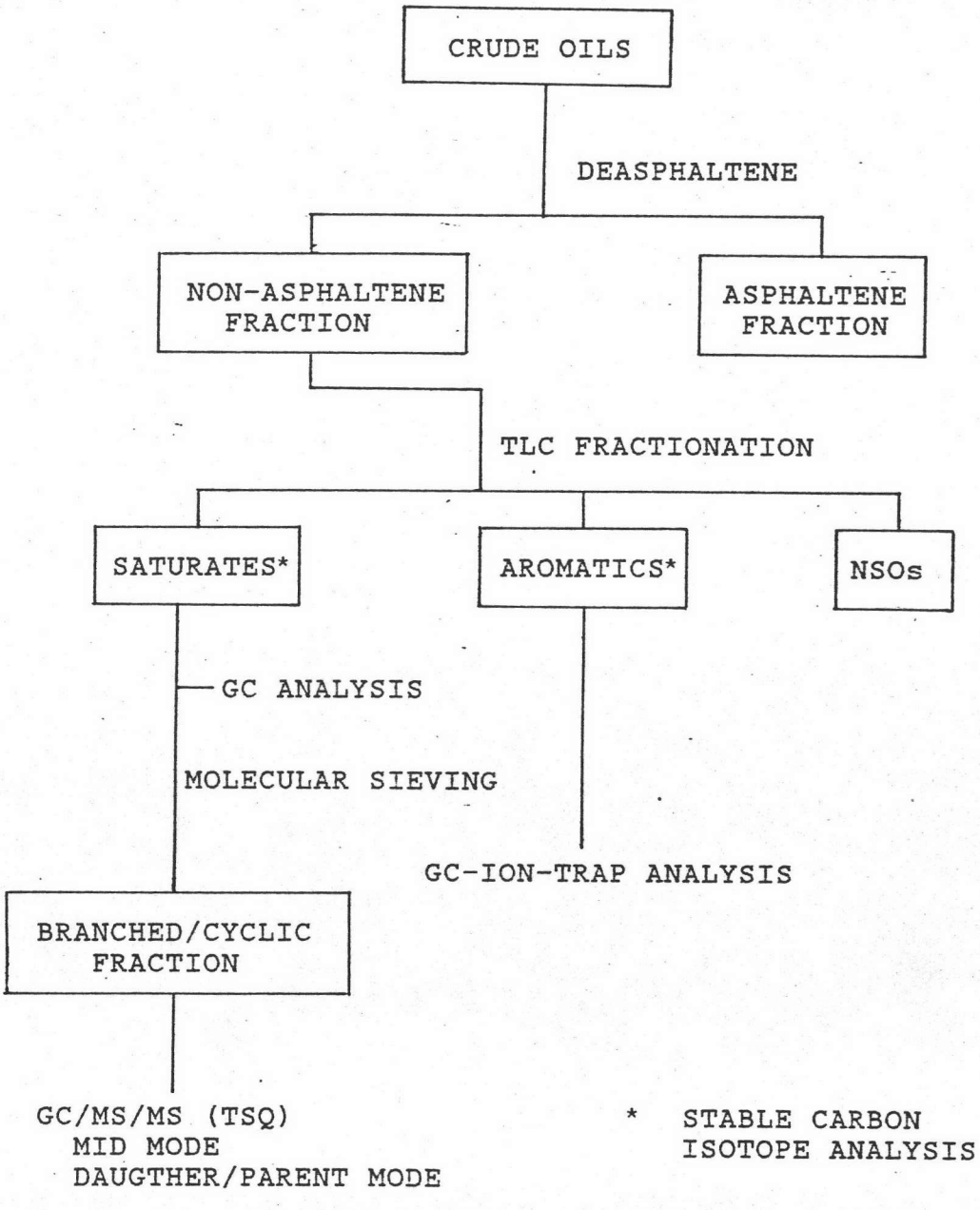

Figure 21. Flow diagram of experimental procedure.

Thin Layer Chromatography

The non-asphaltene fraction was separated into saturate, aromatic and NSO (nitrogen, sulfur and oxygen containing compoumds) fractions by thin layer chromatography (TLC) using n-hexane as developing solvent. The procedure was performed by using 0.25 mm thick and 20 x 20 cm silica gel plate (Merck). Pre-eluting step with ethyl acetate was nescessarily to remove any contaminants from the plates. The fractions on the TLC plate were detected by developing of rhodamine solution in dichloromethane and exposure under UV light. All the fractions were recovered from the silica gel by washing with dichloromethane followed by evaporation on a rotary evaporator. Finally, the dry weights of saturate, aromatic and NSO's fractions were obtained.

Molecular Sieving

Because of the difference in the general structure of n-alkanes and iso-alkanes, molecular sieving is an effective method for separating n-alkanes and iso-alkanes. Union Carbibe S-115 molecular sieves are used after activating at 200°C for 8 hours. Four or five grams of S-115 were added to the sample in 50 ml iso-octane solvent in round bottom flask and left stand overnight after shaking for 10 minutes. The n-alkanes are retained in the molecular sieves and the branched/cyclic hydrocarbons remain in the solution. The branched/cyclic compounds in iso-octane were transferred to a round

bottom flask, solvent removed using a rotary evaporator, and then tranferred to a small tared vial, blown dry with nitrogen and weighed.

Gas Chromatography

The saturate and aromatic hydrocarbon fractions of all sample were analyzed by gas chromatography using Carlo Erba 600 GC which was equipped with a 25 m x 0.22 mm SGE HTS fused silica WCOT capillary column with a 0.1 μm film thickness. The injector temperature and the FID temperature were 400 ° C. The carrier gas was helium with a flow rate of 1 ml/min. The temperature program was the rate 4 ° C/min from 40 ° C to 400 ° C where it was held isothermally for 15 minutes.

For pristane and phytane peak identification, the same saturate fraction of all samples were analyzed by a Hewlet Packard 5890 GC equipped with a 30 m x 0.255 mm J & W Scientific DB-5 fused silica capillary column with 0.25 μm film thickness. Injection and detector tempertsures were 300 ° C. The temperature program for the GC oven was from 40 ° C to 130 ° C at a rate of 15 ° C/min and then 4 ° C/min to 300 ° C where it was held for 20 minutes. The flow rate of the carrier gas, helium, was 1.2 ml/min.

Gas Chromatography-Ion Trap Detector

Biomarkers in saturate and aromatic fractions were initially investigated using Hewlett Packard 5890A

gas chromatography interfaced to a Finnigan Mat Model 700 Ion Trap Detector (ITD). The GC was equipped with a J & W Scientific DB-5 fused silica capillary column (25m x 0.255mm with a 0.25μm film). A splitless injection technique was used with helium as the carrier gas with a flow rate of 1 ml/min. The injection temperature was initially 40°C for 15 min and then increased at a rate of 15°C/min to 130°C and changed to 4°C/min to the final temperature of 300°C and held isothemally for 20 minutes.

The ion trap detector used an emission current of 80 amps, electric energy equal to 70 eV and the multiplier setting depended upon the instrumental conditions. The ITD was generally used in the multiple ion detection mode to monitor m/z 123, 191, 217 and 231 for biomarkers in saturate fraction and m/z 128, 142, 156, 178, 192, 239 and 253 for biomarkers in aromatic fraction. Data collection was on the IBM x T personal computer using Finnigan Mat ITDS V #1.5 and MS DOS 2.1 software.

Component identification was made by comparison of mass fragmentograms with samples that have been analyzed on more sophisticated GC/MS systems as well as the GC-ITD.

Gas Chromatography - Mass spectrometry (GC-MS)

The gas chromatograph used in the GC/MS system was a varian 3400 GC, equipped with a DB-5 fused silica

capillary column (30m x 0.25mm, 0.25μm film thickness). The column was operated in the split/splitless mode. The carrier gas was helium with a flow rate of 1 ml/min and the temperature program was 40 °C to 300 °C at 4 °C/min with a final hold time of 30 minutes.

The GC was interfaced directly to a Finnigan Triple Stage Quadrapole system (TSQ 70). The filament current was 200 °A and the electron multiplier was set at 1600 volts. The collision gas was argon at a pressure of ca. 0.5 torr and a collision offset voltage of -20eV.ICIS (Interactive Chemical Information System), Finnigan Mat Corp., was used for data collection.

The data were collected by operating the TSQ in the multiple ion detection (MID) mode and daughter/parent ion detection (PAR) mode. Normal GC/MS involves the used of one quadrupole, normally Q3. MS/MS analyses were done in the parent mode, with all three quadrapoles in operation. This mode involves the ability of the TSQ to monitor the parent/daughter relationships in the detection of parent, or molecular ions of specific ions (PHILP et al., 1988).

Stable Carbon Isotope Mass Spectrometry

Stable carbon isotope values were determined for the saturate and aromatic fractions of all samples. The sample preparation used the static combustion method of Sofer (1980). Following combustion, the tubes were opened with a tube cracker connected to a vacuum line (2

x 10^{-3} torr). The water that was generated during combustion was removed from the individual gas samples with a trap consisting of an ethanol bath maintained at -70 ^{0}C with a Neslab Cryocool CC-60 unit. The CO_2 fraction of each individual gas sample was collected by submerging a gas sampling ampoule into into liquid nitrogen. The sampling ampoules containing the condensed CO_2 samples were sealed with gas tight values and then transferred directly to the inlet system of Finnigan Delta E isotope ratio mass spectrometer for the stable carbon isotope analyses.

The stable carbon isotopic compositions are expressed as : $\delta^{13}C$ (per mil) = $(R_{sample}/R_{standard} - 1) \times 10^{3}$, where R is the abundance ratio of the heavy to light isotope of carbon ($^{13}C/^{12}C$). The reference that was used was NBS-22 (-29.81 per mil) relative to PDB (Pee Dee Belemnite) carbonate (0 per mil). For the stable carbon isotope values reported in this paper, the average precision was 0.02 per mil.