

CHAPTER II

LITERATURE SURVEY

2.1 General Definition and Structure of Asphaltenes

Asphaltenes, appearing as dark brown to black solids, represent the most polar and heaviest part of petroleum crude. Solvent solubility is a general mean to define asphaltenes. It can be defined as the fraction insoluble in heptane (or pentane) but soluble in toluene or other aromatic solvents (Speight, 1991). Figure 2.1 shows the fractionation and classification scheme of crude oil fractions. The fraction of asphaltenes usually has high molecular weight ranging from 1,000 to 2,000,000. The wide variation in asphaltene molecular weight might be due to the difference of measuring techniques but mostly due to the association of asphaltenes in solvent (Sharma and Yen, 1994). Asphaltenes are composed of polyaromatic nuclei carrying aliphatic chains or rings and other heteroatom including sulfur, oxygen, nitrogen and trace amounts of metal such as vanadium, nickel, and iron (See Figure 2.2).

2.2 Stabilization of Asphaltene in Crude

Asphaltene molecules are simply composed of asphaltene core, resin and maltene. Resin and maltene are parts containing alkyl chains, which are compatible with the bulk crude. These two molecules are responsible for stabilizing asphaltenes (Becker, 1997). Resin and maltene, which are slightly less polar than asphaltene and have less molecular weight, will form micelle as shown in Figure 2.2.

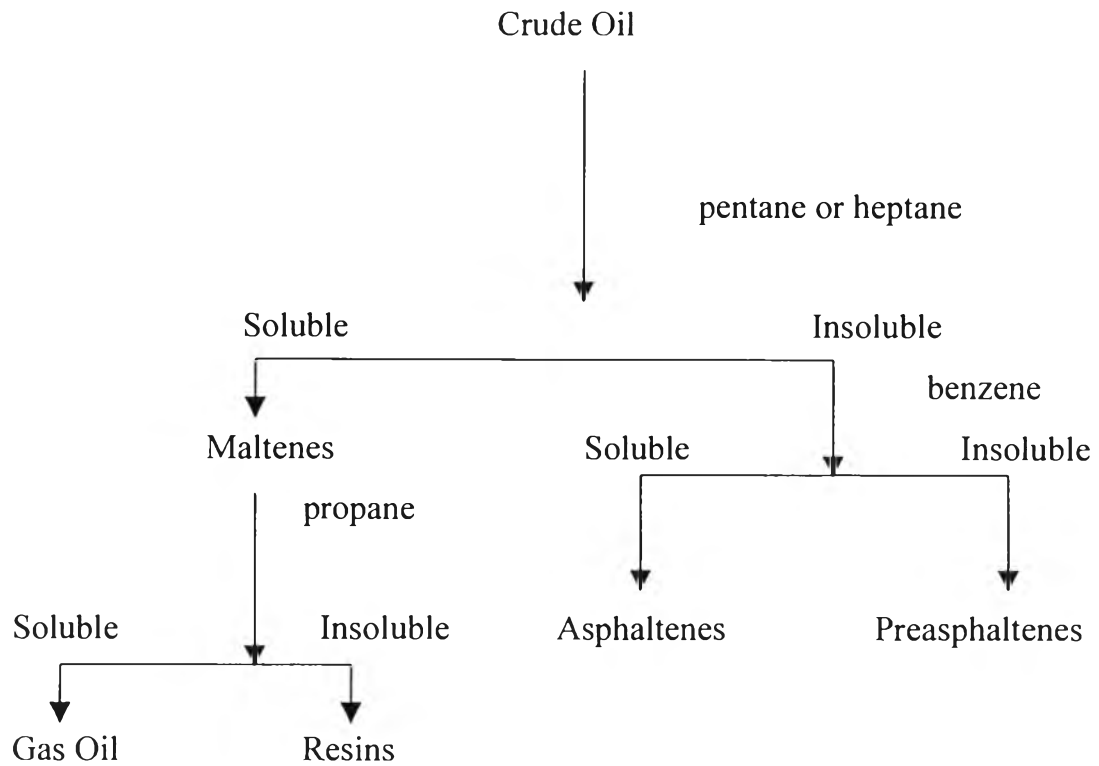


Figure 2.1 Fractionation and classification scheme for crude oil fractions

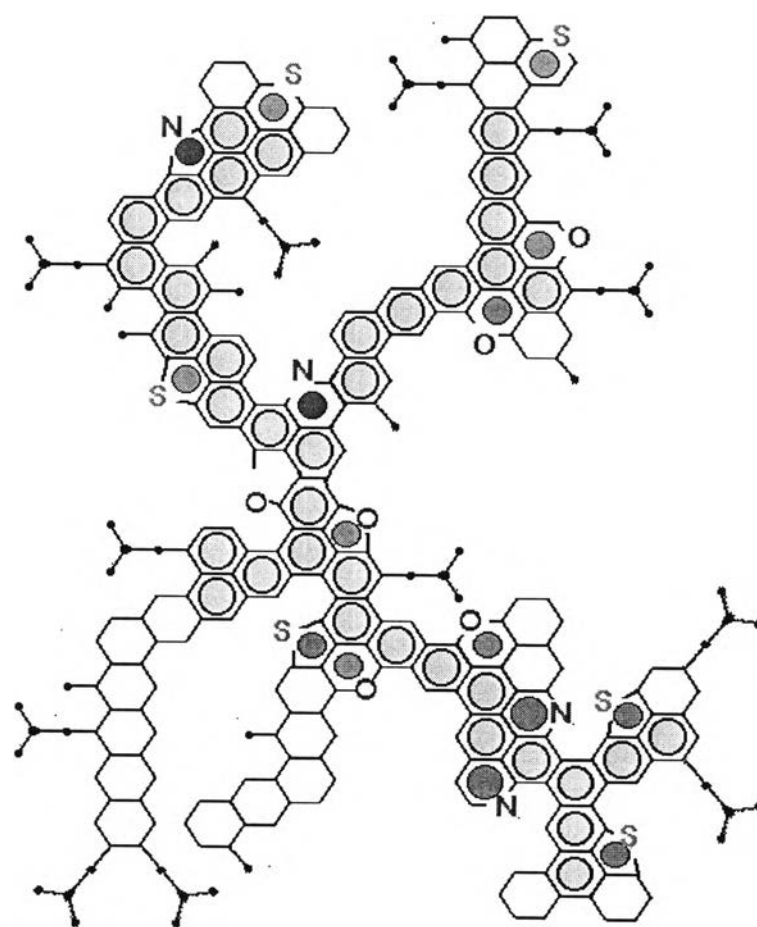


Figure 2.2 Molecular structure of asphaltene proposed for Maya crude (Mexico) (Mansoori, 1997a)

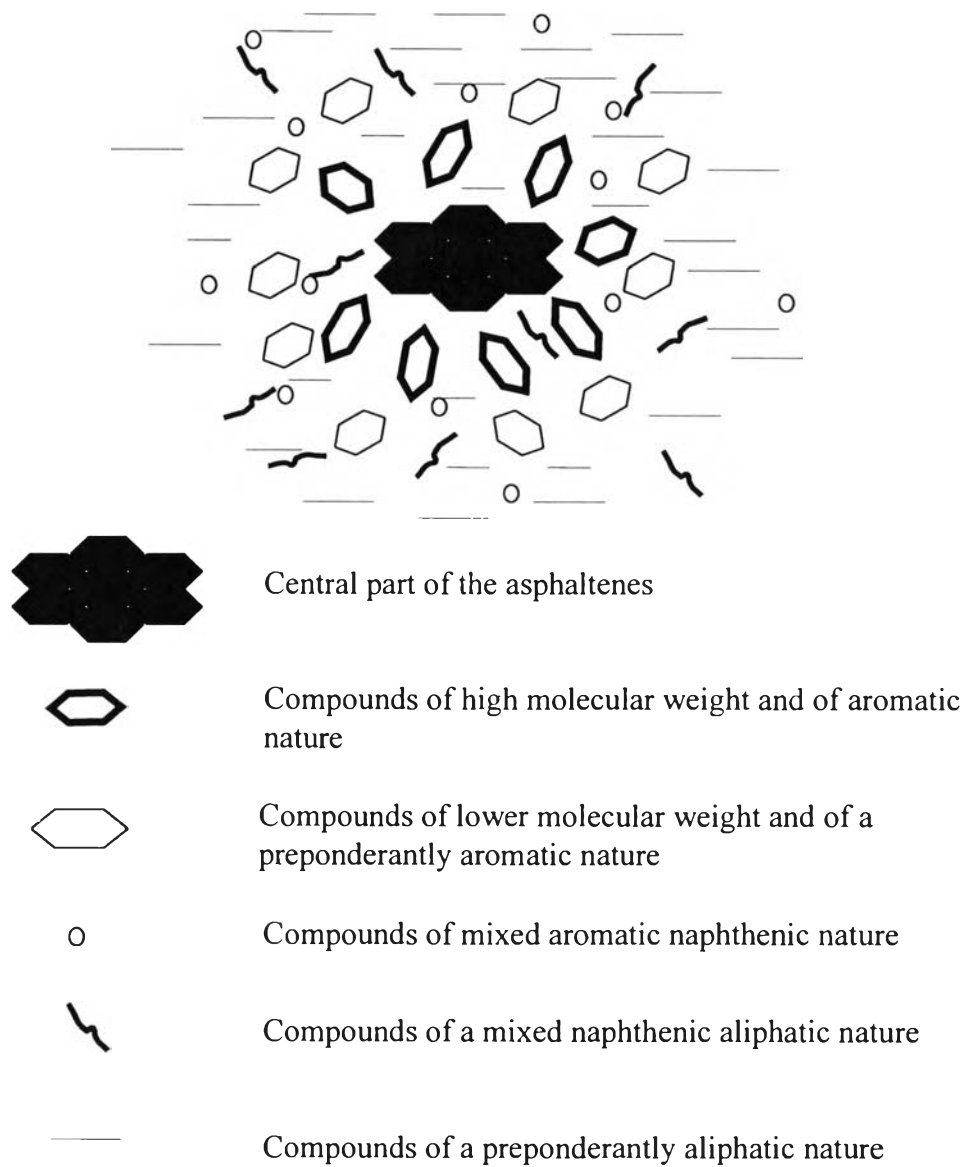


Figure 2.3 The proposed model for asphaltene-resin complexes (Sheu and Mullins, 1995)

By extending their alkyl tail to the bulk fluid and attaching the more polar part to the asphaltene core, the asphaltene can be dispersed in crude.

Once the resins are removed from the asphaltene, it can be no longer stabilized and hence precipitates out of crude.

2.3 Possible Origin and Porphyrin Structures of Asphaltenes

It is believed that asphaltenes are the byproduct of complex hetero-atomic aromatic macro-cyclic structures polymerized through sulfide linkages, as shown in Figure 2.3 (Becker, 1997). Porphyrin structures are important portion in some asphaltenes (Sheu and Mullins, 1995). The porphyrin ring is typically found in nature such as chlorophylls of green plant cells. It is possible for porphyrin to condense with other electrophile and result in the several repeating porphyrin units which are high molecular weight and high viscosity (Becker, 1997).

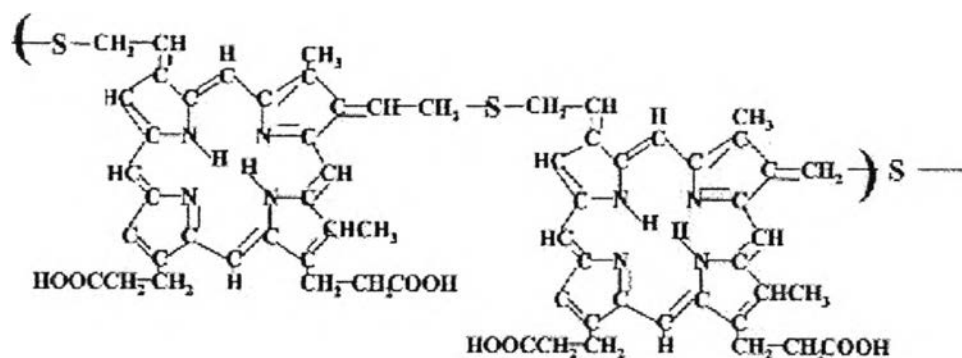


Figure 2.4 Possible product from polycondensation reaction (Becker, 1997)

2.4 Electrostatic Behavior of Asphaltenes

Because of the high degree of delocalized electron associated with asphaltenes, maltenes, and resins, it results in a relatively high charge dispersal effect being negative. These negativity charges can make the asphaltenes being disrupted by electronic forces derived from magnetically induced frictional charges. They are created by their motion with respect to an electron-rich sink such as pipe wall or other asphaltene molecules. The

electrostatic behavior of asphaltenes is considered as one of the reason for destabilization of asphaltenes (Becker, 1997).

2.5 Asphaltenes Flocculation and Deposition

In normal conditions, asphaltenes and other compounds in crude oil are mutually stabilized. Upon variations in pressure, temperature, or composition, the asphaltenes and/or other heavy molecules may separate out either in the form of another liquid phase or solid precipitate. Asphaltenes can be aggregated (or polymerized) which are considered to be irreversible deposits and insoluble in crude oil (Kawanaka, 1991). Flow regime, wall and electrokinetic effect are also responsible for the asphaltenes deposition (Mansoori, 1997). Several studies have been attempted for modeling of asphaltenes stability in crude oil. One of accepted model is to propose that asphaltenes are dispersed by resin. The degree of dispersion depends on the aromaticity and the chemical composition of crude oil (Mansoori, 1997).

2.6 Asphaltenes Dissolution using Amphiphile/Alkane Solution

Aromatic solvents such as toluene and xylene have been used to dissolve asphaltenes deposits because of its effectiveness, availability, and low cost. As increasing the environmental concern, attempts have been done to find other solvents which are not hazardous to environment as aromatic solvents to remove asphaltenes deposits.

Chang and Fogler (1994b) studied the asphaltene-amphiphile interaction and the stability behavior of asphaltenes in amphiphile/alkane solutions by using alkylbenzene-derived amphiphiles. Figure 2.5 shows the chemical structure of alkylbenzene-derived amphiphiles. Dodecylbenzenesulfonic acid in heptane showed the most effective solvent. According to the proposed model of asphaltenes stabilization by resin, dodecylbenzenesulfonic acid acts like a resin in stabilizing asphaltenes. By

attaching sulfonic head to asphaltenes, dodecyl group will create a steric hindrance around asphaltenes molecules and prevent asphaltenes to aggregate.

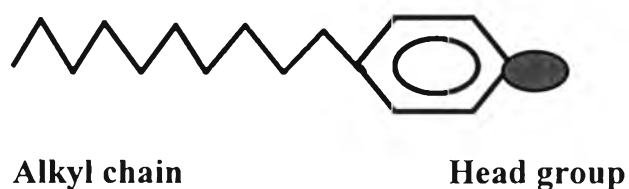


Figure 2.5 Schematic of the chemical structure of alkylbenzene derived amphiphiles

2.7 Study of Asphaltenes through Fractionation

Due to the sources specific character of asphaltenes, the study scope of asphaltenes is limited. In order to specify a universal mean for asphaltenes from a number of difference sources, the fractionation method using polarity difference was then proposed (Nalwaya *et al.*, 1999). A study of fractionation on Mobil crude by dissolving asphaltenes in binary solvent of methylenechloride and pentane was carried out (Nalwaya *et al.*, 1999). By increasing the ratio of pentane to methylenechloride step by step, asphaltenes fractions are obtained. It is clear that the asphaltenes fractions obtained at low pentane to methylenechloride ratio are less polar fraction and vice versa. The physical appearance of the most polar fraction indicates a more ordered structure relative to the least polar fraction which appears to be of a relatively amorphous nature. This method has been proved to be a powerful tool to characterize asphaltenes from various sources (Nalwaya *et al.*, 1999).

From the results of the dissolution studies of each fraction by using both toluene and micellar fluid, DBSA/heptane, it was clearly shown that the higher polar fraction had the lower rate of dissolution and rate constant. It can

be concluded that the higher polar asphaltenes create more severe problem since they are hard to dissolve (Nalwaya *et al.*, 1999).