CHAPTER II
LITERATURE SURVEY

2.1 Asphaltene

Asphaltenes are dark brown to black friable solids, they are defined as the crude oil fractions that are soluble in aromatic solvents (e.g., benzene, toluene, and xylene) but insoluble in aliphatic solvents (e.g., n-pentane). Asphaltenes separated from crude oil using an aliphatic solvent. They include the most polar part and the highest molecular weight species of crude oil. Figure 2.1 shows the fractionation and classification scheme for crude oil fractions. Asphaltenes are generally composed of polyaromatic nuclei carrying aliphatic chains or rings and other elemental including sulfur, oxygen, nitrogen and trace amounts of metal such as iron, vanadium, and nickel (Figure 2.2). These extra elemental atoms (i.e., S, O, N and metal) account for hetero-atoms and variety of polar groups of the asphaltene molecules such as aldehyde, carbonyl, carboxylic acid and amide (James, 1991). Asphaltene isolated from different sources are remarkably constant in terms of ultimate composition. The polyaromatic rings and hetero-atoms of asphaltene tend to associate together through electron donor-acceptor and hydrogen-bonding. On the other hand, asphaltene molecules may perform acid-base interactions as well as π-π orbital associations to form micellar-like aggregates. Resin, the lighter neutral polar component in crude oil, may appear within the asphaltene fraction by adsorption onto the asphaltenes from the supernatant liquid and can be released by re-precipitation in the correct manner. (Yan, 1997)

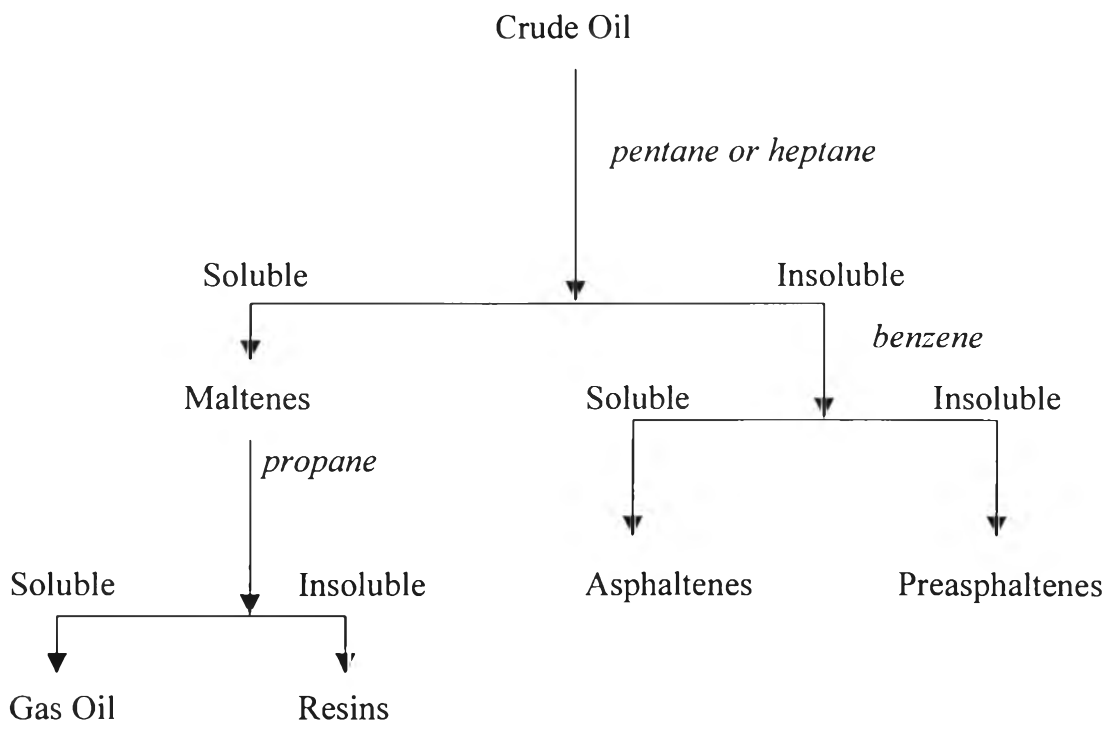

Figure 2.1 Fractionation and classification scheme for crude oil fractions (Gonzalez et. al, 1991).

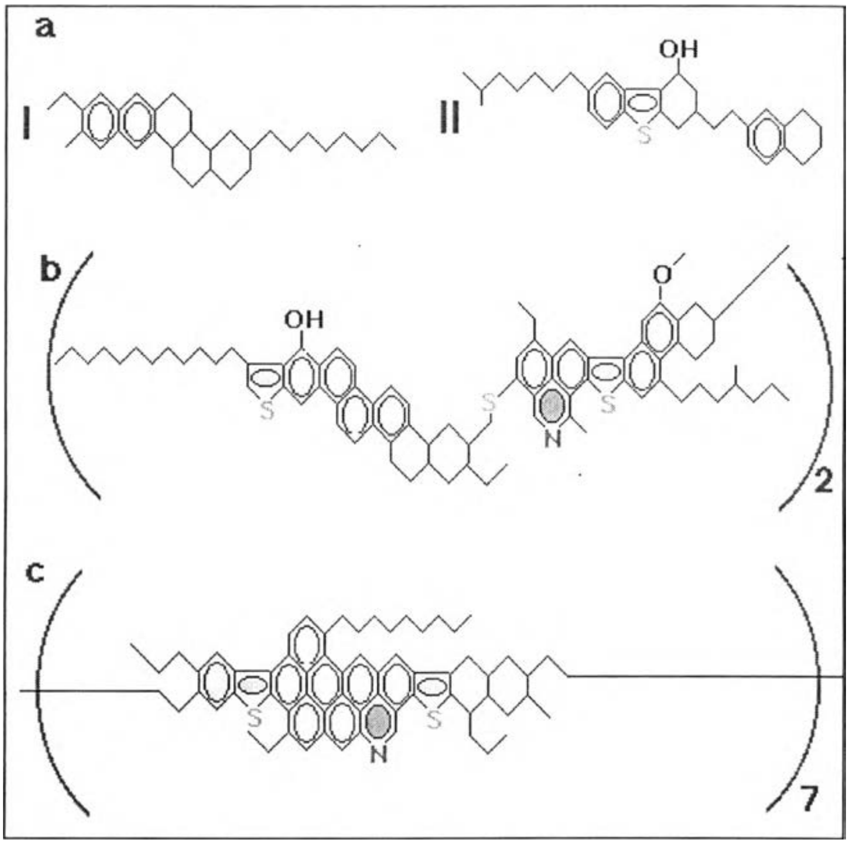

Figure 2.2 Hypothetical structures for the fractions of Athabasca tar-sand bitumen and petroleum (a) resin fraction (b) asphaltene fraction of tar-sand bitumen (c) asphaltene fraction of petroleum bitumen (Suzuki, 1982).

The asphaltene dispersion is mainly attributable to the resin. Because resin molecules contain various polar groups, as asphaltene (the degree of aromaticity of and the proportion of hetero elements in the resin), appear to play an important role in the ability of these materials to bring solubility of asphaltene in oil. It was found that once resin is removed from crude by the method of adsorption chromatography, the remaining oil can no longer solubilize asphaltenes. It has been proposed that resins are essential to the peptization of asphaltenes because they attach to asphaltene micelles with their polar groups and stretch their aliphaltic groups outwards to form a steric-stabilization layer around asphaltene (Figure 2.3). The interactions between asphaltenes and resins have been identified qualitatively using various methods, such as infrared spectroscopy. However, it is extremely difficult to quantify the interaction between asphaltenes and resins because both species contain a distribution of molecules with complex chemical structures (Chang and Fogler, 1994).

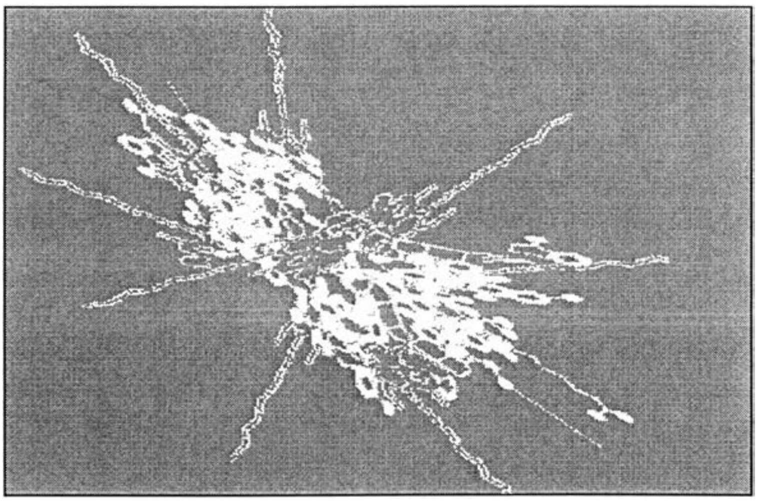

Figure 2.3 Steric-colloid formation of flocculated asphaltenes with resins (Mansoori, 1997).

2.2 Asphaltene Flocculation and Deposition

It is generally accepted that asphaltenes flocculation may take place because of temperature, pressure and composition changes or electrokinetic effects(Leontaritis, 1989). In the case of normal reservoir production, no significant changes in temperature are encountered. In general, pressure drop is accepted to act in the way that inhibits asphaltene flocculation. Consequently, only two dominant mechanisms of asphaltenes flocculation may be considered likely to occur in the reservoir, by composition change and/or by electrokinetic effects(Chang and Fogler, 1994).

2.2.1 Flocculation Due to Composition Changes

Two common ways that the composition of a reservoir fluid (deep in the reservoir matrix) changes, are by normal depletion during which the lighter components of the reservoir fluid are produced in higher proportion (i.e., during primary production by dissolved gas drive) and injection of fluids for enhanced oil recovery.

2.2.2 Flocculation Due to Electrokinetic Effects

The opposing electrical charges are overcome by van der Waal-London attractive (dispersion type) forces and/or, second, generation of the streaming potential due to flow (or application of an external potential) large enough to neutralize the electrical charges and disturb the force balance between the micelles thus causing them to flocculate (Leontaritis, 1989).

2.3 Asphaltic Sludge Precipitation

Formation damage caused by the precipitation of asphaltic sludge when crude oil is contacted by acid is a serious problem after acidizing treatments. The asphaltene will flocculate and precipitate from the crude oil. The asphaltene micelles may depeptize by any chemical, electrical, or mechanical means. In the presence of strong acids such as hydrochloric acid, the colloidal dispersions are destabilized causing the formation of asphaltene precipitate (sludge form) and rigid film emulsion. Weaker acids, such as acetic acid, do not cause significant sludge precipitation. Sludge precipitation has been found to increase dramatically with acid concentration. Sludge precipitation may be due to oxidative polymerization processes in the resin layer. Ferrous iron also contributes on asphaltic sludge precipitation but to a considerably less extent than ferric iron (Brezinski, 1996).

The formation of asphaltic sludge and rigid film emulsions can lead to partial or complete plugging of the formation after an acidizing treatment. While this damage can be removed from the tubing and casings by aromatic solvents, it is extremely difficult to remove from a formation. This difficulty is due to the inability to inject fluids into the formation such that they can contact the sludge particles. Various additives can be used to control sludge precipitation, such as acid corrosion inhibitors, anti-sludge agents, iron reducing agents (to convert ferric iron to the less damaging ferrous iron) along with other additives, such as mutual solvent, wetting agents, and iron chelating agents. These additive can be costly and require testing to ensure compatibility of the various components as well as their effectiveness for prevention of asphaltic sludge precipitation (Jacobs, 1989).

For example, in Venezuela the formation of heavy organics (asphaltic sludges) after shutting in a well temporarily and/or stimulation treatment by acid has resulted a very serious problem (Mansoori, 1997).

2.4 Iron

Dissolved or soluble iron compounds in stimulation fluids can promote unwanted reactions with acids, formation waters, and crude oils. Although some sources of soluble iron exist naturally in the formation, usually the iron source is introduced into the well during drilling and completion operations. This introduction may occur by the addition of raw acid or the placement of tubular goods into the wellbore. Natural sources are from the formation of deposits containing soluble iron in their mineralogical make-up and in the interstitial water of the matrix. Raw acid which is used in stimulation operation may contain iron in the form of the ferric ion (Fe^{3+}). A chemical reactions between HCl and hematite, and HCl and magnetite are respectively (Brezinski, 1996).

$$Fe_2O_3 + 6HCl \rightarrow 2Fe^{3+} + 6Cl^- + 3H_2O$$

$$Fe_3O_4 + 8HCl \rightarrow 2Fe^{3+} + Fe^{2+} + 8Cl^- + 4H_2O$$

Iron concentration in raw acid can vary from zero ppm. (colorless, clear liquid) to several hundred ppm. (yellow to yellow-orange color).

The formation of asphaltic sludge precipitates during acidizing operation, especially in the presence of Fe^{2+} and Fe^{3+} ions, has become more widely recognized over the crude of Western Canada such as the Beaverhill Lake crude, in Alaska and California, as well as in the San Andres crude of West Texas and the Smackover crude of Mississipi (Brezinski, 1996 and Jacobs, 1989).