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Mathematical Modeling of Asphaltene Precipitation: A Review

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Abstract**—**In the Enhanced Oil Recovery (EOR) method, use of Carbon dioxide flooding whereby CO_2 is injected into an oil reservoir to increase output when extracting oil resulted significant recovery worldwide. The carbon dioxide function as a pressurizing agent when mixed into the underground crude oil will reduce its viscosity and will enable a rapid oil flow. Despite the CO_2's advantage in the oil recovery, it may result to asphaltene precipitation a problem that will cause the reduction of oil produced from oil wells. In severe cases, asphaltene precipitation can cause costly blockages in oil pipes and machinery. This paper presents reviews of several studies done on mathematical modeling of asphaltene precipitation. The synthesized result from several researches done on this topic can be used as guide in order to better understand asphaltene precipitation. Likewise, this can be used as initial reference for students, and new researchers doing study on asphaltene precipitation.

Keywords**—**Asphaltene precipitation, crude oil, carbon dioxide flooding, enhanced oil recovery.

I. Introduction

CRUDE oil or commonly called petroleum is a liquid found within the earth and formed naturally through heating and compression of the fossil of animals and plants over a long period of times [1]. It is comprised of hydrocarbons, organic compounds and small amounts of metal. While hydrocarbons are usually its primary component their composition can vary from 50%-97% depending on the type of crude oil and how it was extracted. Organic compounds combining nitrogen, oxygen, and sulfur typically make up between 6%-10% of crude oil while metals such as copper, nickel, vanadium and iron account for less than 1% composition [2]. It is yellow or black in color and can either exist in liquid or solid state [1]. Since crude oil is extracted from different geographical locations all over the world it has different viscosity and appearance. It is graded according to its API gravity which is a measure of how heavy or light a liquid petroleum is as compared to water. The classifications of crude oil are light, medium, heavy and extra heavy as in Table I with the API gravity [3]. This is based on density at 15.6^oC [4]. Also, it can be classified based on the sulfur content such as 'sweet' crude with low content of sulfur, less than 0.5% and 'sour' crude with high content of sulfur greater than 0.5%. In terms of price, light 'sweet' crude is more expensive than heavy 'sour' crude because it requires less processing and produces a slate of products with a greater percentage of value-added products such as gasoline, diesel and aviation fuel. Heavier, sourer crude typically sells at a discount to lighter sweeter grades because it produces a greater percentage of lower value-added products with simple distillation and requires additional processing to produce lighter products [4].

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TABLE I
Classifications of Crude Oil according to API Gravity [3]

No.	Type	API Gravity (^{o})	Density (kg/m^3)
1	Light	>31.1^o	<870.0
2	Medium	Between 22.3^0 - 31.1^o	870-920
3	Heavy	<22.3^o	920-1000
4	Extra heavy	Below 10.0^o	>1000

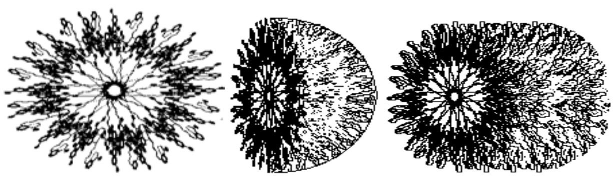
The oil price increase and clamor for petroleum outputs as energy source heightened the effort to lengthen the life of reservoirs. With the oil recovery methods of primary and secondary, only about 1/3 of the stocked oil in place can be regained [5] hence; enhanced oil recovery of oil has been used. During the enhanced oil recovery, more than thirty to sixty percent of the reservoir's originally stored oil can be withdrawn as compared to twenty to forty percent using recovery methods of primary and secondary [6]. EOR is applied to aging oil fields and Carbon dioxide (CO_2) miscible flooding was found to be the most accessible process for this field [7]. The injection of carbon dioxide gas is next only to steam flooding which significantly resulted recovery worldwide. The injected fluids increase the natural energy of the reservoir to displace the remaining oil towards the producing well due to interaction between the injected fluid and the reservoir rock oil system which make a suitable condition for oil recovery. However, these might result in oil swelling interfacial tension and decreasing oil viscosity [8]. When Carbon dioxide and reservoir oil mix, multiphase equilibra may exist including the solid phase i.e., asphaltene [9]. Asphaltene itself is not problematic, but asphaltene precipitation is a big concern. Precipitation may happen during different phases of CO_2 flooding.

Asphaltene precipitation is a serious problem in the oils recovery during Carbon dioxide flooding thus affecting large region in the reservoir [10]. It may start from the wellbore, thus formation damage and then may extend over large distances from its origin and tubing plug-up [11].

For better understanding of asphaltene precipitation several research papers were reviewed. The objective of this paper is to sum up the available method in predicting asphaltene through mathematical modeling and to synthesize the results to be used as guide by the students, engineers and new researchers who would like to dwell on this topic.

II. Asphaltenes

Asphaltenes are the non-volatile and polar fraction of petroleum that is insoluble in n-alkenes [9]. It exists in the crude oil predominantly as a dispersion of very small platelets that will easily pass through pore passages as they flow. These asphaltene particles are held as distinct platelets by chemicals that form “micelle” see Fig. 1 principally maltenes and resins [12], [14]. When these micelles are stable, the asphaltene particles are not significant problem, however when chemical or physical interactions cause micelles to break, the particles will agglomerate (stick together) and can plate out on steel or oil reservoir, forming deposits in piping and creating extremely viscous sludges in the oil [13].



(a) (b) (c)

Fig. 1 Various shapes of asphaltene micelle (a) spherical, (b) paraboloid, and (c) cylindrical

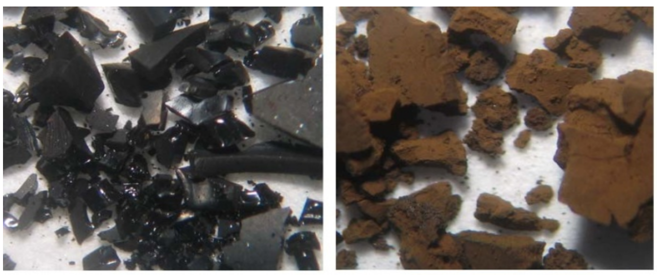


Fig. 2 Left is n-C7 asphaltenes and Right is n-C5 asphaltenes [12]

Asphaltene precipitation happens following three stages (1) the formation of distinct solid particles coming out from the solution could be quite small; (2) flocculation stage where these small solid particles cling together and gets bigger in size; and (3) deposition stage where the particles are so big and later unable to be pushed by the liquid then finally, stick on the surfaces of solid [15], [16].

III. Factors Affecting Asphaltene Precipitation

Srivastava et al. [17] experimented on 3 samples of recombined crude oils to determine asphaltene precipitation using high pressure volume temperature (PVT) instrument at reservoir’s temperature which is between 138^0F and 145^0F. The sample gas and oil separator were recombined to a ratio of gas and oil (GOR) of 107, 129, and 180 scf/bbl respectively. They showed the asphaltene’s destabilization onset happens about 39mol-% to 46mol-% concentration of CO_2.

An evaluation was done by Takahashi et al. [15] regarding precipitation of asphaltene during Carbon dioxide injection using crude oil. They measured the crude oil’s onset pressure using pvt cell with a light scattering method of near infrared. This is done by slowly reducing the mixture’s pressure at each given concentration of CO_2. When the carbon dioxide concentration exceeded 50mol-%, the precipitates of asphaltene became noticeable.

A study done by Verdier et al. on the phase of envelope of their sample crude oil for fixed amount of CO_2 (18 wt%) concluded that when the pressure is higher the asphaltene are more dissolve or meltable. While at higher temperature, the asphaltene’s stability was less [18].

To recreate the CO_2 asphaltene behavior, Gonzales et al. [19], found that the asphaltene’s stability in the crude oil depends on 3 factors and these are pressure, temperature and fluid composition. Any factor’s changes may affect the stability and may incur asphaltene to precipitate [18], [19]. From this study, they used perturbed statistical associating fluid theory (PC-SAFT) equation of state (EoS) which is a simulation tool to find the boundaries of precipitation as liquid-liquid equilibrium. The simulation results agreed with the experimental measurements. The findings showed that CO_2 addition to live oil can control or promote asphaltene to precipitate. This occurrence depended upon certain range value of temperature, pressure, and composition. At constant pressure and composition of live crude oil, adding CO_2 generates the stability of asphaltene below the crossover point which is between 150^0F to 200^0F, whereas above this point, the stability of asphaltene becomes less.

In field situations [20], when pressure in the reservoir is reduced or when light hydrocarbon or other gaseous injectants are introduced, the colloidal suspension may destabilize, resulting in asphaltene and resin molecules precipitating out of oil, thus, forming a separate and visible phase of asphaltenes. Precipitation occurs above the saturation point or bubble-point pressure, reaches a maximum value around the saturation pressure, and decreases as pressure drops further [20].

Alian et al. [21], investigated precipitation of asphaltene from a Malaysian light oil reservoir. Different pressures of injection of CO_2 were used in dynamic flooding experiments to investigate and examine its effect. Study showed that injection of CO_2 in the porous media would change the oil composition and causes asphaltene instability and thus it will precipitate. For continuous increase of CO_2 in the pore volume of injected gas, would result in the more asphaltene precipitation. However, when injection pressure is increased, for CO_2, less asphaltene would deposit. It depicted therefore that in the dynamic flow experiments the presence of asphaltene inside the core samples, porosity and permeability of the porous media would be reduced. The reduction values confirmed the fact that at highest pressure, less asphaltene deposits.

According to Khanifar [22], the initial step to predict and avoid any issues of asphaltene at reservoirs is to evaluate its stability. Since asphaltenes are in equilibrium thermodynamically into solution by colloid state in reservoir conditions, the change in composition and pressure were found to have bigger effect as compared to temperature on asphaltene precipitation. From thermodynamic equilibrium in solution, precipitation is the formation of separate and visible phase [23]. The occurrence of asphaltene to precipitate is when the pressure of the bubble point reaches the saturation pressure and the precipitation reduces as pressure drops [24]-[28] hence, a decrease in bubble point pressure decreases the amount of the precipitate [29].

IV. Categories of Asphaltene Model

There are three categories of asphaltene models [30]. The first is the molecular solubility method. It is described to be a fluid containing asphaltene as a combination of asphaltene and solvents in liquid state. Its characteristics thermodynamically can be determined using the solution theory of Flory-Huggins (see (1)):

$$\Delta G_m = RT\{n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_1 \varphi_2 \chi_{12}\} \quad (1)$$

where:

n_1 , n_2 - number of moles

ϕ_1 , ϕ_2 - volume fractions of components 1 and 2

χ - solubility parameter

R - gas constant

T - absolute temperature

The energy interaction parameter can be estimated from Hilderbrand's solubility (see (2)) [31]-[33]:

$$\chi = \sqrt{\frac{\Delta H_v - RT}{V_m}} \quad (2)$$

where:

$\Delta H_v - RT$ - heat of vaporization

V_m - molar volume or volume of 1 mole of gas or liquid

The second is based on cubic equation of state (EoS) (see (3)) [34], [35]:

$$\left(p + \frac{a}{V_m{}^2}\right)(V_m - b) = RT \quad (3)$$

where:

a & b - specific constants based on critical properties

$$a = 3p_c V_c{}^2, \quad b = \frac{V_c}{3}, \quad V_m = \frac{V}{n}$$

T - absolute temperature

R - ideal gas constant (8.314472 J/mol-K)

V_c - molar volume at critical point

p_c - pressure at critical point

The models were considered as a crude oil with asphaltene, a mild component solution where the heaviest component is divided into two parts such as (a) non-precipitating *i.e.*, resin micelle that remains in the crude oil and (b) precipitating *i.e.*, resin micelles that form the asphalt phase. In the last category the asphaltenes are considered as molecules. The non-polar Vander Waals interactions and size control the asphaltenes' nature [36]. A revised statistical association fluid theory (SAFT) EOS was used to find the thermodynamic properties [37].

V. Conclusion

This paper presents that asphaltene is a complex in nature and needs to be understood and studied The following conclusions have been reached:

1) Precipitation of asphaltene occurs when there is a change in temperature, pressure and composition of oil.
2) Injection of CO_2 into porous media can cause instability in asphaltene, confirming that the higher the pressure in injecting the CO_2 the lesser asphaltene deposits.
3) Asphaltene's instability occurs at about 39 mol-% to 46 mol-% concentration of carbon dioxide (CO_2) and become noticeable when it exceeds 50 mol-% CO_2.
4) Despite several models were presented, no consensus can be reached regarding asphaltene's behavior but the modeling of asphaltene is a way to estimate or predict its presence in crude oil and knowing this can save money invested for EOR.

Our next task is to characterize sample crude oils by using the Gas Chromatography Mass Spectroscopy (GCMS). Then later, conduct a SARA analysis and perform the PVT experiment using the crude oil samples.

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