

CHARACTERIZATION OF CRUDE OILS AND
ASPHALTENES FOR AL-SHAHEEN FIELD

A Thesis

by

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ABSTRACT

Al Shaheen field is the largest oil producing field in Qatar. It is considered as an important strategic asset for the economic growth of Qatar. Hence, it is crucial for the country to explore and analyze ways that could optimize the development process in this oilfield. Scientists and scholars have not been able to completely segregate the crude oil into individual components. Also, huge variations are found in the chemical composition of crude oil from oilfield to oilfield and from region to region. Hence, there is a need of conducting a focused study for the characterization of crude oil and asphaltenes in the context of Al Shaheen field. It is not possible to use experimental data for analytical purposes due to its large volume and the complexities involved. Hence, the researchers use cubic equations of state to predict the composition and behavior of crude oils in different oilfields. Maersk Oil Qatar is operating Al Shaheen field at present under a 25 year agreement with Qatar Petroleum. The company is using Peng Robinson Equation of State for the characterization of crude oil. This study recommends expanding the match of EOS from C20 plus (currently used by Maersk Oil) to C60 plus extended oil analysis using the Peng-Robinson equation. The new approach is expected to address accuracy problems, if there are any, particularly evident for very heavy crude oils.

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NOMENCLATURE

ai	Coefficient
bi	Coefficient
ci	Coefficient
di	Coefficient
API	Oil API gravity
Bo	Oil formation volume factor
Co	Oil compressibility
M	Molecular weight
n	Number of moles
P	Pressure
Psat	Saturation pressure
R	Gas constant
Rs	Solution gas oil ratio
T	Temperature
t	Inverse reduced temperature
V	Volume
Vy	Vapour phase fraction
Wi	Weight fraction
xi	Oil mole fraction
y	Reduced gas density
yi	gas mole fraction
zi	Reservoir fluid mol fraction
Z	Gas compressibility factor
Greek	
μ_o	Oil viscosity
μ_g	Gas viscosity
γ_o	Oil gravity
γ_g	Gas gravity
ρ	Density

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CHAPTER I

INTRODUCTION

Oil has an extensive use in automobiles, different types of machines, and marine engines. It has a crucial role in energy efficiency and friction reduction of the machines. The use of substandard oil may lead to damaging of engines and malfunctioning of machines. The substandard or used oil may have the presence of hazardous materials. These may include heavy metals and additives. There is a growing concern across the world related to health and safety, and potential environmental contamination. Hence, forensic analysis of oil is essential to guard against these hazards. It has derived the attention of researchers to present methodologies and protocols for the characterization of oil. Yang et al. [1] asserts that a comprehensive analysis of oil is necessary for four major reasons. First, it assists in understanding the chemical and physical nature of oil. Second, it helps in the tracking and the identification of the oil source. Third, it helps in finding the source of contamination. Fourth, it helps in making a differentiation between used and fake products of oil.

Scholars have suggested different spectroscopic techniques for the analysis of oil. These include fluorescence, UV-Vis, near-infrared, and infrared spectroscopy [2]. These methods facilitate rapid and convenient screening of oil samples. They are particularly useful in the circumstances when the need of analysis is urgent and the samples involved are large. The drawback of these techniques is that they are unable to present the component resolution. Information of chemical components becomes embedded in spectra's multiple bands. Other techniques used in the oil analysis include chromatographic data interpretation and oil fingerprinting. These techniques facilitate in identifying profiles and distribution patterns of components

There are numerous components present in the reservoir oil. Most of these components are categorized as not being identifiable. In the composition analysis, single carbon number fractions are used for the presentation of non-identifiable fractions. Lumped fractions are also used for this purpose such as C₇₊ and heptane plus. Due to the non-identification of components, an alternative approach is used for the characterization of reservoir oil. The technique involves matching of experimental phase behavior data such as saturation pressures and liquid densities. For this purpose, equation of state (EOS) is used along with some pseudo components. There has been an extensive focus in the literature on characterizing the reservoir oil using cubic equation of state [2].

Makeen et al. [3] conducted a study for characterizing geochemical features of crude oils. They also analyzed their asphaltene and the associated organic matter. The study was conducted for Fula oilfields Sudan in the Muglad Basin. The study provided valuable data on various aspects of the crude oil. These included depositional environment and the source of input for organic matter. The study also provided information about the correlation between the potential source rocks and the crude oils. The non-biomarker parameters as well as biomarker parameters showed presence of a single oil family in the oilfield. The results showed that Fula oils have low sulfur, moderate API gravity, high wax contents, and moderate contents of trace metal. Similar studies need to be carried out in other regions as there are regional variations found in the chemical composition of crude oils.

Offshore Facilities – Qatar

The origins of petroleum boom can be traced back to the end of World War II. Qatar also enjoyed the social and economic rewards of this boom. The oil exploration activities started in

Qatar in 1930s. Geological survey of Qatar was carried out by British Petroleum in 1931. For a long time, the Dukhan field was the only onshore oilfield. Offshore activity initiated in Qatar in 1952. Shell Company of Qatar (SCQ) received a concession for offshore exploration. The company drilled two appraisal wells. This work was carried out between the two domes of Idd El Shargi. However, a heavy storm destroyed the drilling platform. Drilling was restarted in 1959 on Idd El Shargi's northern dome. The production began in January 1964 in the north field. Since then, there were major discoveries mostly centered on the Halul Island. These included Idd El Shargi fields, Maydan Mahzam fields in 1963, and Bul Hanine fields in 1970. There was also a joint exploration of an offshore field in 1969. The name of the field is Al Banduq field and it is located on the maritime border between Abu Dhabi and Qatar. By 1972, Qatar reached at the position where the production from offshore field surpassed the production of onshore field, i.e. Dukhan field [4].

In 1971, the Qatar National Petroleum Company (QNPC) was established with the mandate of handling the oil operations of the country. Another landmark year was 1973, when the Government of Qatar signed participation agreements with two foreign companies. The first participation agreement was signed with QNPC for the onshore Dukhan field. The second partnership agreement was signed with SCQ for offshore fields. In 1975, the government established Qatar General Petroleum Corporation (QGPC). It resulted in the conclusion of participation agreements with QNPC and SCQ [4]. Another landmark was achieved in the Qatar oil sector in the decade of 80s. The government invited applications from the foreign companies. These applications were invited in relation to the exploration rights for the unexplored areas of the Qatar. Figure 1 shows the recent status of the oil and gas fields of Qatar.

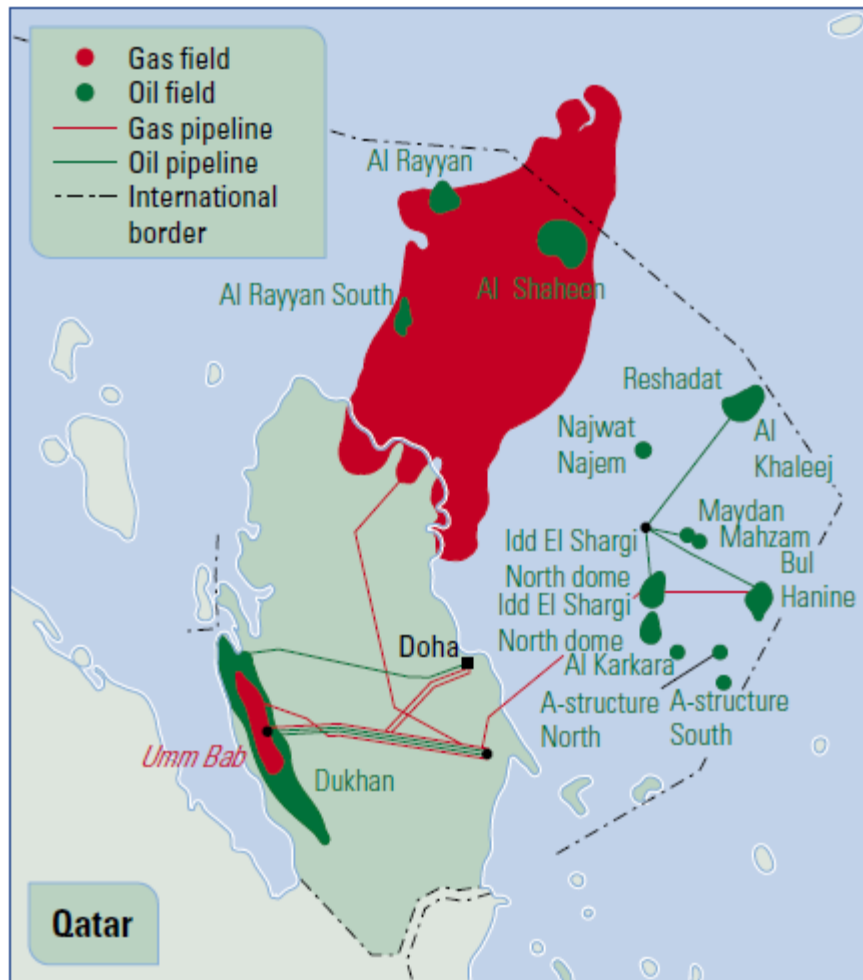


Figure 1: Oil and Gas Fields of Qatar. Reprinted from [4]

Offshore Production Stations

In Qatar, offshore production stations are seven in total (PS1, PS2, PS3, PS4, PS5, PS6, and PS7). The seven offshore production stations operate on eight oil production fields. The details of seven offshore production stations are shown in Table 1.

Table 1: Qatar Oil Production Stations. Reprinted from [5]

Production Station	Description
PS1	<p>Location: North-East of Qatar at a 45 km distance from Al-Rayyan city</p> <p>Oil Production Fields: Idd El Shargi North Dome (Oil production started in 1960) Idd El Shargi South Dome (Oil production started in 1960)</p> <p>Operated by: Occidental Petroleum of Qatar Ltd.</p>
PS2	<p>Location: North-East of Qatar</p> <p>Oil Production Fields: Maydan Mahzam (Oil production started in 1965) Bul Hanine (Oil production started in 1972)</p> <p>Operated by: Qatar Petroleum</p>
PS3	<p>Location: North-East of Qatar</p> <p>Oil Production Fields: Maydan Mahzam (Oil production started in 1965) Bul Hanine (Oil production started in 1972)</p> <p>Operated by: Qatar Petroleum</p>

Table 1 Continued

Production Station	Description
PS4	<p>Location: North-East coast of Qatar</p> <p>Oil Production Field: Al-Shaheen (Oil production started in 1992)</p> <p>Operated by: Maersk Oil Qatar</p>
PS5	<p>Location: 130 km east of the Qatari coast</p> <p>Oil Production Field: Al-Khalij</p> <p>Operated by: Total Exploration and Production Qatar</p>
PS6	<p>Location: North of Qatar in Block 1SE</p> <p>Oil Production Field: Al-Karkara</p> <p>Operated by: Qatar Petroleum Development Company</p>

Table 1 Continued

Production Station	Description
PS7	<p>Location: North-East of Qatar</p> <p>Oil Production Field: Al-Rayyan</p> <p>Operated by: Occidental Petroleum of Qatar Ltd.</p>
	<p>Location: 200 km northwest from Abu Dhabi, 100 km east from Doha</p> <p>Shared Oil Production Field (Shared with UAE): El-Bunduq</p> <p>Operated by: Bunduq Company Ltd.</p>

Production Process of Oil

The term crude oil is used for the unprocessed oil that is exploited from the well. In its crude form, the oil is either semi solid or viscous liquid. Its color is usually brownish black or it may be dark green. Crude oil is a combustible substance. It comprises of different hydrocarbons as well as other elements. These include sulfur, nitrogen, oxygen, and others. After the exploitation of oil from oil well, the next step is to transport the crude oil into oil refineries. It is done through the use of oilers, pipelines, or other methods of transportation. Zhan et al. [6]

argues that classification of crude oils is essential at this stage of transportation. It assists in identifying the types, sources, and properties of crude oils. The classification, in turn, facilitates the subsequent stages of processing. One of the earlier tools of classification was true boiling point (TBP) method. It was a method of batch distillation that was used extensively for characterizing crude oils. Later on, spectroscopy methods were introduced such as mid infrared and near infrared spectroscopy. These methods proved to be effective and fast tools for characterizing crude oils and the associated products [6].

The term oilfield is used for a region that contains numerous oil wells. Crude oil is extracted from the wells, where it is present below the ground. Conventionally, oil fields are located in an area that is far away from the populated area. It is an extremely complicated infrastructure and a challenging task for the oilfield contractor to establish an oilfield. Oilfields that have proven reserves of oil play a key role in the economy of a country. One of the major transportation systems for gas and oil are offshore pipelines. They are differentiated by their operations at elevated pressures and elevated temperatures. Nazari et al. [7] asserts that it is essential to ensure the safety of these pipelines. It necessitates an understanding of the controlling parameters.

Characteristics and Constituents of Crude Oil

There are substantial variations found in the chemical composition of crude oil. The variations in viscosity and color are based on geographical areas and oil fields. There are different chemical compounds present in oil in its raw state. The most prolific among these compounds are the hydrocarbons. A typical percentage of the compounds, as defined by Petroleum UK, are shown in Table 2.

Table 2: Percentage of Key Compounds in Crude Oil. Reprinted from [8]

Compound	Percentage
Carbon	93% to 97%
Hydrogen	10% to 14%
Nitrogen	0.1% to 2%
Oxygen	1% to 1.5%
Sulfur	0.5% to 6%

The characteristics of crude oils are determined by the percentage of four hydrocarbons within the crude oil. These percentages vary based on the oil field and geographic region. A typical range of percentages, provided by Petroleum UK, are shown in Table 3.

Table 3: Percentage Range for each Hydrocarbon in Crude Oil. Reprinted from [8]

Hydrocarbon	Percentage Range
Paraffins	15% to 60%
Napthenes	30% to 60%
Aromatics	3% to 30%
Asphaltenes	Making up the remainder

The percentage of hydrocarbons plays a pivotal role in the chemical composition of crude oil. It gives crude oil a unique compound personality and distinct properties.

Issues Highlighted in Al Shaheen Field

Oil reserves in Al Shaheen field were discovered in the decade of 70s. These reserves were discovered in relation to the appraisal drilling. At that time, the development of Al Shaheen reservoirs was not recommended. The reasons cited for non-recommendation include tight nature and limited thickness of the reservoirs. In 1992, Qatar Petroleum entered into a sharing agreement with Maersk Oil Qatar. The sharing agreement was signed for oil exploration and production at Al Shaheen field. Al Shaheen field is a giant oil field. Oil production from the field started in 1992. The production commenced from different formations. These included a thin sandstone formation and two thin cretaceous carbonate formations [9].

The main targets of Al Shaheen field include Shuaiba carbonate formations, Lower Cretaceous KharaiB B, and Nahr Umr sandstone. KharaiB reservoir is regarded as a carbonate platform. It has a reservoir target of 10 ft and a thickness of 80 ft. Shuaiba reservoir is regarded as a marginal carbonate platform. It has a reservoir target of 20 ft and a full thickness of 200 ft. Nahr Umr reservoir is regarded as a marginal marine sand platform. It has a target of 5 ft to 10 ft [10].

Al Shaheen field consists of a series of stacked and thin reservoirs. The reservoirs are dominated by tight carbonates. The reservoir sequence also has a sandstone unit. These units vary in their quality. There have been a number of feasibility studies related to the development of Al Shaheen field. The findings of these studies showed discouraging results for well tests. The results were discouraging in the vertical appraisal wells. Due to these results, the development of Al Shaheen field was not deemed feasible. According to the technical experts, the majority of the oil was present in thin carbonates. There had been low permeability in thin carbonates [11].

In Al Shaheen field, different reservoir zones may be distinguished based on the

properties and features. The zones differ in structural context, stratigraphic architecture, and sedimentological/lithological facies composition. In order to derive optimal production from these reservoirs, different development strategies have been proposed. The categorization includes the following reservoir units. The first categorization is the Kharab B and Kharab C reservoirs. They are carbonate ramp systems having low angle. The second categorization is the Shuaiba platform. It is characterized by a high variation in lateral facies. It is attributed to platform to basin transition. The third categorization is Nahr Umr shales and sands. The producing sands are below seismic resolution, thin, and exhibit high lateral facies variability [12].

Frank et al. [13] argues that rock typing and permeability estimation are crucial factors in the context of Al Shaheen Field's Shuaiba carbonate reservoir. They play a pivotal role in the development of geological and petrophysical models. Their study showed linkages of permeability variation with the facies. The situation was further aggravated with a relatively high viscosity of the oil of Al Shaheen field. The vertical wells were not in a position to bear the natural flow of the oil. During the artificial lifts, vertical wells showed very low rate. Also, the hydrocarbon distribution in the crude oil of Al Shaheen field was being directed by non-horizontal fluid contacts [11]. It was due to the fact that, in the liquid phases, there were substantial lateral pressure gradients. This made it a highly challenging task to predict the accumulation extent. There was also another challenge faced in Al Shaheen field. The reservoirs were covering a large area of the field. Hence, the development of the oilfield needed a higher number of platforms. Also, the individual reservoirs were not totally overlaid. They were scattered in different areas.

Brink et al. [14] asserts that there are three major challenges faced in Al Shaheen field.

The first challenge is the large areal extent that is observed for the accumulation. The second challenge is the poor productivity of the vertical well. The third challenge is the requirement of a large number of platform locations. The large number of platforms are required if a conventional approach is pursued in which there are either slant or vertical wells. Hence, their study proposed the development of horizontal and long wells.

Due to these challenges, the new development philosophy of Al Shaheen field focused on horizontal and long wells. These wells were developed either in radial or parallel line drive patterns. The patterns were related to oil producers and alternating water injectors [15]. At present the platform locations of Al Shaheen field are nine in total. It was achieved through the drilling process that involved extended reach wells [14]. There has been continuous extension in the horizontal well length. These have been pushed to the limit that is possible through the use of modern technology.

Issues Addressed by Maersk Oil

Maersk Oil signed a sharing agreement with Qatar authorities in 1992. The agreement was a sharing agreement for exploration and production activities, and it was signed with Qatar Petroleum. With the signing of this agreement, Maersk Oil began to operate oil-bearing reservoir of Al Shaheen field. Experts had stated Al Shaheen field uneconomic. They were of the opinion that its reservoirs are extremely tight. They also mentioned that the reservoirs are stretched across vast distances. Maersk Oil took up the challenge in spite of all these complexities. The company made use of its experience and technology. It has achieved the target of producing more than 1.5 billion barrels of oil from Al Shaheen field. The company is making a significant impact to the economic growth of Qatar. The company has gained the distinction of being the

largest offshore producer of oil in Qatar. The daily production capacity of Al Shaheen field is 300,000 barrels [16]. It accounts for one-third of the daily oil production of Qatar. Maersk Oil is committed to respond to the low oil price environment of today. The company seeks to pursue growth opportunities as well as reduce costs.

The sharing agreement between Maersk Oil of Denmark and Qatar Petroleum will expire in mid-2017. Qatar Petroleum has invited applications from international companies for the development of Al Shaheen field after mid-2017. Maersk Oil has also been invited in this regard. Qatar Petroleum values the potential of Al Shaheen field and treats it as a strategic asset. It views the field as an important asset for the exploitation of Qatar's natural resources. It has mentioned on its website that the new agreement will take into consideration the two crucial factors. The first is the capability of the company to offer the best technological solutions. The second is the ability of the company to provide best financial return to Qatar. Qatar Petroleum is a corporation that is owned by the State of Qatar. It was established in 1974 by Decree Law No. 10 [17].

Composition of Crude Oil

During the past five years, there have been remarkable advancements in the techniques of drilling. These advancements have enhanced the marketability and recoverability of crude oil from the deep sea. There is an increased focus of energy companies on deep water drilling. Deep water drilling is defined as the extraction of oil in the deep sea greater than 150 m. It is becoming a new way of expanding the conventional reserves of oil. The U.S. Department of Energy has estimated increase in offshore oil production by 20 percent during 2011 to 2020 [18]. The increase is being attributed to deposits that are found in the explorations of deep water.

The main constituents in the crude oil are saturated and aromatic hydrocarbons. However,

there is also presence in minor amounts of polar compounds. These include NSOs as well as those compounds that contain metals (V, Ni). Despite the fact that polar compounds are in minor amounts, these compounds have significant impact on production, exploration, and refining processes. Their impacts may be observed in the fouling of refinery catalysts, pollution, formation of deposits, formation of emulsions, and corrosion [19].

The extraction of millions of tons of crude oil is carried out across the world annually. The demand of crude oil is due to the expansion in industries and population. The main constituents in crude oil are aromatic and aliphatic compounds. Their percentage is around 80 to 90 percent [20]. Crude oils also have minor presence of complex compounds such as asphaltenes and resins.

Asphaltenes and resins are regarded as heavy oil components. They play a crucial role on the interfacial tension of aqueous solutions and acidic crude oil. The oil producing countries across the world are facing challenges in oil processing. The challenges are particularly evident for increasingly heavier crudes. The complex composition of the crude oils poses problems in transporting them through pipelines. It is due to the fact that heavier crude oils have high viscosity, low flowability, and low mobility. The situation is further aggravated by the fact that crude oils contain high molecular weight hydrocarbons and asphaltenes. These constituents have a tendency to precipitate in the pipelines. They also function as emulsifiers. As a result, there are formations observed as water-in-oil emulsions. These emulsions further increase the oil viscosity [21]. Hence, the oil producing countries across the world have a dire need of developing a technical solution. The solution should be such that it facilitates the transportation of heavy crude oil and extra heavy crude oil.

In the supply chain of oil and gas, the supply process of crude oil forms a crucial part.

The supply process facilitates the link between the upstream stage and the downstream stage.

The upstream stage refers to the exploration and production of crude oil. The downstream stage refers to the refining and distribution of the derivatives of crude oil. Researchers have estimated that there will be a need in the next two decades to enhance the production of crude oil that is highly viscous [22]. The need will arise because of the declining production of light and conventional middle oil.

Fractionation of Crude Oil

Crude oil is one of the main sources of petroleum besides sand oil and shale oil. The compounds present in crude oil can be categorized into four main classes. These include saturates, aromatics, resins, and asphaltenes. Saturate compounds include alkanes and cycloparafins. Aromatic compounds include mononuclear, dinuclear, and polynuclear hydrocarbons. Resin compounds include amides, sulfoxides, pyridines, thiophenes, carbazoles, and quinolines. Asphaltene compounds refer to the aggregates of extended polyaromatics. They include sulfides, naphthenic acids, fatty acids, and polyhydric phenols [23].

Current and Proposed Equation of State

Peng-Robinson Equation of State (PR-EOS), in its original form, is described in Figure 2 below.

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}$$

where

$$a = a_c \alpha(T)$$

$$b = \frac{0.0778RT_c}{p_c}$$

and

$$a_c = \frac{0.45724R^2T_c^2}{p_c}$$

$$\alpha(T)^{1/2} = 1 + k(1 - T_r^{1/2})$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2$$

Figure 2: Peng-Robinson Equations of State. Reprinted from [24]

In the equations, p denotes the pressure, R denotes the gas constant, and T represents the temperature. v denotes the molar volume, p_c represents the critical pressure, and T_c represents the critical temperature. a and b are constants for the equation of state. $\alpha(t)$ represents temperature dependence in a . T_r denotes the reduced temperature, and ω represents the acentric factor.

Currently, Al Shaheen field is operated by Maersk Oil Qatar. The company is using Peng-Robinson equation of state (EOS). This research aims to expand the match of EOS from C20 plus (currently used by the operating company) to C60 plus extended oil analysis using the Peng-Robinson equation. The new model is expected to address accuracy problems, if there are any, particularly evident for very heavy crude oils. The accuracy of modified Peng Robinson Equation of State is illustrated in Figure below. The figure shows a comparison between modified equation of state and experimental data for four systems of heavy hydrocarbon. These

include C₂₂, C₃₂, C₄₀, and C₆₀. These systems demonstrate the higher values in case of acentric factor ($0.95 < \omega < 2.6$). In these cases, there is an excellent agreement between the experimental results and the calculated results. Figure 3 below shows Exp denotes experimental data and MPR EOS denotes Modified Peng Robinson Equation of State.

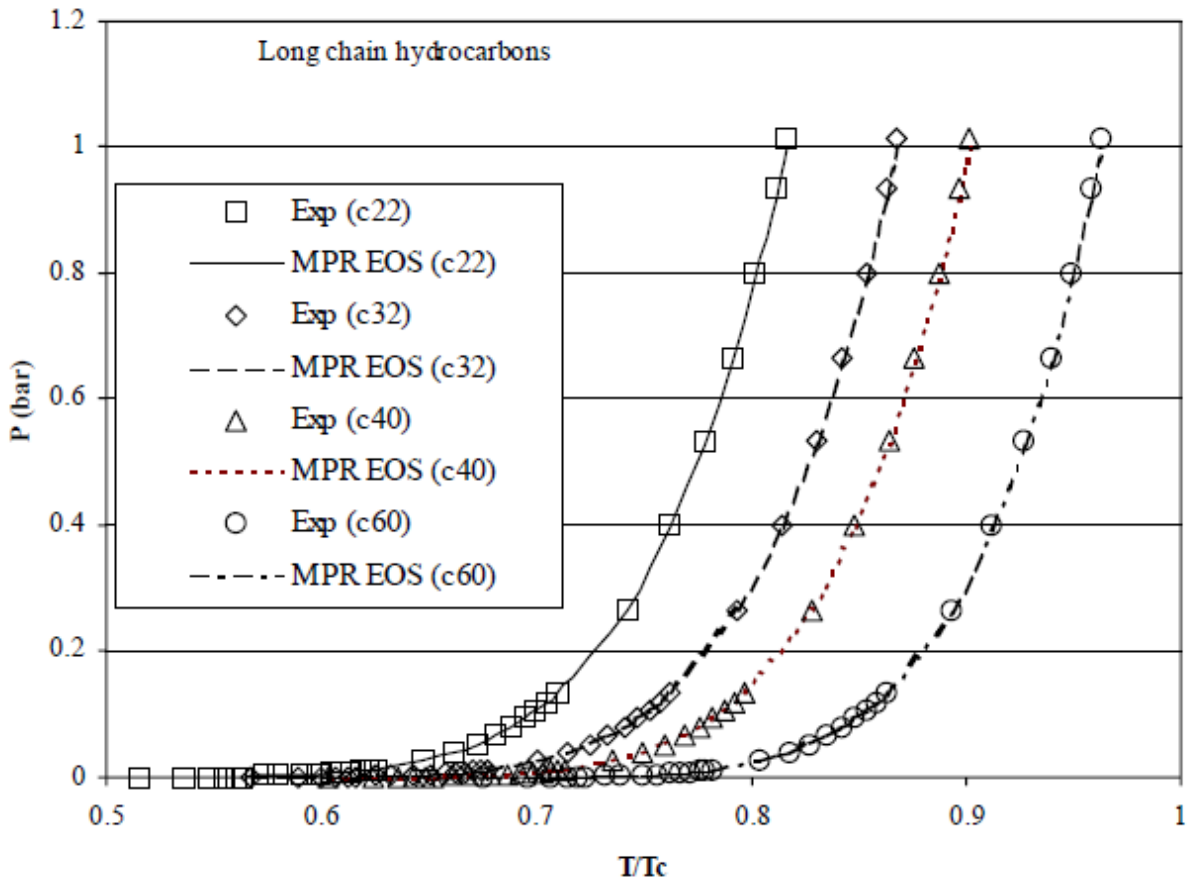


Figure 3: Comparison of Experimental Data with Calculated Results. Reprinted from [25]

Aims and objectives

The aims and objectives of this study are as follows:

1. Characterization of crude oils for Al Shaheen field
2. Characterization of asphaltenes for Al Shaheen field

3. Analyze samples from Al Shaheen field including six crude oil samples, three tar samples, and one condensate sample
4. Analyze variations in the samples in terms of API gravity, Gas Oil Ratio, and the saturation pressure
5. Analyze the samples through GCxGC FID analysis
6. Analyze the samples through APPI FT-ICR MS analysis
7. Analyze the samples through HPLC-2 Quantitation of ring number
8. Analyze the samples through APPI FT-ICR MS analysis of nC5-nC7 asphaltenes dropout distributions
9. Analyze different Enhanced Oil Recovery (EOR) methods
10. Analyze PVT research conducted on 120 datasets to explain the variations
11. Expand the match of EOS from C20 plus (currently used by the operating company) to C60 plus extended oil analysis using the Peng-Robinson equation

Significance of the Study

The transportation and processing of crude oil have become problematic for the oil producing countries of the world. It is due to the high viscosity of heavy crude oils and regional variations found in the chemical composition of crude oil. In the absence of standardization and global standards, the studies focused on specific oilfields and geographical locations are valuable sources of information for researchers, engineers, and others working in oil and gas sector. This study is also significant in this approach as it focuses on a giant oilfield of Al Shaheen that is one of the largest oilfields of the world. Any steps toward the development and advancement of this field must be backed with comprehensive and thorough analysis of the issue. This study conducts

an in-depth analysis of crude oil and the associated samples of Al Shaheen field. The findings of this study will provide guiding principles and approaches for the operators, management, and officials of Al Shaheen field. The incorporation of latest technologies and methods will increase the productivity of Al Shaheen field, which in turn, will increase the pace of economic growth in Qatar.

Scope of Work

The work will focus on the characterization of six crude oil samples obtained from different locations in the Al Shaheen field to represent the API variation observed. The samples will also include one condensate sample obtained from a test separator and 3 tar samples extracted from core plugs. The scope of work includes a C60 extended analysis of the whole crude oil, tar samples and condensate sample.

The samples collected from Al Shaheen field will undergo several advanced level of analysis. These include GCxGC FID analysis, APPI FT-ICR MS analysis, HPLC-2 Quantitation of ring number, and sulfur distributions from APPI FT-ICR MS analysis of nC5-nC7 asphaltenes dropout distributions. In addition to the discussion of these methods of analysis, the review will also test the current Enhanced Oil Recovery (EOR) methods used in the field in a conceptual simulation model based on water alternate gas injection.

Peng-Robinson Equation of State will be used to predict the pseudo component properties of the soluble and insoluble components. The aim is to provide a better match equation of state to the heavy end components than what is currently available for the field. A sector model composed of two injectors and one producer arranged in a horizontal line-drive pattern will be built to represent a portion of Al Shaheen field.

Definitions of the Key Variables

Crude Oil

Crude oil refers to petroleum in its unrefined or raw form. Crude oil is classified into light, medium, heavy, and extra heavy crude oil based on API gravity. API gravity compares the oil density to water.

Asphaltenes

The characteristics of crude oils are determined by the percentage of four hydrocarbons within the crude oil. These include paraffins, naphthenes, aromatics, and asphaltenes. Asphaltenes are present in the crude oil as microcolloid. They are composed of particles of about 3 nm. Every particle of asphaltene has one or more aromatic sheets. The aromatic sheets are of asphaltene monomers.

Oil Field

The term oilfield is used for a region that contains numerous oil wells. Crude oil is extracted from the wells, where it is present below the ground. Conventionally, oil fields are located in an area that is far away from the populated area.

Onshore Oil Field

Onshore Oil Field is an area where the activity of oil extraction is carried out away from the ocean and under the surface of the earth. Dukhan field is the only onshore oil field in Qatar.

Offshore Oil Field

Offshore oil field is an area where the activity of oil extraction is carried out by developing fixed or floating platforms on the bed of the ocean. Al Shaheen field is an offshore oil field in Qatar.

Equation of State

An equation of state is a thermodynamic equation mentioning the relationship between state variables. Under the given physical conditions, the equation describes the state of matter. Cubic equations of state are specialized equations of state as they can be written as a cubic function of molar volume. Peng Robinson equation of state is an example of cubic equation of state.

CHAPTER II

REVIEW OF THE LITERATURE

Conceptual Framework

This research aims to present the characterization of crude oils and asphaltenes for Al Shaheen field. The conceptual framework of the research takes into consideration the economic, demographic and other specific factors that make the review focused. These are important considerations to identify the areas that need to be explored and assessed in the literature review.

The first important consideration is the importance of crude oil and petroleum sector for the State of Qatar. The economy of Qatar is heavily dependent on oil exports. Hence, studies must be conducted which can provide guidelines and recommendations for proper management of oil reserves for Qatar. Another important consideration is the fact that crude oil cannot be segregated completely into individual constituents. Proper characterization of crude oil makes it possible to get enough information about its chemical composition, which is crucial and pivotal in the organized management of crude oil reservoirs and applying relevant safety and precautionary measures.

The third important point of consideration is that the characterization of crude oil varies from region to region. Past studies that might have addressed the characterization of crude oil cannot be replicated exactly in the context of Qatar, and in particular context of Al Shaheen field. There must be a dedicated and focused research to analyze the properties of crude oil and its fractions such as asphaltenes in the context of Qatar. This research will analyze experimental data of Al Shaheen field of a C60 extended carbon analysis. Samples from Al Shaheen field will include six crude oil samples, 3 tar samples, and one condensate sample. The variations in the properties may be found in the API (American Petroleum Institute) gravity, GOR (Gas Oil

Ratio), and the saturation pressure. This research also analyzes the PVT (Pressure, Volume, Temperature) research which was conducted on 120 datasets to explain the variations.

Currently, Al Shaheen field is operated by Maersk Oil Qatar. The company is using Peng-Robinson equation of state (EOS). This research aims to expand the match of EOS from C20 plus (currently used by the operating company) to C60 plus extended oil analysis using the Peng-Robinson equation. The new model is expected to address accuracy problems, if there are any, particularly evident for very heavy crude oils.

The samples collected from Al Shaheen field will undergo several advanced level of analysis. These include GCxGC FID analysis, APPI FT-ICR MS analysis, HPLC-2 Quantitation of ring number, and sulfur distributions from APPI FT-ICR MS analysis of nC5-nC7 asphaltenes dropout distributions. In addition to the discussion of these methods of analysis, the review will also test the current Enhanced Oil Recovery (EOR) methods used in the field in a conceptual simulation model based on water alternate gas injection.

History of Oil Discovery and Development

The oil and gas fields in the State of Qatar are important strategic assets for the government. The development history of hydrocarbons in the state of Qatar can be summarized into two major phases, which are the phase before 1990 and the phase after 1990. Until 1990, Qatar had five areas of production, four located offshore and one located onshore. The offshore areas consisted of three oil fields and one gas field. The three oil fields are located at BulHanine_MaydanMahzam, Idd El Shargi and Al-Bunduq field, which is a shared field with Abu Dhabi. The giant gas field is located at what is known as the North field. Dukhan field is the only onshore oil field and was regarded as the largest oil field in Qatar. In the after-1990 phase,

there have been numerous discoveries in the offshore areas. As a result, new fields were developed which included Al-Shaheen, Al-Rayyan and Al-Khalij. Further efforts and endeavors enabled Qatar to reach the present state [5].

The State of Qatar is regarded as a high-income economy. The country has one of the largest reserves of oil and natural gas. Qatar is administratively divided into seven municipalities. These include Al Khor, Madinat ash Shamal, Al Daayen, Umm Salal, Al Rayyan, Doha, and Al Wakrah. After the municipalities, the next division is zones. There are total 98 zones in Qatar. For the purpose of oil and gas exploration, Qatar was divided into several blocks. From the perspective of these administrative divisions, Al-Shaheen field is situated in offshore Qatar in Block 5, as shown in Figure 4.



Figure 4: The Location of Al Shaheen Field. Reprinted from [26]

Al Shaheen Field

Al Shaheen field started its production in 1994. The production began from a sandstone formation and two carbonate formations. The sandstone formation is also known as NahrUmr formation and the two carbonate formations are known as Kharaib formation and Shuaiba formation. The development philosophy of the field is focused on effective and efficient positioning of extended reach wells in horizontal direction. The field also implements the process of water injection [9].

Al-Shaheen oil field is located offshore at a distance of 80 km northeast the coast of the State of Qatar. It is operated by a Danish company, Maersk Oil Qatar AS, located at Dhoa, Qatar. The company has a production sharing agreement signed with Qatar Petroleum. Maersk Oil entered into this agreement in 1992. Before the agreement, Al-Shaheen field had been declared uneconomic because of the vast distanced and extremely tight and thin reservoirs. Past studies suggested these issues as major drawbacks in oil processing and refining [27]. However, Maersk Oil took up this challenge and first oil production began just two years after the agreement. Currently, the production of Maersk Oil accounts for almost 40 percent of the daily production of Qatar. Al-Shaheen field has a daily production capacity of 300,000 barrels of oil. During the development of the field, 320 wells were drilled [28].

Maersk Oil Qatar has reached several milestones since the beginning of Al Shaheen field in 1992. During the exploration and appraisal stages of the Al Shaheen field, a well was drilled and oil production was achieved in 1994 and in 1996, a field development plan was permitted to the company. In 1998, Maersk Oil Qatar initiated the first offshore facility. Since then, Al Shaheen field has been in continuous development through various field development plans. In 2001, the company was sanctioned a field development plan for providing additional facilities

and production platforms for gas export pipeline and gas compression. In 2005, the company was permitted another field development plan. The plan aimed a major expansion in the Al Shaheen field infrastructure. The expansion included 15 wellhead and process platforms. It also included 160 water injection and oil production wells. The expansion resulted in the enhancement of Al Shaheen field production to 300,000 bopd. The latest field development for Al-Shaheen was approved in 2012 and another 51 new wells were drilled. According to the plan, the recovery process should be optimized and stability should be attained in the production plateau of the field. The plan also included debottlenecking of current facilities of production [28].

Challenges in Al-Shaheen Field

Al Shaheen field was explored in the 1970s. At that time, the experts were of the opinion that developing the Lower Cretaceous reservoirs was uneconomic. The major issues that had rendered the development project uneconomic were the tight nature, low permeability and limited thickness of the reservoirs. Also, the oil present had a high viscosity. Hence, the vertical wells drilled during that time lacked the capability to sustain the pressure of natural flow and the artificial lifts resulted in very low rates [11]. Another major challenge was that the reservoirs were occupying substantial areas. For carrying out the development work, there was a need of the deployment of numerous platforms. However, these reservoirs were developed in 1992, when the agreement reached with Maersk Oil Qatar and they introduced the horizontal well technology in the field.

SARA Methodology

The presence of natural gas can either be noticed in crude oil or it is found in gas

reservoirs. In the former case, the natural gas is called associated gas, and in the latter case non-associated gas. Associated gas comes out of the solution when there is a release of pressure on the oil. The gas reserves of Qatar mostly comprise of non-associated gas. In 1974, the government of Qatar acquired full control of the hydrocarbon industry. It was manifested by the establishment of Qatar General Petroleum Corporation [27], which is a national oil corporation. The economic development of Qatar is heavily dependent on the proper management of natural gas and oil resources.

There are a variety of ways of division of the crude oil into its constituents; one of them is known as SARA (Saturates, Aromatics, Resins, Asphaltenes). This classification is derived on the basis of the solubility level of different components. Saturates comprise of non-polar paraffin compounds. Aromatics comprise of soluble that are not included in saturates. Resins are polar compounds that are sticky and semi-solid. Asphaltenes are similar to resins; however they differ in their appearance, ring structure, and molecular weight. In the SARA procedure, the first extraction is of asphaltenes. When the crude oil is diluted, asphaltenes are precipitated. An n-alkane such as n-hexane is used for the purpose. The crude oil left after this process is known as maltenes. Afterwards, aromatics, saturates, and resins are eluted through the use of solvents [29]. Fractionation of Crude Oil is shown in Figure 5 below.

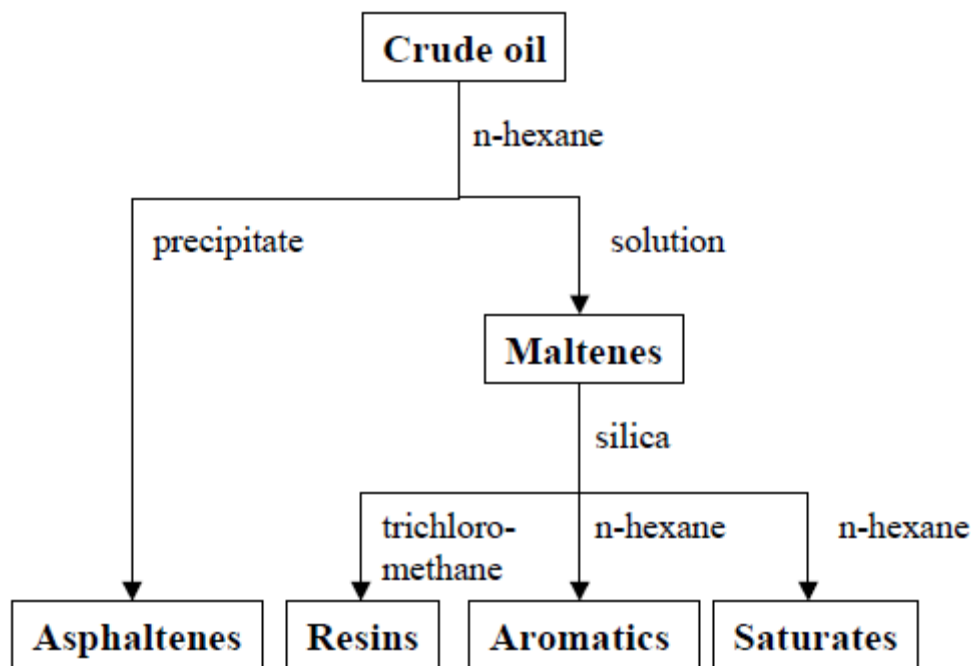


Figure 5: Fractionation of Crude Oil. Reprinted from [30]

The introduction of SARA analysis is attributed to the work of Jewell. Since then, three approaches were introduced to separate crude oil into SARA fractions. The first approach is known as claygel adsorption chromatography method. This method is less preferred because it requires large sample, large quantities of solvents, and is time consuming. The advanced methods fall into two groups. The first group employs methods of High Pressure Liquid Chromatography (HPLC). The issue with this method is that it requires removal of asphaltene fraction before beginning the process of chromatography. The most advanced method uses Thin Layer Chromatography (TLC) [31]. This method does not require removal of asphaltenes before the process of chromatography.

Characterization of Crude Oil

The characterization of crude oil is regarded as an important area in the field of oil refining. The characterization is of crucial importance especially in upstream operations. The conventional method of characterization takes into account the crude oil gravity. However, there is a need to gather additional information to analyze the volume of crude oil in the reservoir and estimate the recoverability of crude oil. There is a great variation in the appearance of crude oil based on its chemical composition. Usually, it is found in dark brown or black appearance. In the reservoir, its presence is conventionally observed along with natural gas. Since gas is lighter than oil, there is a formation of gas cap over the oil. Oil is used as a major source of energy due to its various benefits. For the extraction of crude oil, wells are drilled into the reservoirs of oil.

One of the classifications of crude oil is to classify it as light crude oil, heavy crude oil, and bitumen. Light crude oil is characterized by its low viscosity. It is easier for the light crude oil to flow in pipelines. It contains heteroatoms in lower proportions. Heavy crude oil is characterized with its high viscosity. As a result, enhanced recovery techniques are required to remove heavy crude oil from reservoirs. Heavy crude oil has more heteroatoms and ring systems than light crude oil. When the crude oil reaches a state, where it has a density more than ~ 960 kg/m³, it is termed as bitumen. Bitumen is characterized by extremely high viscosity. Its presence is observed along with clay, sand, and water. The mixture is often termed as oil sands. Figure 6 shows snapshots of light crude oil, heavy crude oil, and bitumen [32].

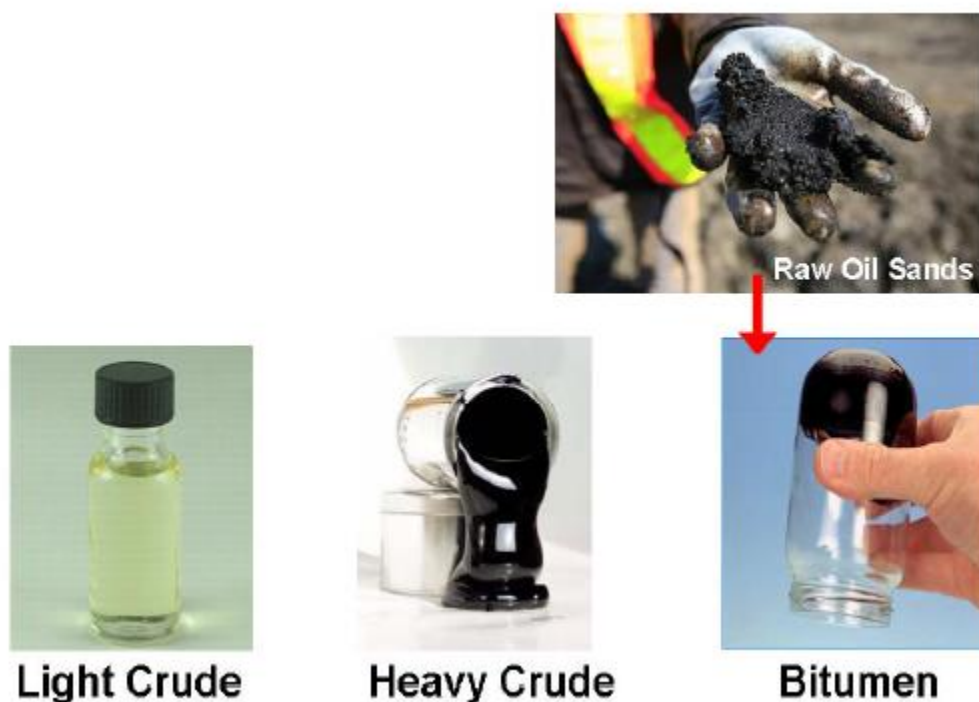


Figure 6: Images of Light/Heavy Crude Oil and Bitumen. Reprinted from [32]

Characterization of Asphaltenes

There are several factors that play a key role in the intrinsic composition of asphaltene. Muhammad [33] mentions three criteria for asphaltenes. The first criterion is its precipitation from oil and solubility in toluene. The second criterion is its capability to be filtered at 1 μm to 1.5 μm . The third criterion is that there are no contributions present in asphaltenes from waxes and resins. It has been established by scholars that asphaltenes precipitate out in presence of non-polar solvents. Hence, the characteristics of asphaltenes are heavily dependent on the quantity and type of solvent.

When asphaltenes are separated through the process of precipitation, a complex mixture of components is obtained. The complete molecular analysis of asphaltenes has not been achieved yet because of its tendency to self-aggregate. Asphaltenes are enriched with ring

groups. There are also bridges found between the clusters that enable larger molecules. It also results in extreme diversity of composition. In case of asphaltenes, molecular interactions result in forming stable aggregates. These interactions include acid-base interactions, coordination complexes of metals, hydrogen bonding, association of cycloalkyl, alkyl, apolar groups, and aromatic stacking. Asphaltenes are present in the crude oil as microcolloid. They are composed of particles of about 3 nm. Every particle of asphaltene has one or more aromatic sheets. The aromatic sheets are of asphaltene monomers. They have adsorbed resins that function as surfactants. Their role is to enable stability in the colloidal suspension. The bonding that keeps these molecules together includes hydrogen bonds, π bonds, and electron donor acceptor bonds. The most important characteristic of asphaltenes is their tendency to self-aggregate. This tendency is considered as a major problem during the processing phase and refining phase of crude oil. It can cause a number of problems including equipment plugging, formation damage, catalyst deactivation, and affecting the emulsion stability [30].

PVT Properties

Past researches have attempted to study correlations related to PVT (Pressure, Volume, Temperature) properties. Specific patterns and trends can be extracted from these studies, in the chemical composition of crude oils based on different regions [34]. These studies classified regional variations to chemical compositions into the groups of aromatic, naphthenic, and paraffinic. The studies emphasized that since there are regional variations in chemical composition, regional samples of one chemical base may not predict accurately the chemical properties of the crude oils of other regions. Hydrocarbon is also an important attribute in the characterization of crude oil. It is classified primarily based on the molecular structure. Examples

of paraffin hydrocarbons include decane, propane, ethane, and methane.

Crude oil also contains resins and asphaltenes. They are distinguished by their properties of being polar, high-molecular-weight, aromatic ring compounds, and polycyclic. Asphaltenes in their pure form are dry, non-volatile, black powders, and solid. Resins in their pure form are either sticky solids or heavy liquids. Asphaltenes are insoluble in oil; whereas resins are soluble [32]. It has not been possible so far to completely separate crude oil into individual components. However, scientists have been able to identify various components in crude oil. Even with complexities involved in the chemical composition of crude oil, its various properties can be identified using PVT correlations. In PVT lab, scientists employ different instruments to identify the fluid behavior of the reservoir. It is also aimed to analyze the properties from gas and oil samples. The ultimate objective of this exercise is to simulate the condition of the reservoir and the condition of the surface during production. The central point of consideration in PVT analysis is to observe the evolution of gas from the oil when the pressure reaches below the bubble point. Researchers denote these processes with two terminologies; differential liberation and flash liberation. In flash liberation, although the gas comes out of oil due to a sudden drop in pressure, yet it remains confined with the remaining oil. In differential liberation, gas comes out of solution due to a gradual decrease in pressure, and is permanently removed from the oil. It is observed that there is a domination of flash liberation when the pressure in the reservoir is reduced below the bubble point. The tests of flash and differential liberation are useful in the establishment of parameters related to the surface volumes.

PVT properties are used to denote the volumetric behavior of a reservoir fluid. It is expressed as a function of temperature and pressure. PVT properties are useful because of the variations in the chemical composition of crude oil from one region to another region. These

properties are important indicators for petroleum engineers and geophysicists. The properties are utilized in inflow performance calculations, material balance calculations, determination of reserve estimates, and well log analysis. These properties are considered through experimental measurements on crude oil samples by researchers. If experimental measurements are not available for PVT properties, an alternate approach is recommended. The approach recommends using of empirically derived correlation or EOS (Equation of State) [35]. Theoretical computations are also called oil system correlations together. The important parameters in these calculations include pressure, temperature, solubility, gas gravity, and API gravity. Often, correlations have not been found reliable because of their dependence on the range of data and the geographical area.

API Gravity

The API (American Petroleum Institute) gravity evaluates the lightness/heaviness of petroleum liquid in relation to water. If the value of API gravity comes out to be larger than 10, liquid petroleum is considered as lighter and it is predicted that it will float on water. If the value of API gravity comes out to be less than 10, liquid petroleum is considered as heavier and it is predicted that it will sink in water. API gravity has gained the distinction of being the preferred gravity scale in the petroleum sector [36]. Its formula is as follows:

$$\gamma_{API} = \frac{141.5}{\gamma_o} - 131.5.$$

Where, γ_{API} refers to Degrees API gravity and γ_o refers to Specific Gravity (at 60°F). From the equation, it is evident that lower specific gravity results in higher API gravity. The U.S. National Bureau of Standards recognized Baume scale in 1916. It was recognized as the standard

for the evaluation of specific gravity. However, later on, errors were reported in temperature and salinity controls. Due to these errors, variations were found for these values with the published values. It led to the manufacturing and distribution of hydrometers in the U.S. These hydrometers had a modulus of 141.5. In comparison, Baume scale had a modulus of 140. Due to the variations between these two moduli, the American Petroleum Institute presented a remedy. The remedy was the establishment of API gravity scale. For obtaining the value of API gravity, first the specific gravity needs to be measured. The specific gravity can be measured using the oscillating U-tube method or the hydrometer.

API (American Petroleum Institute) is a major trade association in the United States. The association works in the natural gas and oil industry. It works for the establishment of standards for refinement, production, and distribution of oil products. The most famous standard introduced by API is the standard for evaluating oil density, which is popularly known as API gravity. Its formula also involves a variable specific gravity. Specific gravity provides density of oil in relation to water. API gravity is similar in concept to specific gravity. The only difference is in calculation that ensures consistency in measurement. It works on the principle that light crude oil is better than heavy crude oil because dense oil has large quantity of hydrocarbons. There are not units for the values of API gravity. However, the usual approach is to denote them in degrees. API gravity of 10 is considered equivalent to water. Due to this reason, it is stated that for any values of API gravity above 10, the oil will float on water. The oil will sink in water if it has API gravity value of less than 10. On the basis of the API gravity values, crude oils are classified as light crude oil, medium crude oil, heavy crude oil, and extra heavy crude oil. The crucial importance of API gravity lies in the fact that the weight of the oil determines its value in the market. American Petroleum Institute provides the classification as follows [37]. Extra heavy

crude oils are the one that have the API gravity values of less than 10. Heavy crude oils are those that have the API gravity values between 10 and 22.2. Medium crude oils are those that have the API gravity values between 22.3 and 31.1. Light crude oils are those that have the API gravity values greater than 31.1.

Crude Oil Processing and Refining

The composition of crude oil can be seen from the elemental, as well as, fractional perspective. From the elemental perspective, its constituents include carbon, hydrogen, nitrogen, oxygen, sulfur, nickel, and vanadium. From fractional perspective, the constituents include asphaltenes, resins, aromatics, and saturates. The refining process of crude oil can be divided into three categories. The first stage is separation that involves the division of feedstock into different fractions. The second stage is conversion, which involves altering of the molecules of feedstock so that viable products could be formed. The third stage is finishing. It involves the purification of the product stream [32].

The reserves of petroleum across the world are evolving continuously, and going towards heavier crude oils. Crude oils are becoming rich with heteroatomic content. Recent studies emphasize the need of effective and efficient processing of heavy petroleum [38]. Heavy petroleum is regarded as a mixture composed of numerous hydrocarbon molecules. Hydrocarbon molecules have different aromatic rings. There is a direct effect on all processes of oil refinery of the chemical composition of petroleum. Hence, a high importance is placed on the compositional information of crude oil for effective petrochemical processing.

Despite the fact that crude oil contains numerous hydrocarbon molecules, there are variations in the proportions of elements found in crude oil. These variations are prevalent in the

highly asphaltenic crudes, as well as, the lightest crude oils. There is an existence of carbon content in the range of 83 percent to 87 percent. The presence of hydrogen content is in the range of 10 percent to 14 percent. Other elements such as oxygen, nitrogen, metals, and sulfur are also present in crude oils with variations. The complexity in the chemical composition of crude oil makes its characterization difficult by the individual molecular types. Elemental analysis is also not preferred due to the constancy of the elemental composition. The preferred approach that is usually applied is hydrocarbon group type analysis [30]. It requires information related to the distribution of hydrocarbons' structural classes. One of the most famous examples of this type of group analysis is SARA separation. This analysis divides the crude oils into four classes. The classes are made on the basis of polarity and solubility. The four classes include saturates, aromatics, resins, and asphaltenes. Figure 7 exhibits a hypothetical asphaltene molecule.

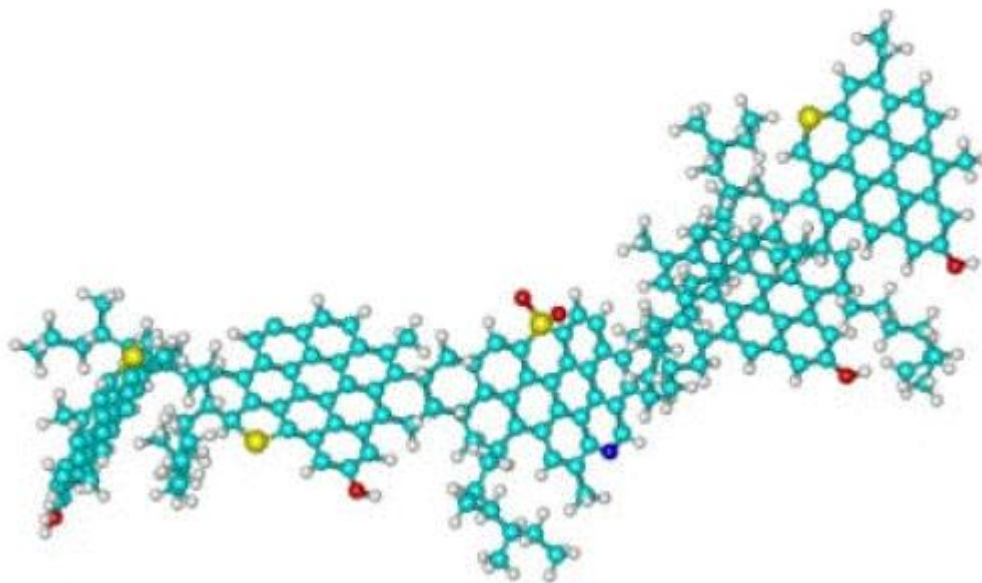


Figure 7: Asphaltene Molecular Representation. Reprinted from [30]

Analytical Methods

GC x GC – FID

GC x GC – FID is a comprehensive analysis related to gas chromatography. It is considered a powerful technique of analysis when complex samples are involved in the analysis. The analysis is useful for the quantification of individual chemical components. The technique was introduced by J.B. Phillips in 1991, and is a good replacement of the conventional technique. The analysis enhances the separation capacity, detectability, and sensitivity using modified form of standard gas chromatograph [39].

FT-ICR

Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry has the benefit of providing higher accuracy in mass measurement and mass resolution than other mass analyzers. The technique is considered powerful because of being effective in dealing complex samples. The technique is useful in determining the elemental compositions in highly complex mixtures such as crude oils. The development of FT-ICR mass spectrometry theory is attributed to Melvin Comisarow and Alan Marshall. They collected first mass spectrum in 1973 on methane ions [40].

HPLC

HPLC fluorescence detection has become a standard method in the analysis where there is a requirement of high selectivity and high sensitivity. The technique is used widely for samples that are associated with high impurities. In its advanced form, the technique facilitates a temperature controlled cell that ensures stability in the analysis during temperature fluctuations.

The technique also has benefits of minimal capital equipment and ease of analysis [41].

Peng-Robinson Model

In the chemical industry, it is essential to predict the phase equilibrium of mixtures accurately. It is useful in the optimization and design of separation processes. Ideally, experiments should be conducted for obtaining accurate data. However, in the real world, the researchers find the experiments expensive and time consuming. It raises the need of developing models that could give reliable and accurate prediction of mixtures. For this purpose, the chemical industry extensively uses cubic equations of state such as Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) [42]. These equations are used to perform process design calculations and reservoir simulations due to their characteristics of being efficient and simple. Peng-Robinson Equation of State (PR-EOS), in its original form is described Figure 8 below.

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}$$

where

$$a = a_c \alpha(T)$$

$$b = \frac{0.0778RT_c}{p_c}$$

and

$$a_c = \frac{0.45724R^2T_c^2}{p_c}$$

$$\alpha(T)^{1/2} = 1 + k(1 - T_r^{1/2})$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2$$

Figure 8: Peng-Robinson Equations of State.(Original Form) Reprinted from [24]

In the equations, p denotes the pressure, R denotes the gas constant, and T represents the temperature. v denotes the molar volume, p_c represents the critical pressure, and T_c represents the critical temperature. a and b are constants for the equation of state. $\alpha(t)$ represents temperature dependence in a . T_r denotes the reduced temperature, and ω represents the acentric factor.

There have been various efforts to improve the PR-EOS. Gasem et al. [24] mentions that acentric factor dependence is a linear function. Due to this reason, there is no improvement in the predictions of phase behavior through higher order polynomials. Saffari and Zahedi [43] developed a new alpha function for PR-EOS and applied it to natural gas. The optimization of parameters was specifically analyzed in the context of the components of natural gas. In the study, there was a generalization of parameters as a linear function of ω (the acentric factor). The authors compared the results with the original PR-EOS. The comparison showed that there was a good accuracy with the new alpha function. There was an average deviation of 1.42 percent for the components of natural gas.

Cubic equations of state are very help in the simulations of reservoir; however, there have been inaccuracies in the prediction of liquid densities. It is attributed to the binary nature of the parameters. Due to the two-parameter nature, the equation results in a constant factor for critical compressibility. Consequently, there are significant errors, when calculations of liquid phase densities are involved. Some studies recommended three-parameter cubic equations of state. However, it resulted in a larger critical compressibility factor than the actual fluids' value. Other studies suggested a method of volume translation [44]. This approach emphasizes applying translation in the axis of volume. As a result, predictions may be improved without changing the predictions of Vapor Liquid Equilibrium (VLE).

Baseri and Lotfollahi [45] presented a modified PR-EOS for explaining the vapor liquid

equilibrium (VLE). The study was conducted on systems containing salts and water. There were three terms employed in the modified PR-EOS. These included a Margules term, a Born term, and a term used for predicting electrostatic interactions. The comparison of findings with the original PR-EOS showed that the applied mixing rule resulted in a more accurate value of vapor liquid equilibrium. Costa et al. [46] asserts that PR-EOS is a good solution when VLE data is not present in the literature. Conventionally, PR-EOS is used with two-parameter approach along with classical mixing rule (CMR) of van der Waals. However, there is a need of parameter optimization through the use of experimental data.

Literature Summary and Remarks

The literature review focused on the history of oil development and discovery, Al Shaheen field, SARA methodology, characterization of crude oil, characterization of asphaltenes, PVT properties, API gravity, crude oil processing/refining, analytical method, and PR-EOS model.

The review of oil development and discovery history discussed two important phases in the context of Qatar. These are pre and post 1990 eras. It was found that there was a substantial improvement in the development and discovery activities after 1990. It was evident in the addition of offshore fields that also include Al Shaheen field. The review of Al Shaheen field showed that the field is being operated by Maersk Oil Qatar. The company proved successful in running the oil and gas field that had been declared uneconomic by the professionals earlier. The major challenges were related to well structures in relation to oil viscosity and the substantial areas occupied by reservoirs. The literature review also evaluated SARA methodology which divides the crude oil into fractions of saturates, aromatics, resins, and asphaltenes. This

methodology is useful as it provides insight into the chemical composition of crude oil.

The characterization of crude oil was also discussed in relation to light crude oil, heavy crude oil, and bitumen. The major variations in these cases are in the viscosity of the oil. The next topic discussed was the characterization of asphaltenes. It was found that an important characteristic of asphaltene is its tendency to self-aggregate. It can cause a number of problems including equipment plugging, formation damage, catalyst deactivation, and affecting the emulsion stability. The discussion also highlighted the importance of PVT properties. The research of these properties is useful because chemical composition of crude oil varies from region to region. The discussion emphasized that in absence of experimental measurements of PVT properties, Equation of State should be used.

API gravity is also an important indicator in crude oil characterization. It is useful for the evaluation of oil density. Based on the values of API gravity, crude oils are classified as light crude oil, medium crude oil, heavy crude oil, and extra heavy crude oil. The refining process of crude oil can be divided into separation, conversion, and finishing.

The review also discussed analytical methods used in this research. These include GC x GC – FID, FT-ICR, and HPLC. GC x GC – FID analysis is useful for the quantification of individual chemical components. FT-ICR mass spectrometry determines the elemental compositions in crude oils. HPLC technique is used extensively for samples that are associated with high impurities. The review also discussed benefits of PR-EOS model over conventional approach to cubic equations of state. The model was found more reliable and accurate than the conventional approach.

There are major developments in Qatar in the development of oil and gas fields. The scientific and advanced management of these strategic assets require characterization of crude

oils. The chemical composition of crude oil is heavily dependent on regions where the reservoirs are located. Past studies have discussed characterization of crude oils and asphaltenes. However, they have not been conducted in the Al Shaheen field. It creates an element of rethinking that further studies are needed so that the chemical composition specific to Al Shaheen field could be evaluated. So far it has not been possible to segregate crude oil into individual components. Also, the characterizations of crude oils into constituents are not a single one. Instead, many characterizations have been proposed. Past studies have stressed on the utilization of SARA methodology. Hence, this research takes into consideration not only the characterization of crude oil in general, but also one of the fractions of SARA methodology, i.e. asphaltenes. Asphaltenes have the tendency to self-aggregate and they precipitate during the process of fractionation. It is important to research their properties so that a holistic approach could be employed for the characterization of crude oil. Due to the regional variations in chemical composition, it is important to research several terms related to crude oil such as PVT properties and API gravity.

In the light of this research, conventional approach of cubic equations of state (EOS) is not feasible for the proper analysis of crude oils. The Peng-Robinson Equation of State (PR-EOS) will be used in this research to overcome the limitations of traditional approach.

CHAPTER III

RESEARCH METHODOLOGY

Description of Oil Samples (Al Shaheen Field)

Maersk Oil took up the challenge of developing Al Shaheen field since 1992. It started producing oil from this field in 1994. Another landmark project was implementing water injection that was completed in 1996. Al Shaheen field has five producing reservoirs. One of the reservoirs is known as Kharab B reservoir. It started oil production from the very beginning in 1994. Technical experts had declared Al Shaheen field uneconomic due to three major challenges. The first challenge is the large areal extent that is observed for the accumulation. The second challenge is the poor productivity of the vertical well. The third challenge is the requirement of a large number of platform locations [14]. Hence, Maersk Oil took into consideration all these issues in the development of reservoirs. Its development philosophy focused on long horizontal wells. The company opted for radial well patterns for the older wells. It developed parallel line drive patterns for newer wells. The parallel lines pertained to alternating oil producers and water injectors. In the placement of well, care was taken for avoiding fractured regions. The fractured regions may be present in the reservoir within graben zones [47]. The company also authenticated the successful placement of wells. It was ensured through the observation of only few short circuits of water injection and the good water flood performance.

When the PVT properties of the oil of Al Shaheen field are observed, it becomes evident that they show large lateral variations. The API gravities of the oil range from 16 degree to 38 degree. Also, large variations are found in saturation pressures and gas oil ratio (GOR). Scholars have hypothesized that there is an existence of complex fluid variations in the Al Shaheen field [47]. It is attributed to the fact that separate oil pulses charge the reservoir. The charging is

followed by biodegradation and gas influx.

In 2006, a landmark was achieved in the context of Al Shaheen field. Enhanced oil recovering (EOR) study was conducted in this year [47]. The study focused on methods that could enhance the recovery of oil beyond water flooding. The findings of the study showed that four processes could be used to enhance oil recovery from the reservoir. The first of these processes is known as gas injection with CO₂ gases or hydrocarbon. The second of these processes is known as ASP (Alkaline Surfactant Polymer) flooding (Air Injection). The third of these processes is known as in-situ combustion (Chemical Flooding). The fourth process is known as microbial EOR.

Gas injection process was regarded as a promising EOR process. There were two potential benefits in this approach. The first benefit is that the reservoirs have relatively low temperature. The second benefit is that the oil properties of the samples of Al Shaheen field show that the oil favors gas injection. For this purpose, water alternating gas (WAG) injection method may be used. Mogensen et al. [48] implemented successfully a gas injection trial in the carbonate reservoir of Al Shaheen field. There were several important aspects of the gas injection trial. These included prior data gathering, careful well selection, and the attentive daily monitoring. The results were inspiring and the study recommended implementing the process of gas injection as water alternating gas scheme. The authors suggested there is a significant scope in the Al Shaheen field for enhanced oil recovery. The main factors in this respect are improved sweep due to the combined effect of gas and water.

In order to identify the benefits of air injection process, a study was conducted to ascertain the ignition characteristics of Al Shaheen crude oil under reservoir conditions. In the method of air injection, oxidation reactions may occur in two types. The first is known as oxygen

addition reaction. The second is known as bond scission reaction [47]. In oxygen addition reaction, there is a chemical combination of hydrocarbon with molecules of oxygen. The result is a hydrocarbon product that is oxygenated and heavier. In bond scission reaction, hydrocarbon and oxygen react in a traditional combustion. The resultant products are heat, water, and carbon dioxides. The study confirmed that spontaneous ignition in the oil reservoir through air injection is a recommended approach. It results in the improvement of process stability and the simplification of process initiation.

In case of chemical flooding, it needs to be recognized that the injection water in case of Al Shaheen field is sea water. Al Shaheen field is an offshore field. This water is incompatible for using with alkalis such as sodium carbonate, organic alkalis, and sodium metaborate. Hence, the enhanced oil recovery method recommended using a surfactant solution. The surfactant solution can work without alkalis.

In case of microbial EOR, microbial alterations were proposed in interfacial properties. The findings of the study showed that enhanced oil recovery would be modest [47]. The IFT achieved was two orders magnitude higher than the IFT achieved with abiotic surfactants. The study, however, noted that the amount of input material needed would be greater than the enhancement achieved in the recovery of oil.

Methods of Sample Preparation

This research analyzed experimental data of Al Shaheen field of a C60 extended carbon analysis. The scope of work included a C60 extended analysis of the whole crude oil, tar samples and condensate sample. Samples from Al Shaheen field included six crude oil samples, 3 tar samples, and one condensate sample. One condensate sample was obtained from a test separator

and 3 tar samples were extracted from core plugs. The variations in the properties were observed in the API (American Petroleum Institute) gravity, GOR (Gas Oil Ratio), and the saturation pressure. This is shown in Table 4 below.

Table 4: Sample Preparation

Method/Number	Description	Source
1	Crude Oil Sample One - Al Shaheen Field	Reservoir
2	Crude Oil Sample Two - Al Shaheen Field	Reservoir
3	Crude Oil Sample Three - Al Shaheen Field	Reservoir
4	Crude Oil Sample Four - Al Shaheen Field	Reservoir
5	Crude Oil Sample Five - Al Shaheen Field	Reservoir
6	Crude Oil Sample Six - Al Shaheen Field	Reservoir
7	Tar Sample One - Al Shaheen Field	Core Plugs
8	Tar Sample Two - Al Shaheen Field	Core Plugs
9	Tar Sample Three - Al Shaheen Field	Core Plugs
10	Condensate Sample One - Al Shaheen Field	Test Separator

Table 4 Continued

Method/Number	Description	Source
Analysis	C20 plus (currently used EOS used by Maersk Oil) C60 plus (proposed - using the Peng-Robinson equation)	Peng – Robinson Equation of State
Properties to be observed	API, GOR, Saturation Pressure	

There were total 10 samples for the study (six crude oil samples, three tar samples, and one condensate sample). One sample was collected per day. Hence, it took 10 days to complete the process of sample collection from Al Shaheen field. The volume of samples was kept as per the standard sampling method ASTM. During the transportation, it was considered that the samples are kept carefully at a moderate temperature. The study acknowledged that the representative samples are needed for the identification of physical and chemical properties. The representation of the samples was achieved through manual sampling method adhering to ASTM. According to the description of manual sampling, it should be collected from the selected area in a small portion [5]. The small portion is also known as spot sample. The sample should be collected in that container that could represent the material of the selected area.

There were several steps involved in the characterization of oil samples. The first step involved the collection of data related to minimum and maximum carbon numbers. The maximum carbon number used in the study was 60 and the minimum carbon number used in the study was 1. The second step involved calculating pseudo components and the limits. The third step involved calculating molar functions, specific gravities, and molecular weights. The fourth

step involved calculating critical pressure, critical temperature, and critical volume. Saturated boiling temperature was also recorded. The fifth step involved calculating the acentric factor. The sixth step involved calculating thermodynamic properties. These calculations resulted in complete information about PVT properties.

The component, molar fractions, molecular weight, and thermodynamic properties are given in Table 5 below.

Table 5: Carbon, Molecular Weight, and Molar Fractions. Reprinted from [25]

Carbon Number	Molecular Weight	Molar Fractions
C ₁	16	0.0013
C ₂	30.1	0.0050
C ₃	44.1	0.0047
C ₄	58.1	0.0117
C ₅	72.1	0.0158
C ₆	86.2	0.0189
C ₇	90.9	0.0534
C ₈	105	0.0854
C ₉	117.7	0.0704
C ₁₀	132	0.0680
C ₁₁	148	0.0551
C ₁₂	159	0.0500
C ₁₃	172	0.0558
C ₁₄	185	0.0508

Table 5 Continued

Carbon Number	Molecular Weight	Molar Fractions
C ₁₅	197	0.0380
C ₁₆	209	0.0267
C ₁₇	227	0.0249
C ₁₈	243	0.0214
C ₁₉	254	0.0223
C ₂₀	262	0.0171
C ₂₁	281	0.0142
C ₂₂	293	0.0163
C ₂₃	307	0.0150
C ₂₄	320	0.0125
C ₂₅	333	0.0145
C ₂₆	346	0.0133
C ₂₇	361	0.0123
C ₂₈	374	0.0115
C ₂₉	381	0.0109
C ₃₀	624	0.1828

Equation of State is one of the ways of predicting thermodynamic properties of hydrocarbon mixtures that are complex in nature. The equation helps in predicting the volumetric and phase behavior of hydrocarbon mixtures. For the predictions, it is essential to determine some of the critical properties. These include critical pressure, critical temperature, molecular

weight, and acentric factor. For the petroleum engineers, the interest lies less on the behavior of pure components than the behavior of hydrocarbon mixtures. Also, it is easier to calculate specific gravities, normal boiling points, and molecular weights. These properties back up the parameters that are required for the simulations of the equations of state (critical pressure, critical temperature, and acentric factor). The thermodynamic properties from C₁ to C₁₀ are given in Table 6 below.

Table 6: Thermodynamic Properties for C₁ through C₁₀ Reprinted from [25]

Carbon Number	Critical Temperature T_c (K)	Normal Temperature T_b (K)	Critical Volume V_c (cm³/mol)	Acentric Factor ω	Critical Pressure P_c (bar)
C ₁	190.6	111.7	98	0.008	45.4
C ₂	305.4	184.5	148	0.098	48.2
C ₃	369.8	231.1	203	0.152	41.9
C ₄	425.2	272.7	255	0.193	37.5
C ₅	469.6	309.2	304	0.231	33.3
C ₆	507.4	341.9	370	0.296	29.3
C ₇	570.3	399.7	487.13	0.396	24.58
C ₈	653.13	483.45	705.72	0.548	18.52
C ₉	723.7	564.86	1011.85	0.726	13.56
C ₁₀	806	662.69	1398.14	1.022	8.72

Oil Analysis by GC x GC – FID Gas Chromatography

In GC×GC-FDI experiments the process of separation is conducted over two columns, and the interface is defined as the modulator that is located among the two capillaries. The separation of GC is obtained at the point where all the components from the conventional column are re-analyzed over the second column through a short micro-bore capillary segment [49]. The GC×GC-FDI system then generate separation peak capacity equal to the product of the two peak capacities within both the dimensions, and in the final phase the visualization and data processing is carried out. GCxGC-FID chromatogram oil analysis is shown in Figure 9.

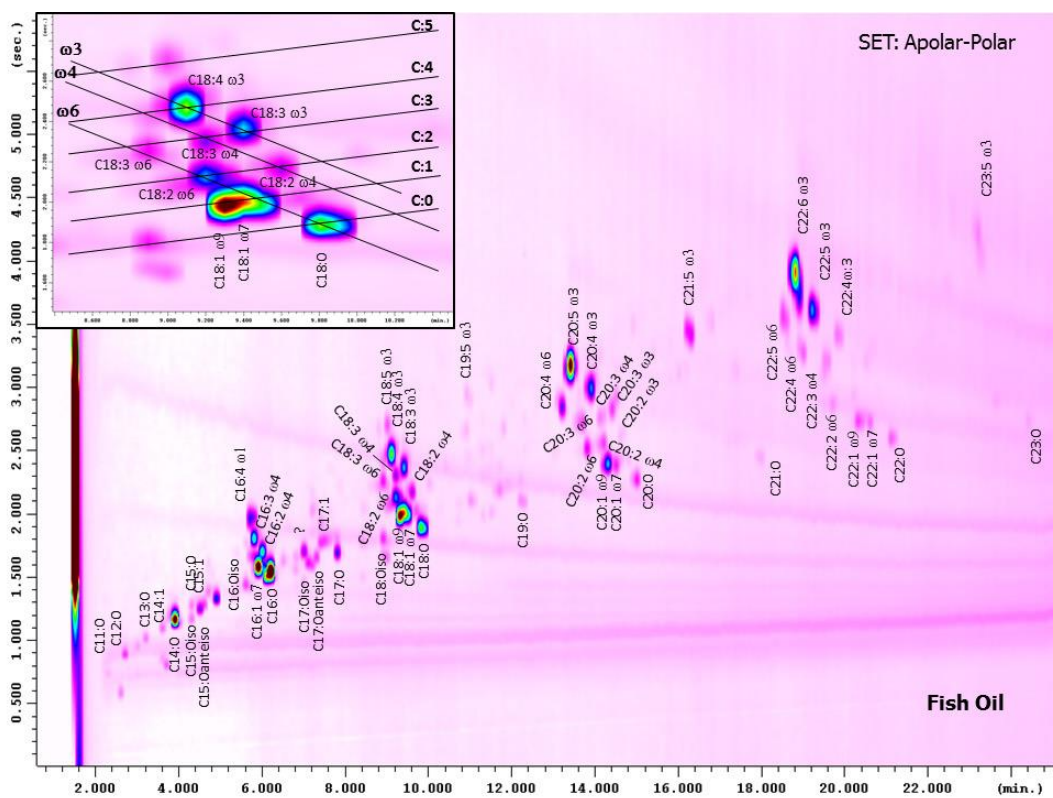


Figure 9: GC×GC-FID chromatogram oil analysis

The utilization of GC×GC-FDI detection for oil analysis enables to perform both

quantitative and qualitative analysis within a single chromatographic run. Along with that this method also provides a high separation power which plays an essential role in simplifying the preparation step [50]. A simple illustration of this could be the unsaponifiable fraction of a series of oils, which can be subjected to derivatization [BSTFA–1% TMCS]. This helps in avoiding the tedious thin-layer chromatography step that is usually performed by other methods. Along with that through this method the unsaponifiable constituents are spread out over the ²D plane, under which every chemical class is located within a particular position.

Oil Analysis by HPLC Preparative Separation Technique

The high-performance liquid chromatography (HPLC) is a highly significant tool which can be utilised for oil analysis [50]. Through utilisation of the HPLC method the profile of the fatty acid can be obtained quickly. A simple illustration of this is given in the Table 7 below.

Table 7: High Performance Liquid Chromatography

		High-Performance Liquid Chromatography (HPLC)		Gas Chromatography (GC)
		COSMOSIL C ₁₈	COSMOSIL Cholester (HILIC)	
Free fatty acids	Short fatty acids	Good	(HILIC)	Poor
	Middle and long fatty acids	Excellent		Poor
Fatty acid ester	Short fatty acids	Fair		Poor
	Middle and long fatty acids	Good		Excellent
Position or geometrical isomers of unsaturated fatty acids		Fair	Good	Excellent
High sensitive analysis		Fair [labeling] Excellent		Excellent
Preparative separation		Excellent		Poor
Lipids composed of complex fatty acid mixture		Using both HPLC and GC to achieve better fatty acid profiling (*1)		

Oil Analysis by FT-ICR Mass Spectrometry

It is a type of mass spectrometer that is used for the determination of the mass to charge ratio of the ion keeping under consideration the ions cyclotron frequency within a fixed magnetic field [51]. Under this method the ions are trapped within the Penning trap, which is magnetic

field consisting of electric trapping plates in which the ions are excited at the resonant cyclotron frequency to a far bigger radius of the cyclotron. This is done through oscillating the orthogonal electric field with the magnetic field. After the removal of the field of excitation, in the next phase the ions are left rotating within the cyclotron frequency within the phase in the form of ion packets, these ions then induce the charge which is detected in the form of image current over a pair of electrodes as the ion packets passes closer to them. Finally, the signal which is received in result is known as the free induction decay (FID), consisting of the superposition of sine waves. This signal is highly useful and it is extracted from the data through performing the Fourier transform for the utilization of the mass spectrum.

Characterization of crude oil in the samples using Peng Robinson Model

The model considers the alpha function as the Soave, however, in this model the function of m is re-calculated along with that this model also had certain modification regarding the dependency of the volume of the attractive term:

$$\text{SRK: } P(T, v) = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \text{ with: } \begin{cases} a(T) = a_c \cdot \alpha(T) ; b = \Omega_b RT_c / P_c \\ a_c = \Omega_a R^2 T_c^2 / P_c \text{ and } \alpha(T) = [1 + m(1 - \sqrt{T/T_c})]^2 \\ m = 0.480 + 1.574\omega - 0.176\omega^2 \\ \Omega_a = 1 / [9(\sqrt[3]{2} - 1)] \approx 0.4274 \\ \Omega_b = (\sqrt[3]{2} - 1) / 3 \approx 0.08664 \end{cases}$$

The Peng Robinson model is used for effective presentation of the crude oil phase behaviour of the smaller number of associated and the polar molecules.

Characterization of Asphaltenes in the Samples Using Peng Robinson Model

For the characterization of the asphaltenes, the Peng Robinson Model utilizes a cubic equation and the two phased flash calculation of the state, the model further describes the mixture of vapor-liquid equilibria and the asphaltene toluene mixture, under which some of the critical properties of the pure asphaltene component are adjusted, the equation of asphaltenes is:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)}$$

$$a_i = 0.457235 \frac{R^2 T_{c_i}^2}{P_{c_i}} \lambda_i$$

$$\lambda_i = [1 + m_i (1 - T_{r_i}^{1/2})]^2$$

$$m_i = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2$$

$$b_i = 0.077796 \frac{RT_{c_i}}{P_{c_i}}$$

n-d-M Method

This method was initially developed by Koninklijke, the applications of the method includes raffinates, and lube feedstock's. Almost all the application of the method is applicable to the solvent refined stocks [52]. It is an empirical method that is used for the determination of the carbon type distribution (%C_p, %C_N, %C_A) through the simple measurement of the samples molecular weight, its density, and the refractive index. The n-d-m method provides the result of correlations between the actual and physical constants of the oil fraction composition that the determined through the utilization of the direct method. These correlation are based specifically over the data from the thirty four oil fractions, which are taken from five different crude oils. With the help of these correlations physical data constant from the oil fraction are utilized for the calculation of the aromaticity, % CA. Through this method the percentage of the paraffinic

carbons and the naphthenic carbons are calculated through the utilization of the ilar equations [53]. Furthermore, the method also provides the mean number of aromatic, and the naphthenic rings per molecule. However, the calculations that are obtained through this method usually include certain assumptions like all the cy molecules are six membered condensed in the specific manner. Toulene with aromacity of %CA -86 is shown in Figure 10.

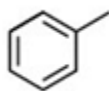


Figure 10: Toulene. Aromacity: %CA -86

Group Contribution Method

It is a method that is used to estimating and predicting the thermodynamics along with the several other properties of the molecular structures. The group contribution model is based on the principle that there are certain simple aspects associated with the structure of the chemical components which always remains the same in a wide range of molecules [54]. In all of the molecules the smallest constituents are the bonds and the atoms, and a huge majority of the organic components are composed of oxygen, sulfur, carbon, nitrogen, and halogens. Along with that together with a single, double, and triple bond there are only ten type of atoms and three types of the bonds that builds more than a thousand components. Afterwards, the next highly complex building blocks associated with the components are the functional groups that are built themselves consisting of very few number of atoms and bonds. The group contribution method is also used for the prediction of the properties of the mixtures as well as pure components through utilization of the properties of single or a group of atoms [55]. This results

in the reduction of the huge amount of data needed, and despite of gaining the knowledge regarding the properties of million and thousands of the compounds, the only data that is required to be known through this method is the hundred or less than a dozen of groups that are to be known.

Hence, the group contributions are usually obtained through experimental data that is known and consisting of well-defined mixtures or pure components. Some of the common source that is used for this method includes the thermophysical data banks such as the Beilstein database. Once the data is retrieved the next phase the properties of the mixture and the pure components are assigned to the groups through statistical correlations. These methods are based strictly over the additive principle, which means that no matter what the type of compound is it can easily be divided into small fragment, and all of these fragments consist of value known as contribution. Through this method the contribution are calculated with the help of experimental data. The property of the compound is obtained through summing up values of all the contributions that are associated with the molecule. An example of the division of the molecule is presented in Figure 11. In which the molecule is divided into various atomic fragments, and the total value of the property X of the ethanol is achieved through adding the values of the two carbon atom contributions, one hydrogen atom contribution, and finally the six hydrogen atom contribution.

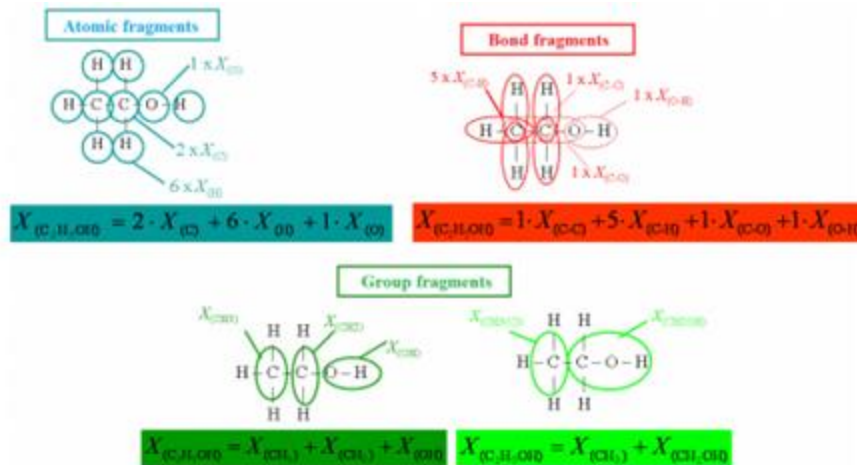


Figure 11: Division of molecule of Ethanol

Group contribution methods are the methods that are used for conducting empirical investigation. In the past few centuries' wide range of models have been designed [56], which are different in their application and in the set of experimental data. These models can be utilised for pure compounds, as well as inorganic compounds.

Cavett Correlations

It is a method that was developed by Cavett (1962) through the utilization of the set of equations for the evaluation of the properties of the petroleum fractions that are not defined [57]. Keeping under consideration the boiling point and the specific gravity of the petroleum fraction, the critical properties along with the molecular weight can be estimated as follows.

Soreide Correlation

For a true boiling point the soreide correlation is solved in an iterative manner for the determination of the molecular weight, the major function of the non-linear solver is presented as

follows:

$$f(MW) = 1071.28 - 9.417 \times 10^4 MW^{-0.03522} SG^{3.266} \\ \exp(-4.922 \times 10^{-3} MW - 4.7685 SG + 3.462 \times 10^{-3} MW SG) - k = 0$$

Structured Oriented Lumping

It is a method that is used for the description of product, compositions, reactions, and properties of the hydrocarbons. In this model the rate of a specific reaction is the function of the type of catalyst, structure of the molecule, and conditions of the reaction are used for the estimation of the kinetics. In this model the molecules are represented as the collection of the structural increments, and the model also utilizes the group contribution method for the estimation of the kinetics. The model provides a detailed stock of the feed along with the characterization of the molecular lump. Through this model the reaction networks are generated for every single molecular type rule based system as per the theory of carbon ion, along with the reactivity and the stability of the secondary as well as the primary and the tertiary carbenium ions. Hence, the structured oriented lumping method provides a representation of the individual molecules of the hydrocarbons, and these are represented as a set of vectors, and each vector is presented with an associated percentage of weight. The structured lumping method provides the basis for the molecular based modelling. Hydrocracking reaction scheme is shown in Figure 12.

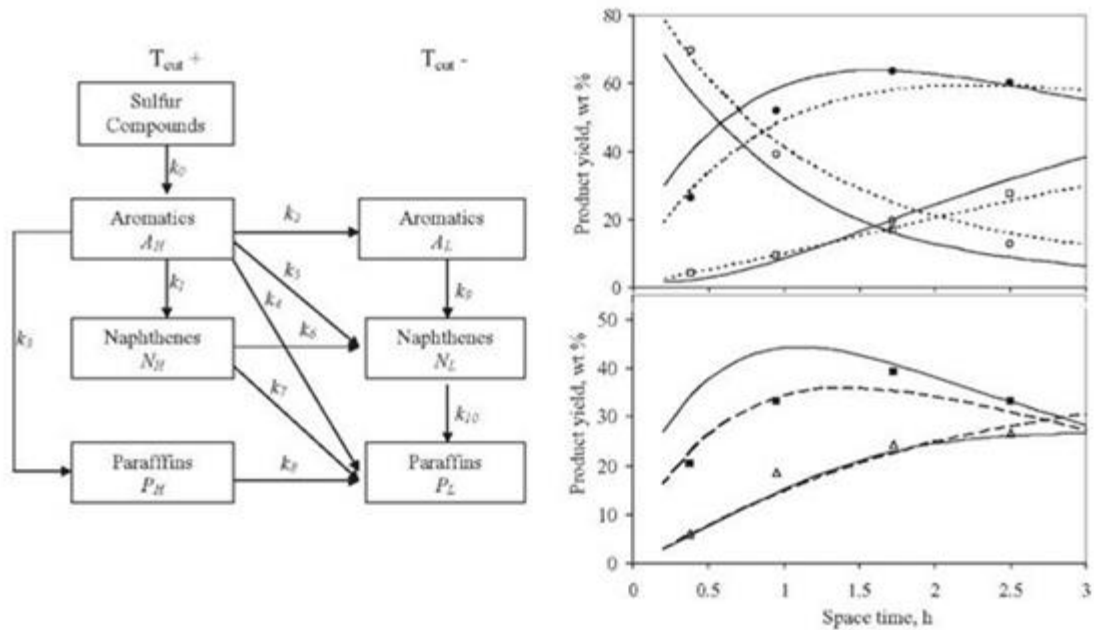


Figure 12: Hydrocracking reaction scheme

Corresponding-States Methods

The corresponding states method provides an indication of all the fluids, on the comparison of the reduced pressure and the reduced temperature that have approximately somewhat similar compressibility factor, which deviates from the ideal behavior of the gas at somewhat the same degree. According to the principle corresponding states method the dimensionless property of a particular substance is equal to another reference substance in case where both are evaluated under the reduced condition [58]. In the corresponding states method each fluid is characterized with the help of the energy parameter, and the shape distance parameter. In case two fluids are under corresponding states, then under such a scenario the reduced viscosity of the fluid is then expressed in the terms of the fluid reference ν and is given as:

$$\eta_{Ri}(V_{Ri}, T_{Ri}) = \eta_{Ro}(V_{Ro}, T_{Ro})$$

Corresponding-states principle is among some of the highly effective and widely utilized method for the correlation and estimation of the thermo physical property. Even though the two parameter [59]. Corresponding-states principle have established quite meticulous base for the spherical non-polar fluids, however, the property of other distinct types of the fluids have been correlated in an effected manner through the introduction of three parameter model. [60] utilized a three parameter model which proved to be extremely useful in making prediction regarding the thermodynamic properties of the slightly polar as well as the non-polar fluids. The reason behind the success of the three parameter CSP model was due to the utilization of the accurate analytics equations of the state, which represents the two references fluids.

CHAPTER IV

MAERSK OIL MODELING APPROACH

Introduction

This section describes the development of a unified fluid model that was built and currently being used by Maersk oil Qatar for Al Shaheen field development. The model is based on PVT data acquired by Maersk Oil Qatar from Al Shaheen reservoirs, in order to support the Enhanced Oil Recovery studies (EOR).

The field of Al Shaheen has been categorized by large horizontal variations in the properties of fluids. The performance of production has a large impact due to the fluid property variations of the reservoir. Al Shaheen field consists of a series of stacked and thin reservoirs. The reservoirs are dominated by tight carbonates. The reservoir sequence also has a sandstone unit. These units vary in their quality. There have been a number of feasibility studies related to the development of the field. The development of the field model started with 120 samples of data sets collected from different parts of the reservoirs. The data set included conventional PVT experiments required to support the waterflooding development as an enhanced Oil recovery method (EOR). The EOR study was further supported with additional four samples taken with gravities of 18, 23, 29 and 36 API which has been subjected to a practical program including gas injection experiments. Overall, 124 samples were included in the database. 49 samples were found representative and good for the in-situ reservoir fluids which were based on the whole analysis.

Maersk Oil Qatar is using Peng-Robinson equation of state (EOS) to correlate properties in different reservoirs across a range of API gravities. It is important to note that the model developed is using a 10 pseudo component EOS which was correlated to describe and predict

the behavior of the gas cap, gas condensate and Oil API range from 28 to 36 associated with the reservoir. Subsequent exploration to the flank areas of the field led to the discovery of heavier hydrocarbons where the oil gravity segregate to the API range from 28 to 16. Therefore, the current pseudo components could not be used to predict the asphaltenes.

Objective

The main objective of Maersk Oil in this work was to establish a consistent fluid models for black oil simulation for water flooding modeling and compositional simulation models for the investigation of using gas injection. The work has established that the oil composition and oil properties can be characterized based on saturation pressure, oil API gravity and solution gas Rs. Those three key properties are mapped for each reservoir in the field based on data obtained from fluid sampling, cutting sampling and initial production performance. Those maps then are converted to compositional maps using a workflow developed internally by Maersk Oil.

EOS Development

For the purpose of EOS modeling, Maersk oil has developed a specific set of correlations for properties such as formation volume factor, oil viscosity and saturation pressures based on AL Shaheen database and did not use other correlations in the industry that were developed for specific areas or other types of oils.

The aim of the EOS model is to explain the behavior of basic PVT and swelling behavior during the injection of gas across the API gravity ranges, with fewer components. The hydrocarbon WAG as well as Carbon dioxide WAG is included in the gas injection studies. For the reason of equation of state tuning, a group of spanning fluids were nominated which were

based on the outcomes of quality process and the availability of appropriate data of PVT including MMP data and swelling data.

The tuning was generated by fitting the Peng-Robinson EOS to experimental data for 12 selected samples spanning the range of oil API gravities from 18 to 36 °API as will be covered in later sections. The EOS was validated against all available data. The experimental data also included conventional PVT data as well as swelling tests and minimum miscibility pressure (MMP) measurements.

Black Oil Model VS Compositional Model

The descriptions of black oil models are not appropriate for the modeling of gas injection procedures. Black oil tables describes property changes which are resulting from the mixing of gas and oil at fix compositions in different ratios. Where as in a gas injection case, oil and gas change composition as a result of mass transfer between phases. In order to model a gas injection, a compositional model has been developed.

The black oil is used to generate the full field forecast and the water flood developments. The fluid property variations was handled either through the tracking of API or through the use of PVT discrete regions which was generated based on the fluid property maps. The API tracking is more attractive since the fluid retains its properties as it is moving through the reservoir whereas the in the PVT regions methods, the fluid property changes as it moves from region to region. In the compositional modeling, the fluid properties changes are tracked through the change in the fluids compositions while using a single EOS. The black oil model is initialized based on the property maps of the three key properties, API, R_s and P_{sat} . Whereas the compositional model is initialized by specifying the composition of each grid block using a

composition predictor workflow.

Sampling

Overall, 124 samples were collected using bottom hole samples (MDT) and Separator samples. A quality check was applied and the two types of samples were observed to investigate whether they are consistent or representative. The consistency of data was checked through the verification of composition and properties of fluids. The R_s was related with the samples to check whether it is representative or not. The bottom-hole samples had the higher confidence relation as compared to the separator samples.

The results of this process were summarized and a total of 42 samples passed for both the representative and consistency. All the samples which were consistent can be used for the equation of state and black oil modeling, regardless of the samples if they are representative of the in-situ reservoir fluid or not.

True Boiling point (TBP)

The technique of true boiling point was also then introduced, which helps the fluid sample to be separated into cuts of physical boiling points according to the normal boiling point of the normal alkanes series. Each cut will be then assigned to a specific number fraction of carbon. For example, a C9 fraction would contain all compounds with a boiling point between n-C8 and n-C9. This technique provided an advantage over the GC analysis in which each cut would have the physical properties in terms of density and molecular weights measured. The disadvantage of the (TBP), it requires a larger sample volume, for example, in a standard system for the distillation column around 5 liters of sample is used, and it is a time consuming experiment. The

measured properties of the boiling cuts resulted in a better interpretation of the compositions which was also a better input for the (EOS) characterization. The quantity of plus residue fractions was also determined without the losses in GC analysis when heavier molecules are trapped in the chromatographic column. The accuracy of the composition by mass is comparable to that of GC analysis for the separated cuts, but for heavier cuts the separation of cuts becomes poorer. This is resolved by analyzing the composition of the individual cuts by GC.

The EOS calculations required the composition in mol%; the composition in weight% was converted by using the molecular weight followed by each component in cuts. When no TBP data is available in case of using GC analysis, the conversion of Mol % is done by first measuring the average molecular weight of the crude oil and then the molecular weights for the resolved cuts are assigned using the Katz and Firoozabadi correlation [Katz and Firoozabadi, 1978]. Finally, mass balance is used to calculate the plus fraction molecular weight. If the fluid system in question does not follow the trends of the Katz and Firoozabadi correlation, the composition reported in mol% will be incorrect. Having determined the appropriate correlation between carbon number fraction and molecular weight by TBP analysis thus improves the quality of the compositional analysis data. In conclusion, the TBP data provides the cut molecular weights and the densities needed for the correlations used to calculate the EOS parameters i.e. T_c , acentric factor i.e. ω and the critical pressure P_c . More tuning typically is required to make the EOS model match measured PVT data for a fluid when no TBP data are available which may lead to a less predictive EOS.

TBP distillations were carried for AL Shaheen Oils. The atmosphere conditions were found suitable for the distillation separating fractions up to C20 according to ASTM-D2892 and vacuum was used to get separation up to C36+. The columns with 15 plates were used which

allowed cuts up to C9 to be separated to individual cuts, while the remaining cuts covered border distribution. GC analyzed each cut individually to resolve the distribution of components and the molecular weights were measured by cryette. ASTM D-4052 measured the densities and the outcomes were transformed to 15 degree centigrade using a table.

The average carbon of each cut was calculated based on the cut component measured and the cut properties correlated was then plotted against the average calculated carbon number as shown in Figures 13 and 14.

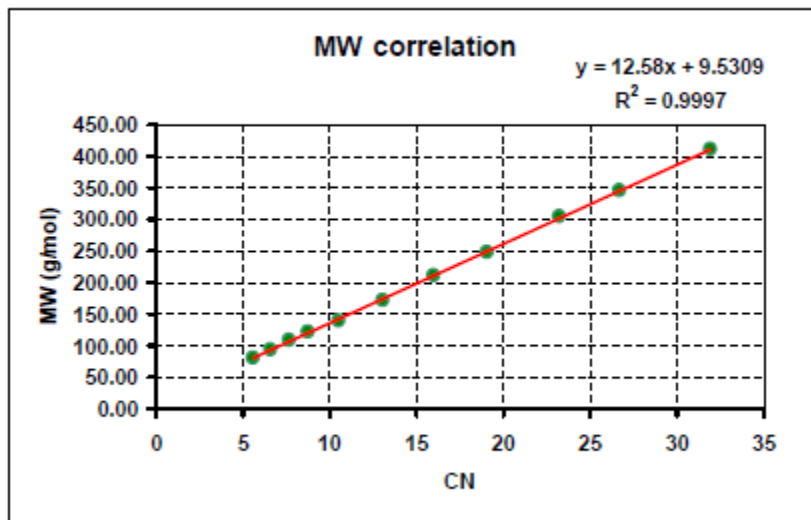


Figure 13: Example of correlation between cut MW and cut average carbon number

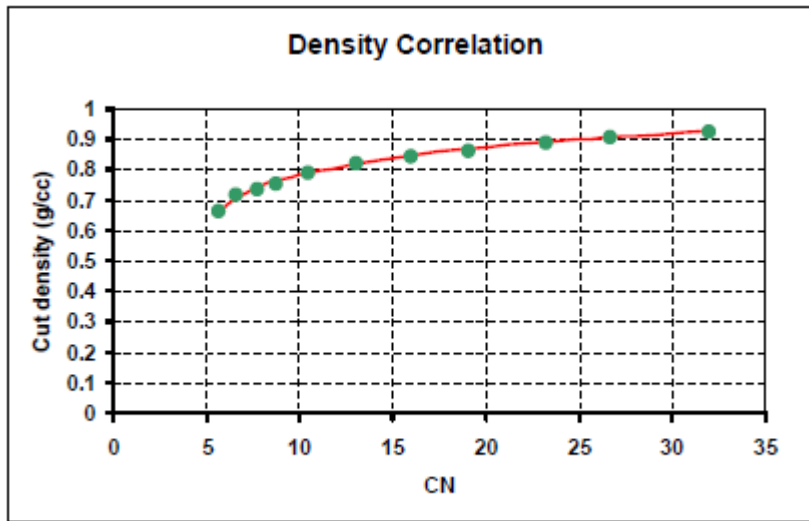


Figure 14: Example of correlation between cut density and cut average carbon number, based on Soreide correlations

There was a linear correlation found as expected, of the molecular weight. The correlation of density was obtained by the fitted coefficients of Soreide correlation.

$$\rho_i = c_0 + c_i * (M_i - M_0)^2$$

ρ_i is the density, M is molecular weight and c_0 , c_1 and a are coefficients in the correlation.

Subscript i refer to the cut number. The results of the cut properties calculated using the correlation is plotted in Figures 15 and 16 below.

As expected, the fluids of Al Shaheen do not follow the Katz and Firoozabadi correlation since the later was developed for crudes with a more paraffinic composition. In general Al Shaheen fluids are more aromatic in nature than the fluids used to develop the Katz and Firoozabadi correlation.

The fluid in figure 16 appears to follow a different density trend than the other fluids measured. This fluid API is around 18 API and is heavier than the other measured fluids which have API range from 24 to 34. It is important to note that the trend of this fluid has not been included in this model.

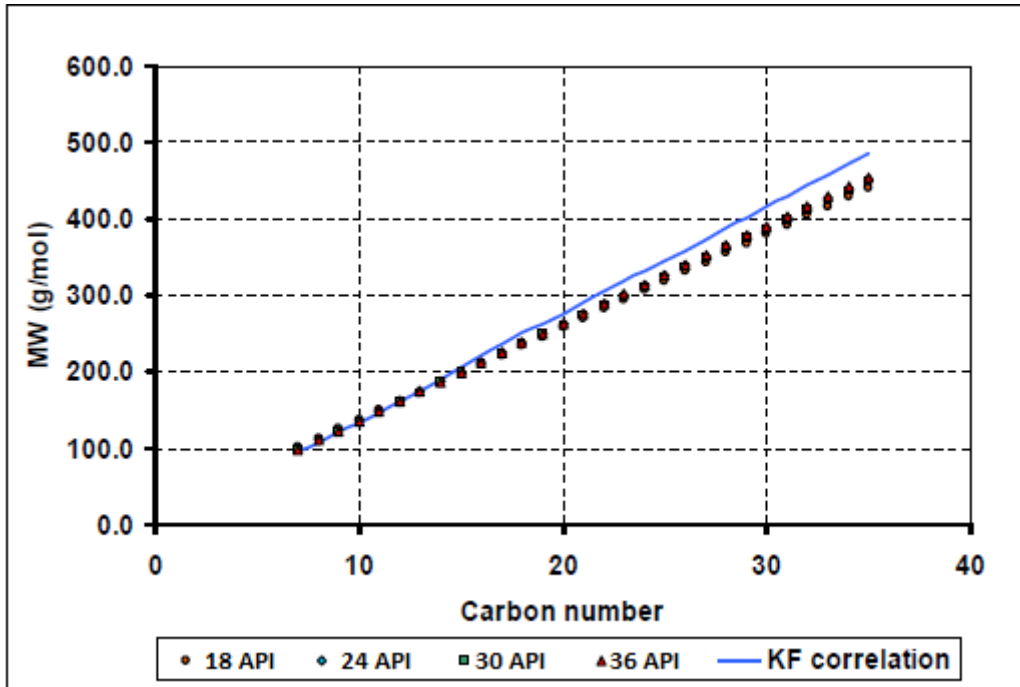


Figure 15: MW vs carbon number for the four EOR fluids, compared to the Katz Firoozabadi standard correlation

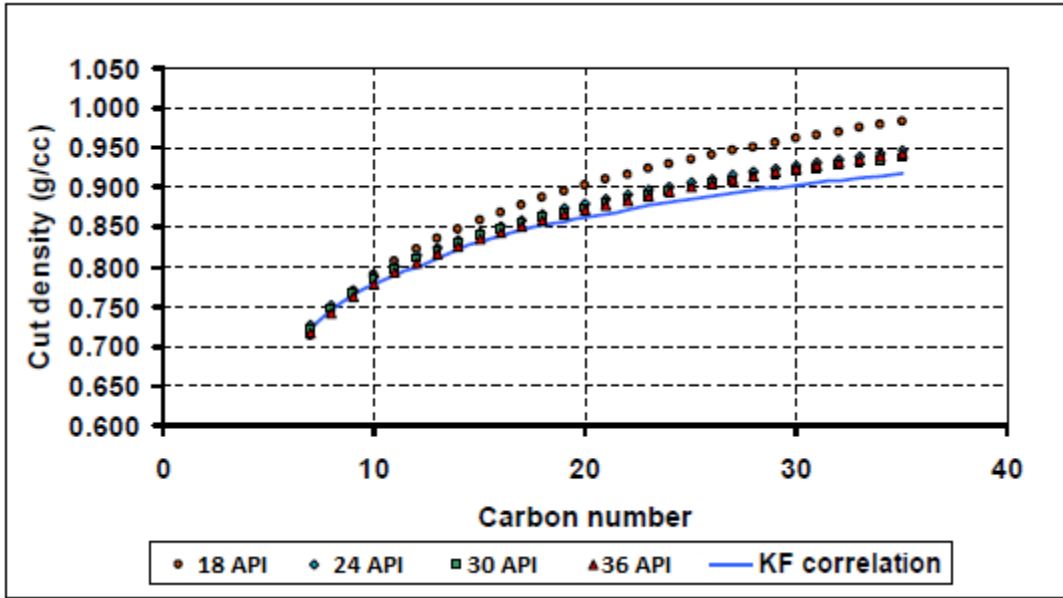


Figure 16: Density vs carbon number for the four EOR fluids, compared to the Katz and Firoozabadi Standard correlation

CHAPTER V

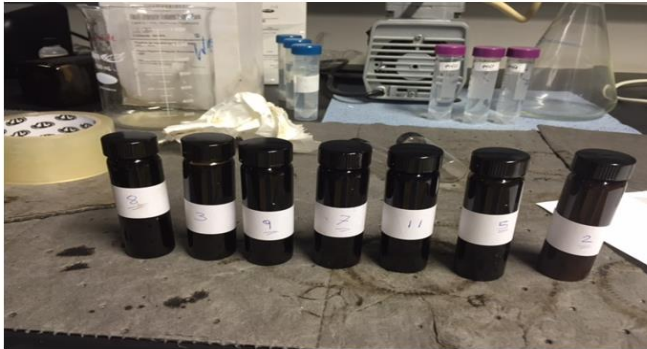
A STUDY TO IMPROVE MODELING

Introduction

This study was carried on hoping to improve the analytical approach used by the operating company. The study includes six crude oil samples obtained from different locations in the Al Shaheen field to represent the API variation observed. The samples also include one condensate sample obtained from a test separator and 3 tar samples extracted from core plugs as shown in Figure 17.

Al Shaheen Oil Field – API 36 to 18 Gravity Segregation Study

Sample Number	API
3	36
5	29
8	19
9	23
7	20
2	26
(Back Up) 11	19



Samples used to extract Tar

Figure 17: Samples collected from Al Shaheen Field.

The samples went through the following analysis:

- Sample analysis through GCxGC FID analysis
- Sample analysis through APPI FT-ICR MS analysis
- Sample analysis through HPLC-2 Quantitation of ring number
- Sample analysis through APPI FT-ICR MS analysis of nC5-nC7 asphaltenes dropout distributions

Objective

The aim of this study is to provide a better representation to the hydrocarbons with the heavy end components than what is currently available for the field by including a C60 extended analysis of the whole crude oil, tar samples and a condensate sample.

The current data base available for the field is a C1 to C20+ GC analysis which records the Average MW, API Gravity, Saturation Pressure, GOR, Weight % (C1-C20) and MWC20+. The MWC20+ was obtained using an MWD sample. The fluid API in the field varies laterally in a range between 36 to 16 API. Based on the C20+ analysis, it is determined that the Percentage of unknown hydrocarbon components is estimated to be between 27% for the higher API range to 79% for the lower API range identified in the filed fluids. The SARA Analysis to divide crude oil in to components was applied using a sample obtained from the inlet separator and based on that the percent of unknown components is identified as

- API 36(74% S, 20% A, 5% R, 1% A)
- API 18(21% S, 51% A, 18% R, 10% A)

Where S: Saturates (Single Bonds)

A: Aromatics (Sigma Bonds) forming rings

R: Raisins (Bitumen) soluble in heptane

A: Asphaltenes (bitumen) insoluble in heptane

Finally, the True boiling point used in Peng Robonson EOS is identified to be very similar to the crude oil assay used at the refinery as shown in Figure 18

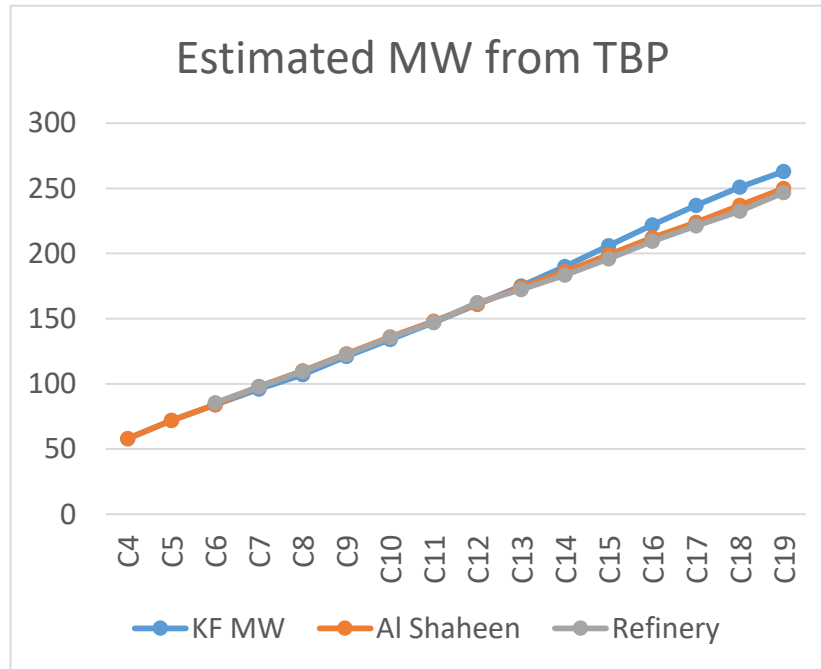


Figure 18: Crude Oil Assay comparison

Experiments Results and Discussions

The current C20+ analysis is not enough to estimate or represent the homologous series such as P, IP, N+, A+, N+A+, S1P+, S1N+, S1A+ . Over 50+ weight % is not characterized for fluids with API gravity less than 28 and the TBP and SG is only measured up to C50 as shown in Figure 19.

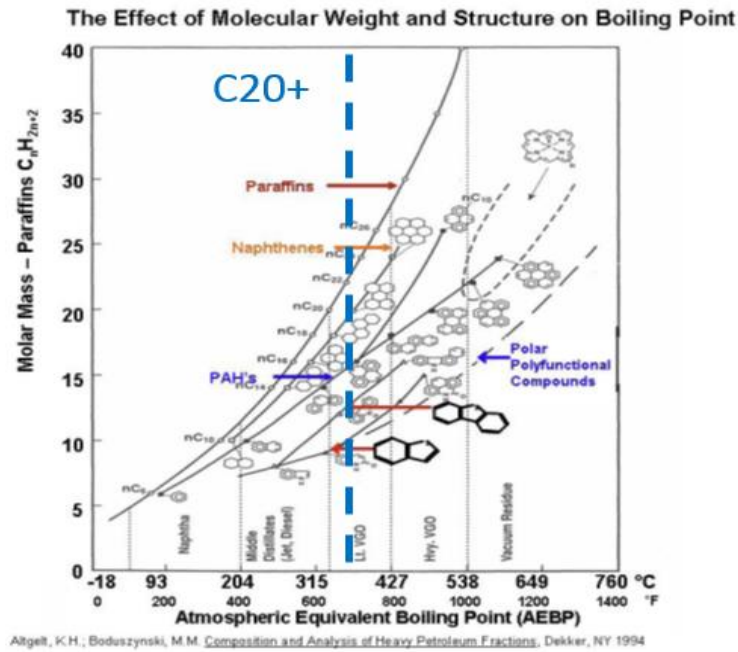


Figure 19: Molecular Weight Vs Boiling Point

In order to have a better understanding and modeling of the heavy crude oil ends including the asphaltene and the EOR methods to be applied, a physical measurement to the Homologous MW distribution versus the coarse crude oil cuts need to be generated as shown in Figure 20.

R<C30, GC x GC with FID Identification Map

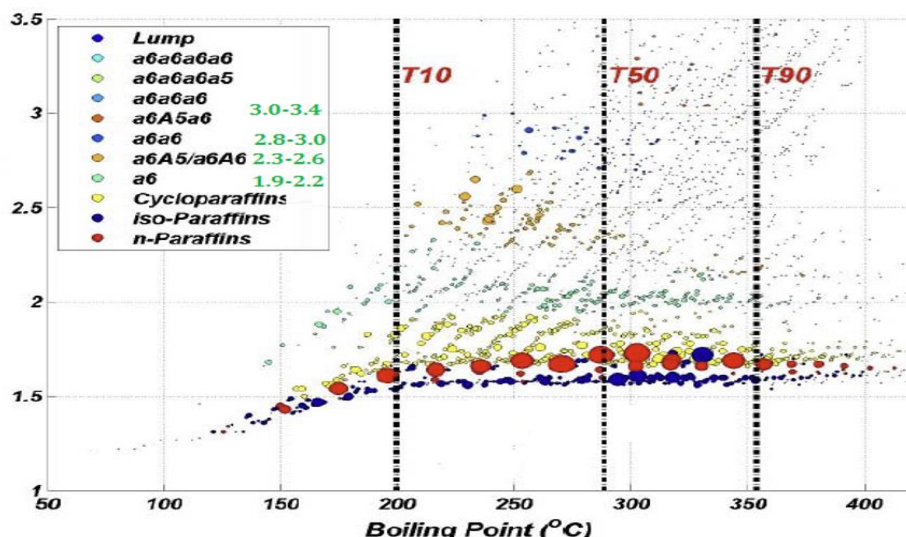


Figure 20: C30 GC XGC Identification Map

The first part of the experiment included a molecular-level analysis of a series of reservoir samples of varying API gravity by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR MS), Comprehensive 2D Gas Chromatography, and HPLC-2. The following goals were outlined:

- quantitative, molecular analysis of the light ends, up to ~ 400°C was achieved by Comprehensive 2D Gas Chromatography.
- quantitative, molecular progression of the saturates, and 1-5+ ring aromatic species into the heavy ends was achieved by HPLC-2 analysis with Photo-Diode array and Evaporative Light Scattering detectors.
- molecular-level characterization of the most abundant PAH, PASH, PANH, and PAOH species in the reservoir samples as a function of API gravity was achieved by FT-ICR MS via Atmospheric Pressure Photo-Ionization.

- molecular-level progression from maltenic species into the asphaltenic species was achieved through back cutting the C5 asphaltenes with C7 to isolate the C5 – C7 asphaltenes, and subsequent analysis by APPI FT-ICR MS.
- True boiling point helps the fluid sample to be separated into cuts of physical boiling points according to the normal boiling point of the normal alkanes series
- Each cut will be then assigned to a specific number fraction of carbon. For example, a C9 fraction would contain all compounds with a boiling point after n-C9 and before n-C10.
- The crude oil assay TBP curve n-Cx is used to calibrate the GC x GC analysis

The 30-GCxGC-FID Chromatogram

Gas Chromatography is applied to measure the true boiling point of the hydrocarbon samples. TBP helps the fluid sample to be separated into cuts of physical boiling points according to the normal boiling point of the normal alkanes series. Each cut will be then assigned to a specific number fraction of carbon. For example, a C9 fraction would contain all compounds with a boiling point after n-C9 and before n-C10. The crude oil assay TBP curve n-Cx is used to calibrate the GC x GC analysis. Figures 21, 22, 23, 24, 25, 26 and 27 show the 30-GCxGC-FID Chromatogram of results of Maersk fluids for API 51, 36, 29, 26, 23, 20 and 19 respectively.

30-GCxGC-FID Chromatogram of Maersk Condensate, API 51

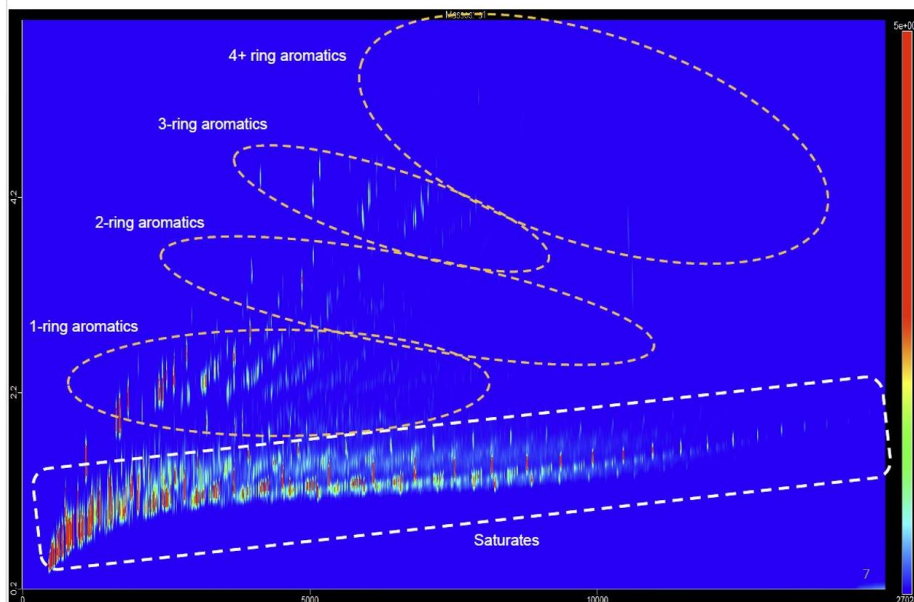


Figure 21 C30 GC X GC, API 51

30- GCxGC-FID Chromatogram of Maersk Oil, API 36

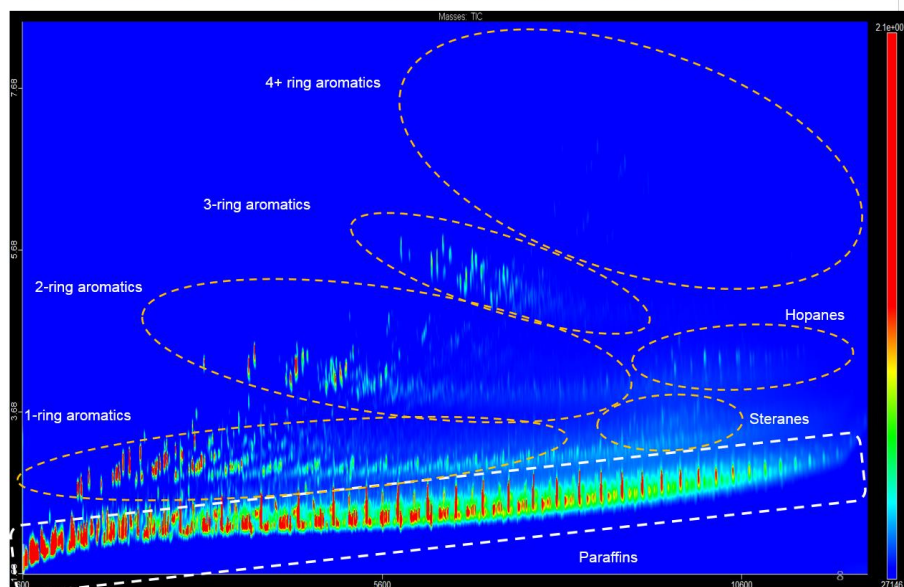


Figure 22 C30 GC X GC, API 36

C30- GCxGC-FID Chromatogram of Maersk Oil, API 29

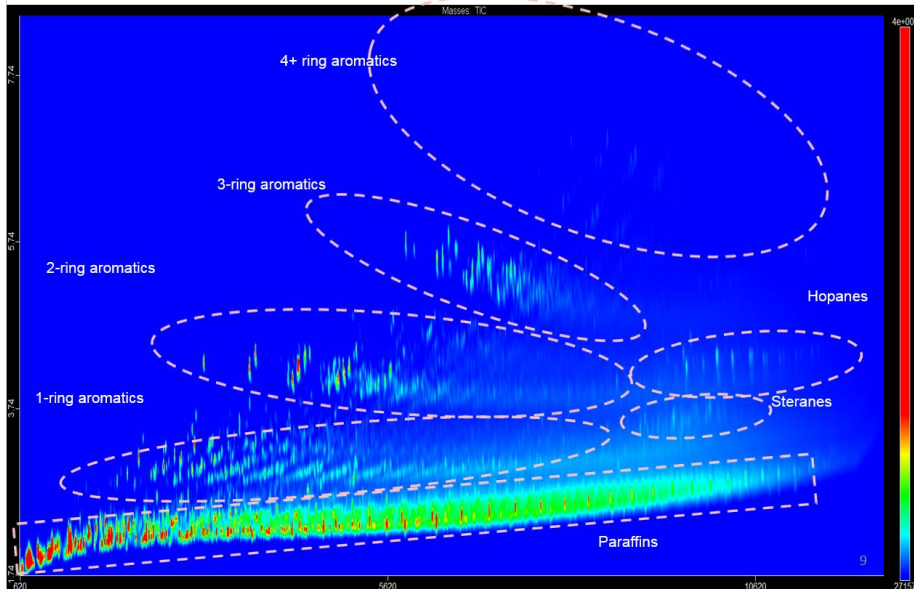


Figure 23 C30 GC X GC, API 29

C30- GCxGC-FID Chromatogram of Maersk Oil, API 26

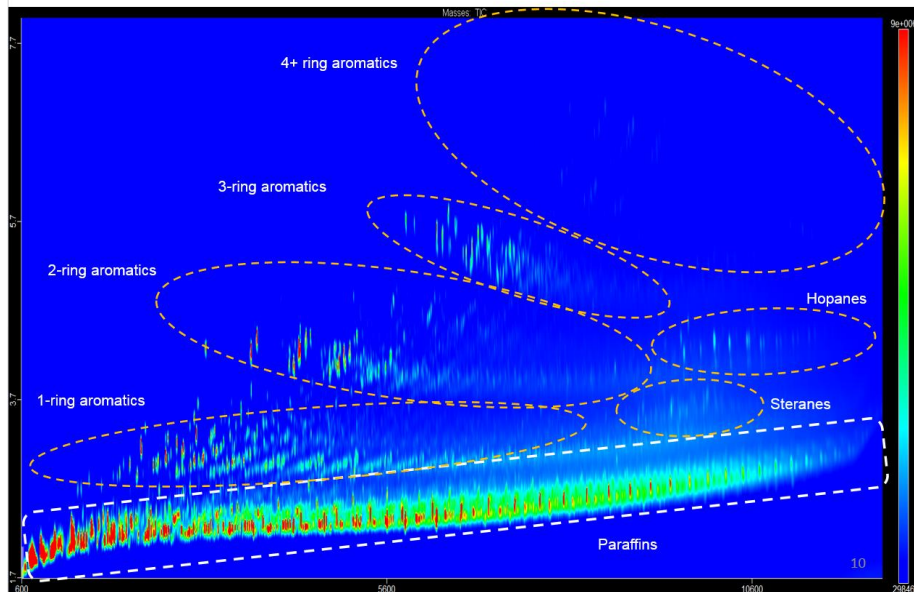


Figure 24 C30 GC X GC, API 26

C30- GCxGC-FID Chromatogram of Maersk Oil, API 23

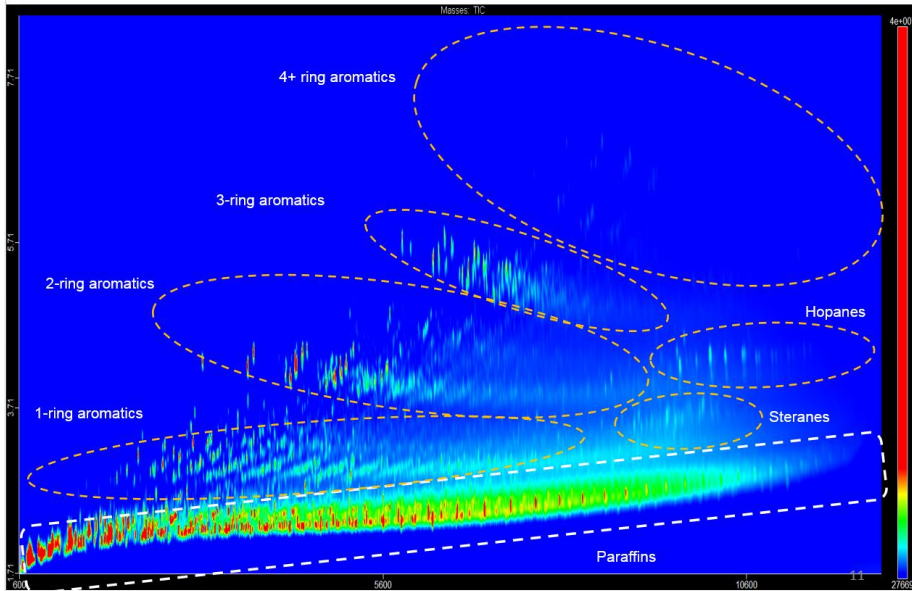


Figure 25 C30 GC X GC, API 23

C30- GCxGC-FID Chromatogram of Maersk Oil, API 20

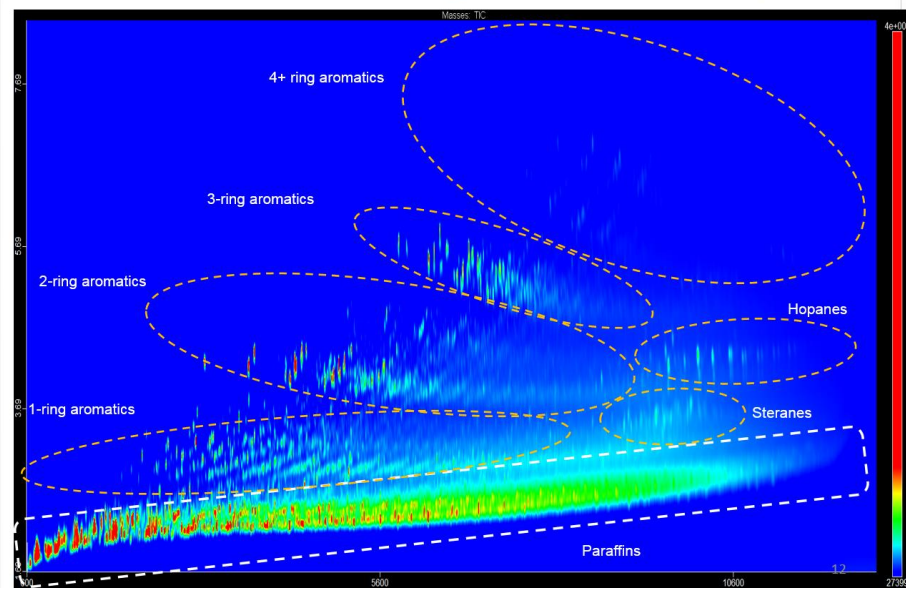


Figure 26 C30 GC X GC, API 20

C30- GCxGC-FID Chromatogram of Maersk Oil, API 19

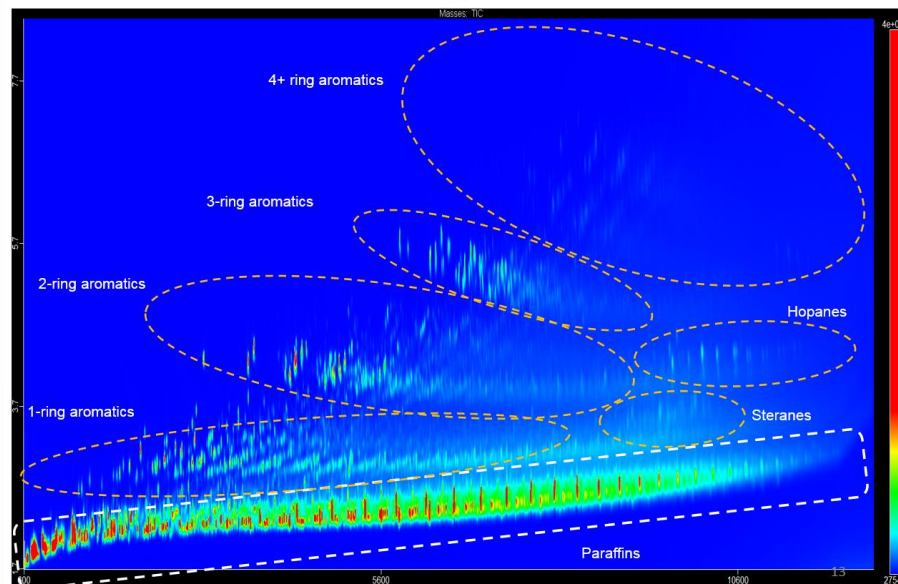
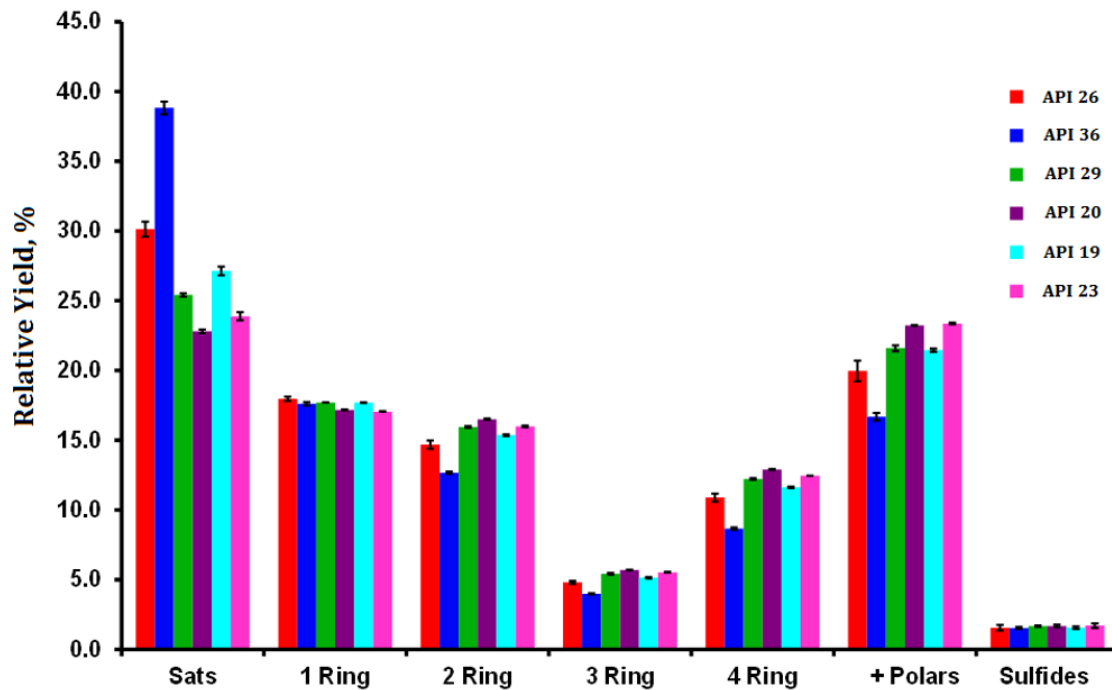


Figure 27 C30 GC X GC, API 19

C30 GC X GC Summary Results

Figure 28 shows a summary of all the results based on experiments done for API 36-19. The results was good enough to determine what type of families and series we have and to give quality check of the fluids. It is very difficult to get a quantitative analysis by compound or by family from this data. The conclusion is GC analysis is not good enough for us to make a quantitative analysis and we have to go with a more accurate methods. It was only good for quantitative, molecular analysis up to~400°C and 1-4 ring aromatic species into the beginning of heavy ends. There is no way to calculate an average MW of the compound beyond that and for asphaltene study this is not good. Over all with this C30 analysis will not give enough data for API 28 or less. For example. We could not tell the difference in sulfide content in each sample. The results shows the same level. Crude oil assay shows that API sulfide content will increase as hydrocarbon becomes heavier at lower API.

Summary of C30-GC x GC with FID



Note, the C30+ material is not transported through the C30-GC

Figure 28 C30 GC X GC Summary Results

Comparing the C30-GC analysis to the C20-GC analysis, it is determined that the Percentage of unknown hydrocarbon weight percent went down from 27% as estimated by the C20-GC to 13% as estimated by the C30-GC analysis for the higher API range. Respectfully, the Percentage of unknown hydrocarbon weight percent went down from 79% to 47% for the lower API range. The C30-GC also over predicts the Asphaltene composition.

9.4 Tesla Mass Spectrometer Analysis

The Mass Spectrometer can provide up to C80 analysis and can be used for whole oil and tar samples. For a given class of compounds, plots of carbon number vs. DBE (a measure of Aromaticity) are used to reveal compositional differences. Comparisons of the classes revealed a gradual shift to higher carbon numbers at a given aromaticity as one progresses from oil API 19 to oil API 36. The most notable compositional trend is the gradual increase in higher heteroatom species as a function of API gravity. For example, the S3 class is first observed above 1% total abundance is in sample API 29, and gradually increases in Samples with API 26-19. Similar plots, and molecular level data are provided for the pre-asphaltene fractions as well. Figures 29, 30, 31, 32, 33 and 34 show the summary of the plots (DBE vs. Carbon Number) for the most abundant classes detected by APPI FT-ICR MS.

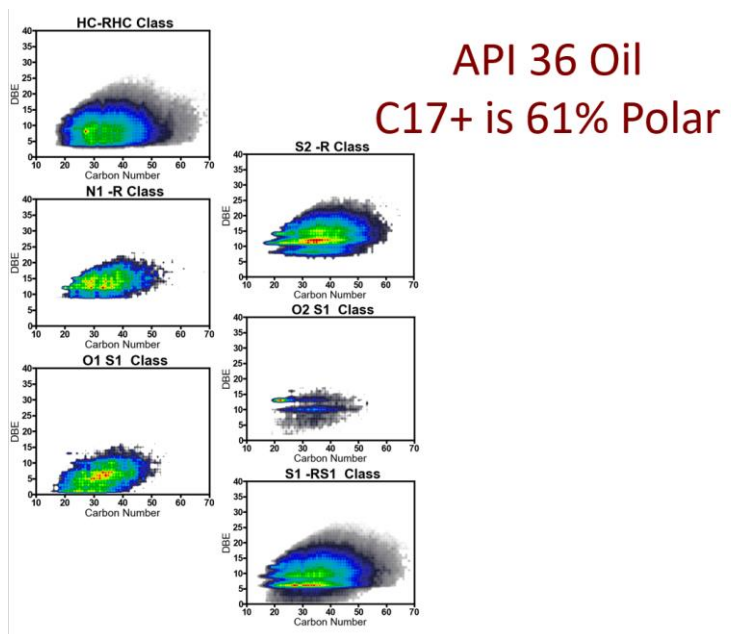


Figure 29 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry API 36 (Polar)

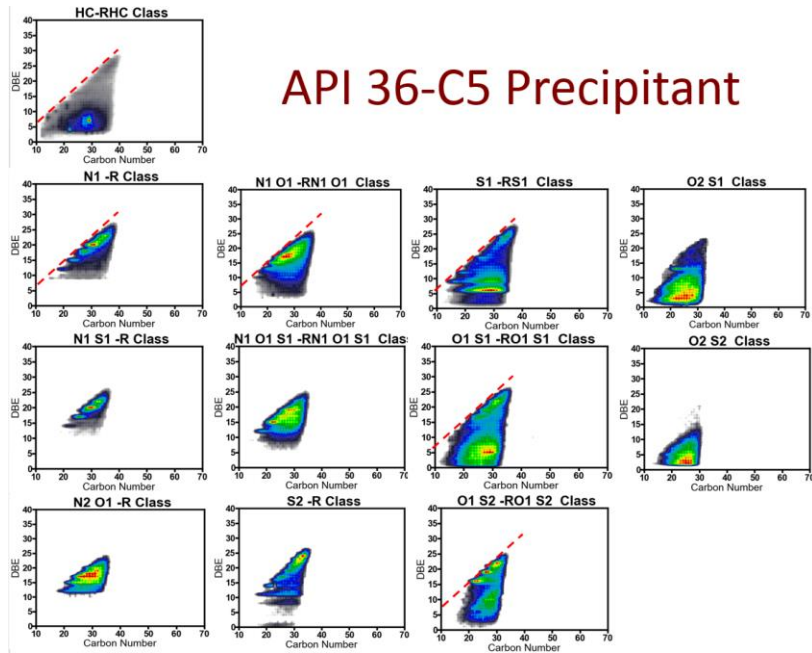
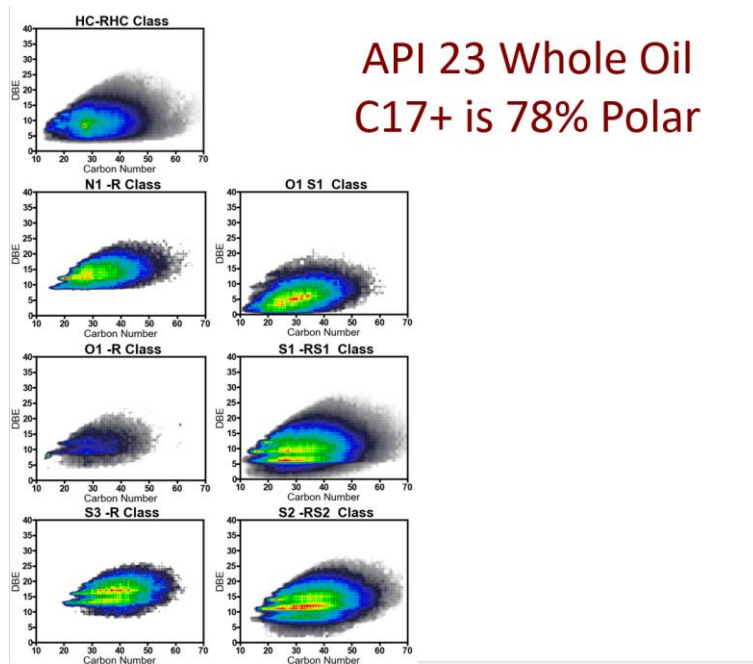


Figure 30 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry API 36 (Precipitant)



**API 23 Whole Oil
C17+ is 78% Polar**

Figure 31 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry API 23 (Polar)

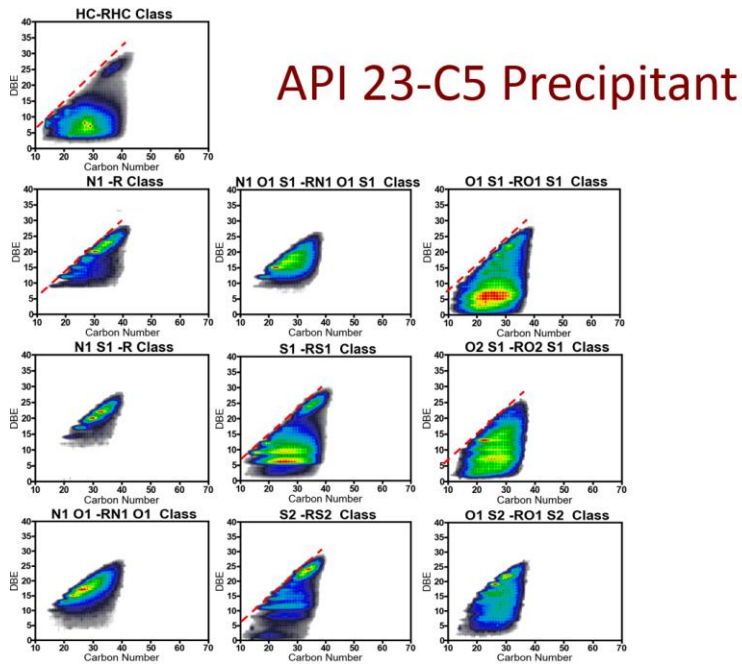


Figure 32 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry API 23 (Precipitant)

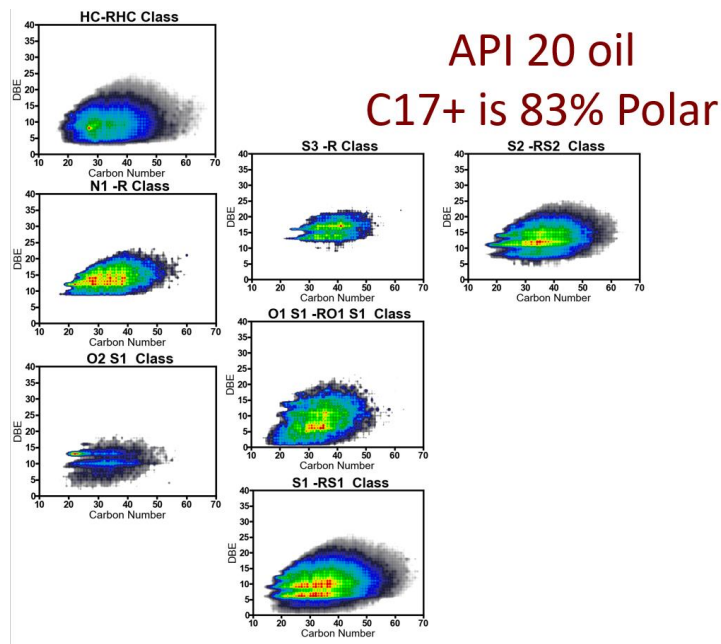


Figure 33 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry API 20 (Polar)

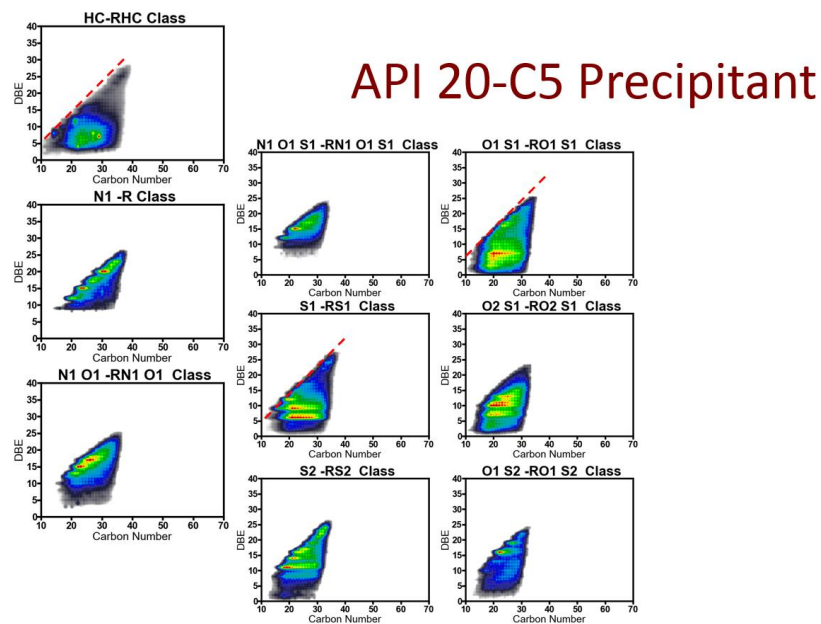


Figure 34 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry API 20 (Precipitant)

Summary results of the 9.4 Tesla Mass Spectrometer Analysis

In summary, the plots of carbon number vs. DBE (a measure of aromaticity) are used to reveal compositional differences. We noticed a gradual shift to higher carbon numbers at a given aromaticity as one progresses from API 36 to API 20 oil gravity. The most abundant hetero-atom for oil are S1 plus two or three benzene rings class and for asphaltene are S1 & S1O1 + 2 or 3 benzene rings. We also notice gradual increase in higher heteroatom species as API gravity decreases. For example, the S3 class is first observed above 1% total abundance is API 23, and gradually increases to API 19.

Tar Mat Samples Measurement

The samples were Grinded and solubilized in Toluene as shown in Figure 35. The CS2 used to solubilize the tar material does not transport through the C30- GC x GC columns.



Figure 35 Tar samples from Core logs obtained downhole

The 9.4 Tesla Mass Spectrometer Method was applied up to C80+ Figures 36, 37 and 38 show the results of the crude oil analysis of KB2, KB3 and KB4 Tar samples respectfully. It is accurate to isotopes of H,C, S, N, O level – 103 component families.

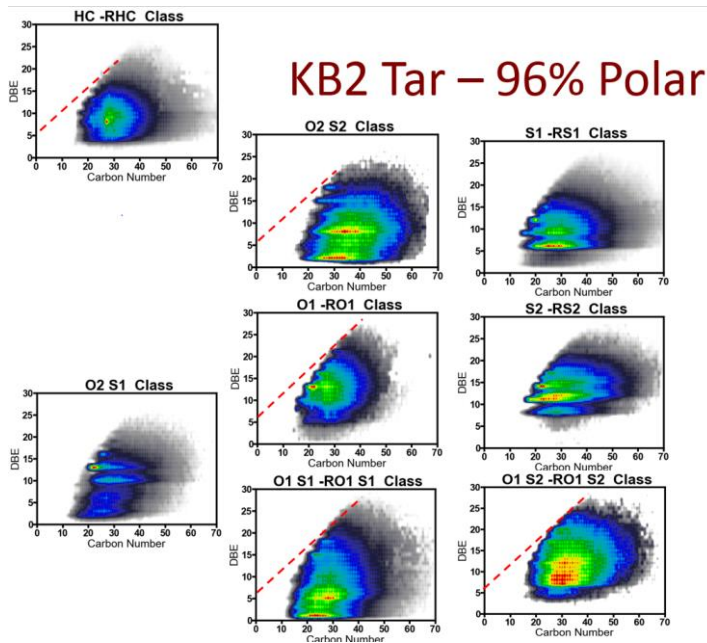


Figure 36 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Tar sample KB2 formation

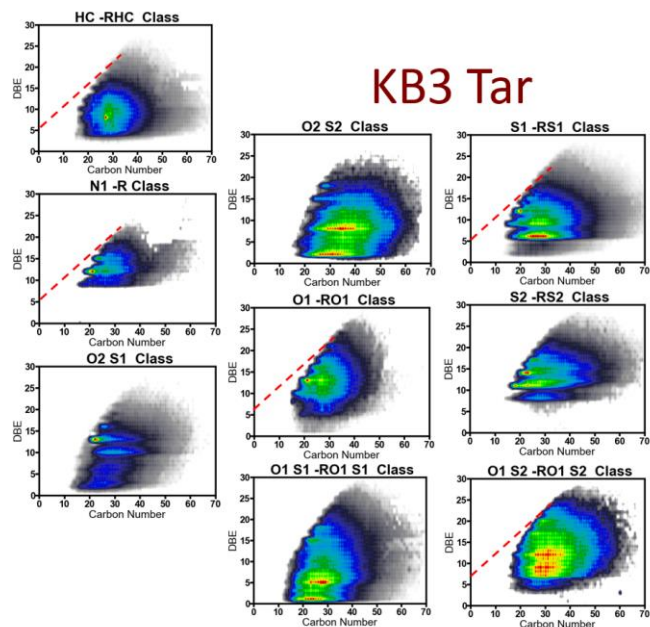
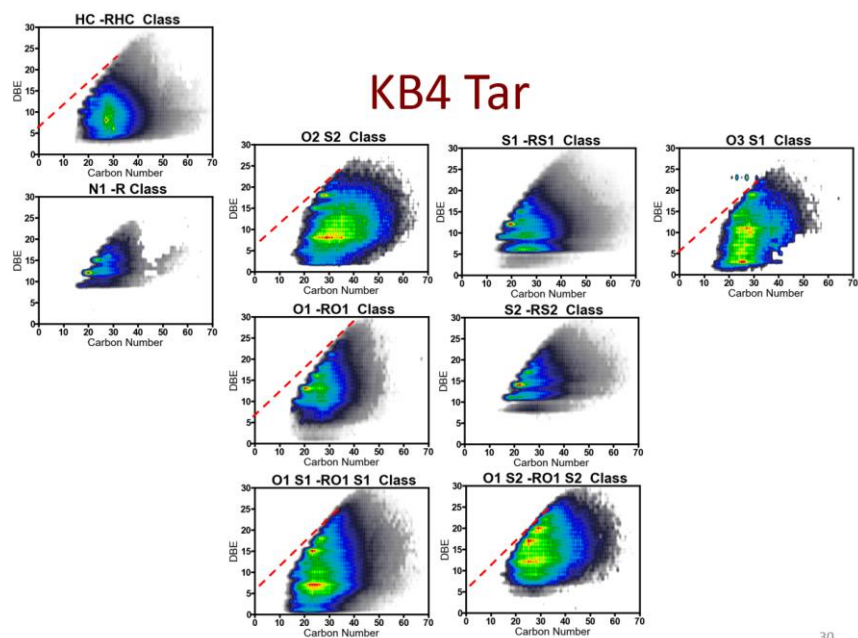


Figure 37 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Tar sample KB3 formation



30

Figure 38 Crude Oil Analysis by (+) APPI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Tar sample K4 formation

Summary results of Tar Mat Samples

- Molecular-level characterization of the most abundant PAH, PASH, PANH, and PAOH
- Species as function of API gravity was achieved by FT-ICR MS via Atmospheric Pressure Photo-Ionization.
- The most probable components are O1, S2 with oxygen or sulfur rings
- The tar has more Hetro atoms than the asphaltene phase in the oil and that is why it participated with methane influx
- KB4 (deepest tar mat) has the maximum concentration of hetro atoms

CHAPTER VI

RESULTS, SUMMARY AND CONCLUSION

Data Analysis

We managed to gather mega data set for 6 oil samples and 3 tar samples using the APPI FT-ICR MS (9.4 Tesla Mass Spectrometer Method). For our analysis, we decided to pick data for 1 oil sample with API 29 and generated Hydrogen number Vs Carbon number plot to help us in identifying families of hydrocarbon components measured as shown in Figure 39. The plot represent data for an API 29 oil sample.

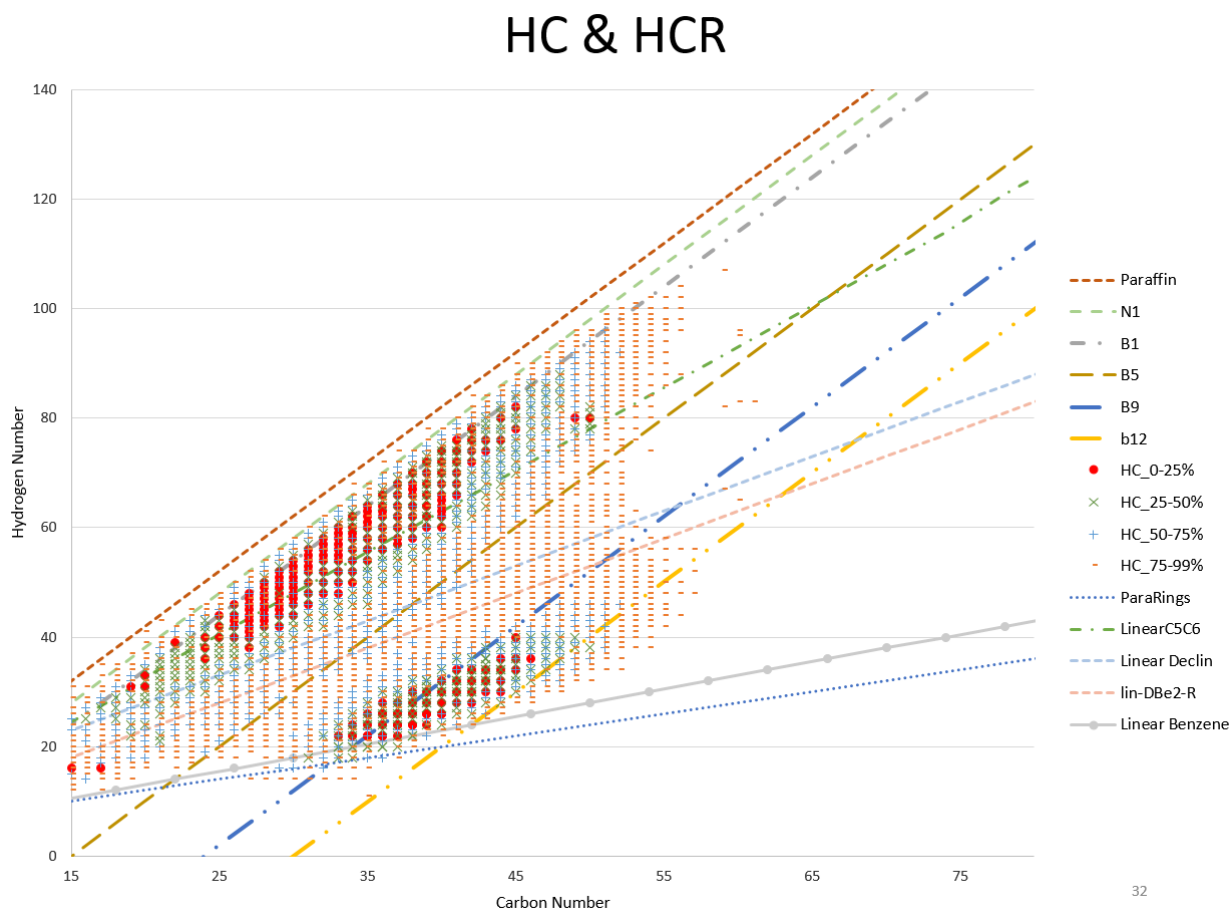


Figure 39 Hydrogen number Vs Carbon number for 29 API oil sample

Each of the straight lines represents different hydrocarbon families. For instance, the line on the top represent the paraffin series, the line to the bottom represent the para rings and the one in the middle is the linear Declin. We also have lines to represent, Linear declin, Linear benzene, 5 benzene rings, nine benzene rings and so on.

Looking at the plot and based most abundant of the data we managed identify two data saturation in a form of islands. One in the top left corner and the other is to the bottom right. Based on that we focused our data analysis on the following groups. The Island on the top represented by the Linear Cyclo-paraffin and paraffin Molecules. The island on the bottom represented by the linear Benzene rings and linear cyclo paraffin and in between we identified linear benzene rings and paraffin molecules groups. We then generated plots that measured True boiling points Vs carbon number for the identified groups as shown in Figures 40, 41 and 42.

Linear Benzene Rings and Paraffin Molecules

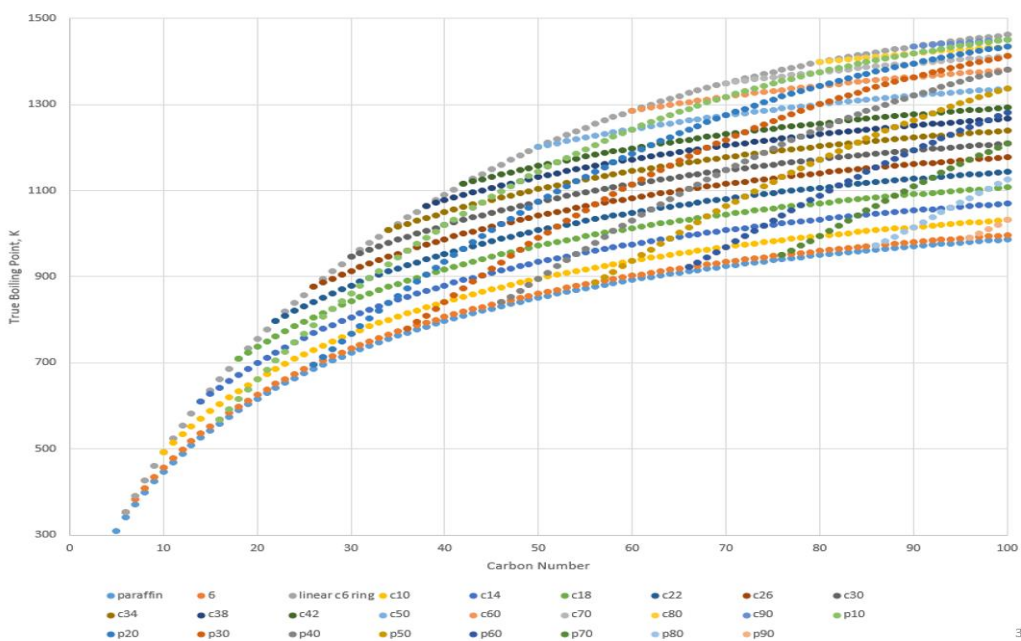


Figure 40 True boiling points Vs carbon number (Linear Benzene & Paraffin)

Linear Cyclo-paraffin and Paraffin Molecules

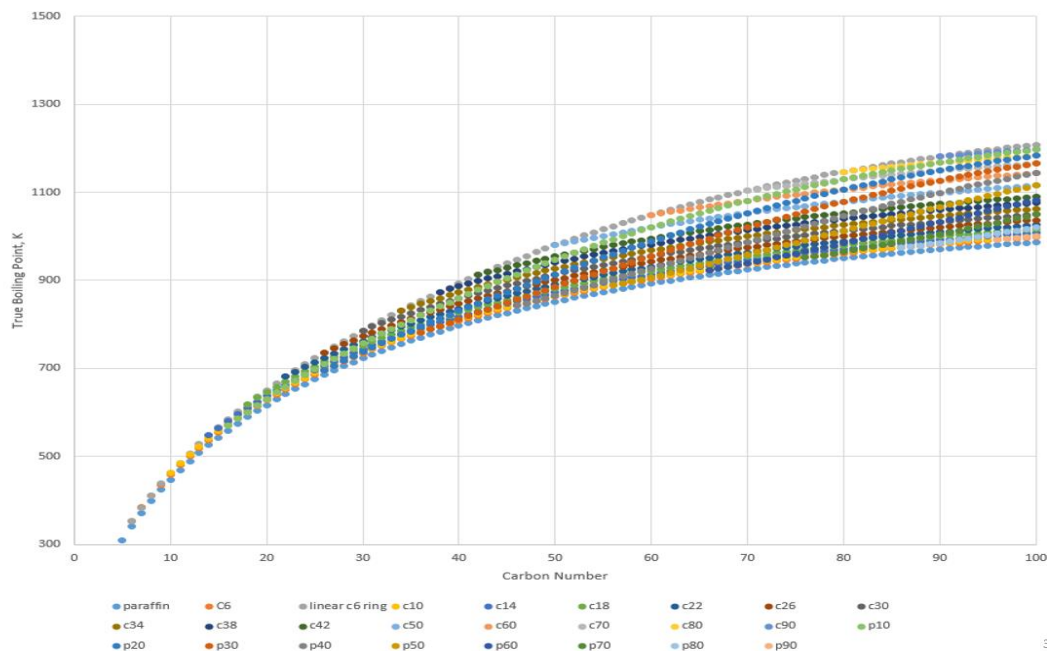


Figure 41 True boiling points Vs carbon number (Cyclo-Paraffin & Paraffin)

Linear Benzene Rings and Linear Cyclo-paraffin Molecules

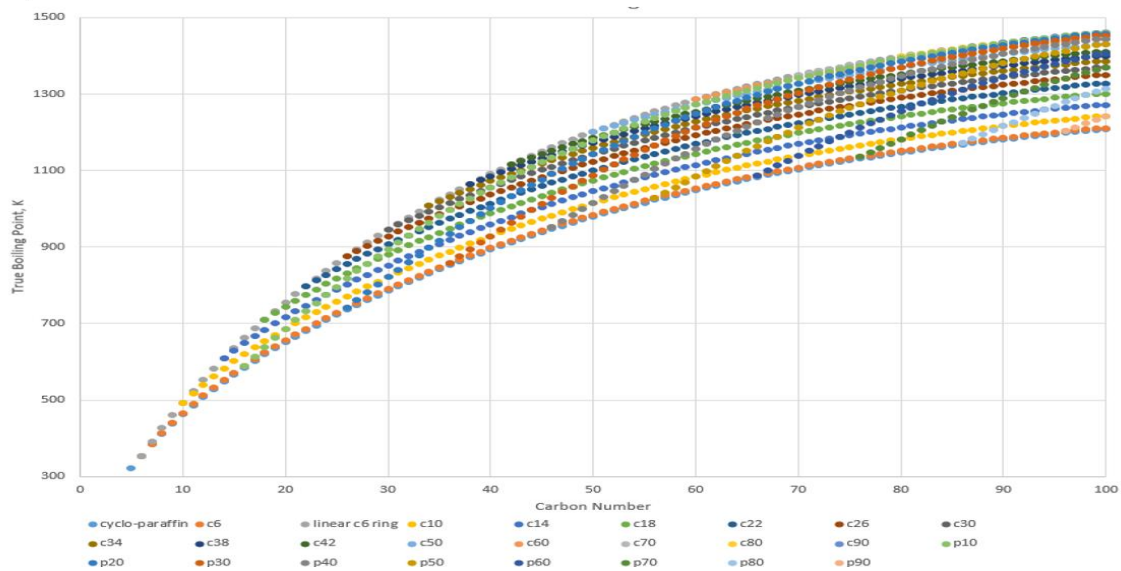


Figure 42 True boiling points Vs carbon number (Linear Benzene & Cyclo-Paraffin)

Conclusion for the True Boiling Points Measured vs Modeled

A Molecular Mass vs True boiling point plot of actual data measured was generated in Figure 43. The blue plot represents the KF correlations used by Al-Shaheen model. We can identify that KF fails to capture a lot of the actual data measured in yellow color which we believed that caused the over estimation of the model results.

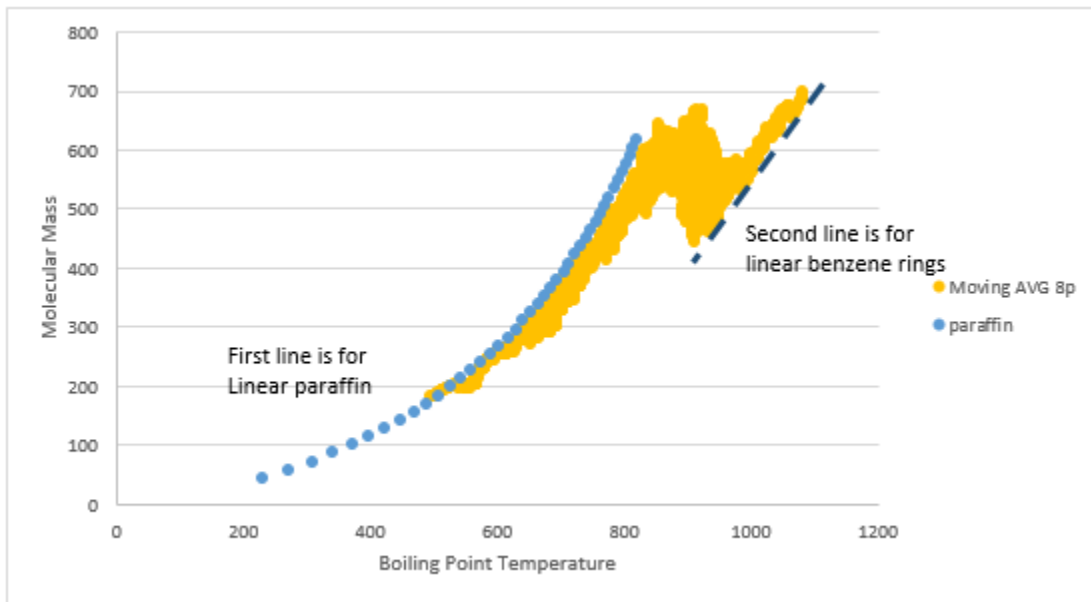


Figure 43 A Molecular Mass vs True boiling point

We can conclude :

- Katz & Firoozabadi developed for crudes with a more paraffinic composition.
- Al Shaheen fluids are more aromatic in nature than the fluids used to develop the Katz and Firoozabadi correlation
- TBP curve needs hetro-atom correction for high sulfur content heavy ends

- TBP Correlation based on average actual compounds to 5 benzene/paraffin rings with endpoint being a commercial polymer

For the measured true boiling points for API 29, we calculated Vapor Pressure for Paraffin [69] as shown in Figure 44, Critical and Triple Point Temperature[70] for Paraffin as shown in Figure 45, Critical and Triple Point Pressure for Paraffin[70] as shown in Figure 46 and finally we calculated Z factor as shown in Figure 47 below.

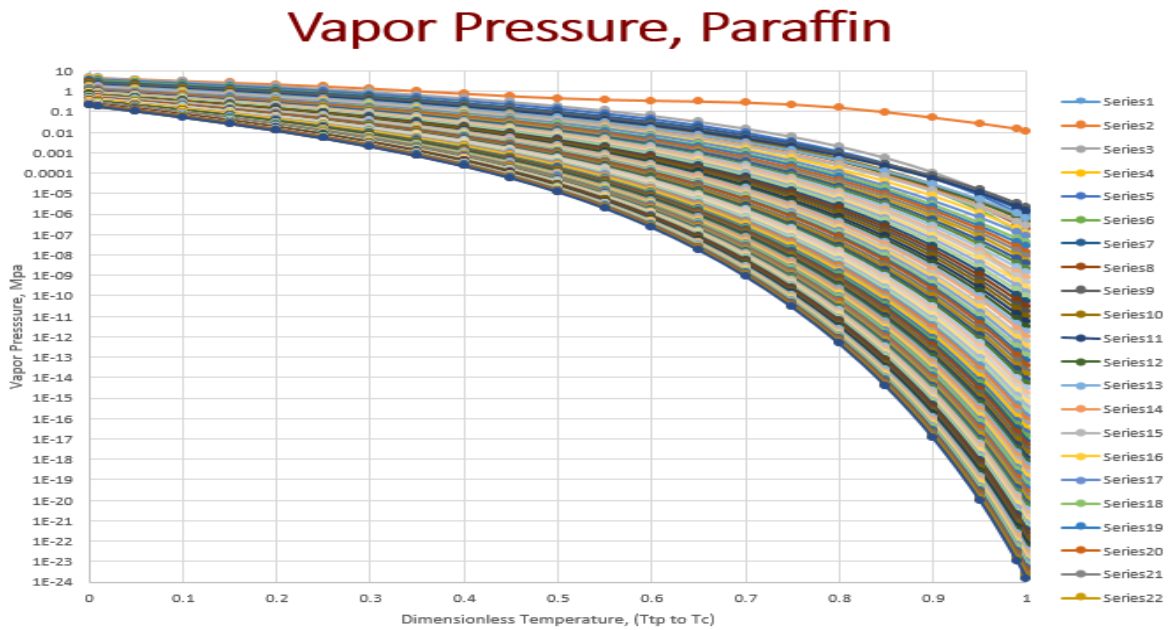


Figure 44 Vapor Pressure for Paraffin

Critical and Triple Point Temperature, Paraffin

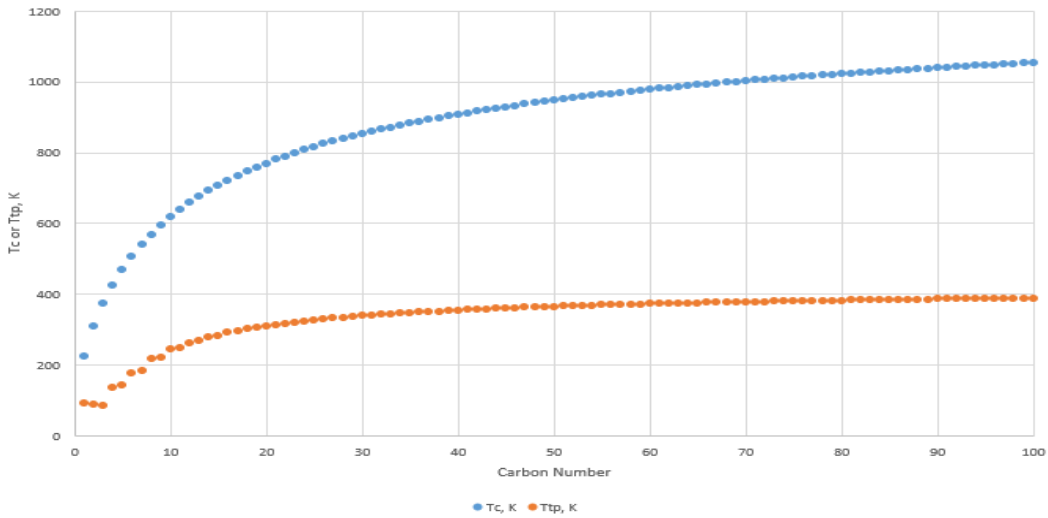


Figure 45 Critical and Triple Point Temperature for Paraffin

Critical and Triple Point Pressure, Paraffin

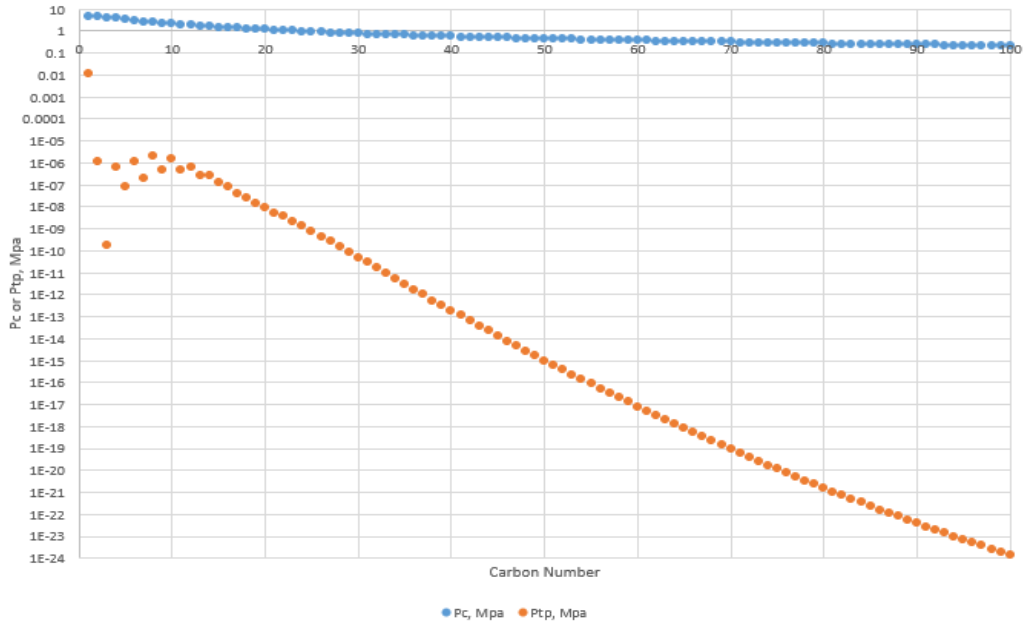


Figure 46 Critical and Triple Point Pressure for Paraffin

Z Factor with Vapor and Liquid Roots

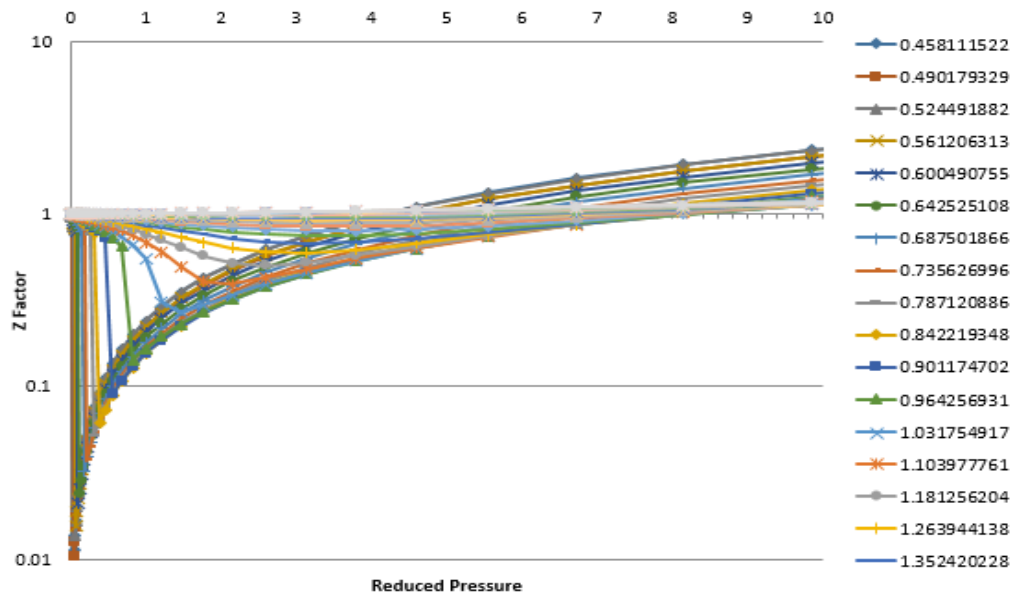


Figure 47 Z Factor

Steps to Simulate API (36 to 18)

- A Minimum of 8 C₇₊ pseudo components are recommended
- Heavy oil viscosity is better modeled by addition of a heavier component
- Heavy components can cause Winprop and Eclipse 300 instability with a solid phase root
- Eclipse 300 is best for testing gas compositions for WAG flooding in the large heavy transition oil zone.

Steps to Simulate Asphaltene Deposition

- Need compositional calibration for C₁, n-C₃, n-C₅, n-C₇, n-C₉, CO₂, and H₂S asphaltene dropout and CS₂ and toluene solvents
- Need additional 4-8 heavy pseudo components (A1, A2, A3, A4)

- A1 to A2 represent Asphaltenes in the oil C20-C30
- A3-A4 represent the Tar leg which is C25- C40
- Need to model heavy components with *-SAFT version such as VLXE/BLEND which was beyond the scope of the project
- Differential scanning calorimetry can be used to map the melting and deposition temperature
- WinProp with solid phase option can model basic asphalt deposition
- Eclipse with solid phase drop out is very slow and unstable at large time steps (negative asphaltene composition).

C7+ Pseudo Component Workflow from Crude Oil Assay

- Simulated Distillation Curve, divide into weight percent cuts
- Estimate structure based on probability from hetro-atom family (1S, exist as 2 benzene rings or hydrogen number = carbon number - 10)
- Molecule weight = CN + HN + Hetro-atom
- Estimate Tc, Ttp, Pc, Ptp, acentric factor and Zc as a function of carbon number, hydrogen number and hetro-atom assuming compounds a built from linear benzene ring, linear paraffin ring or linear paraffin for carbon atoms.
- Using the vapor pressure correlation for Tc, Ttp, Pc, and Ptp and acentric factor calibrate Z-factor equation, Pr-78 EOS, or SAFT EOS
- Asphaltene must use Para-ring line instead of linear benzene ring line
- Tar mat must use Para-ring line and test for precipitation with methane addition to estimate hetro-atom content

Work Flow for Fluid Composition with Gravity Segregation

- Determine reservoir pressure versus true vertical depth from oil gradient or well test and reservoir temperature
- From fluid sample test determine API gravity, gas-oil ratio and bubble point pressure versus true vertical depth. Smooth numbers with gravity segregation correlation from GOC to tar mat
- Build pseudo components from WOC to GOC oil samples
- Build asphaltene pseudo components from C20+ and only use for asphaltene precipitation studies
- With an estimate of nitrogen, carbon dioxide and hydrogen sulfide gas contaminants, calculate methane to hexane composition by matching gas-oil ratio, bubble point pressure and primary separator gas gravity.

Conceptual Study

To demonstrate the error of under estimating the heavy components in developing a dynamic model we created an idealized model as shown in Figure 48. This idealized box model represent the current state of MOQ model.

The object of this model is to show the error we see in the hydrocarbon recovery using the C20 characterization with a huge number of unknown components that were determined using extrapolation instead of actual measurement. We also assume a more paraffinic behavior of the fluid where in fact the fluid have an aromatic behavior. The company promised state of Qatar to deliver 516 kbb/d based on the results of their idealized model. In reality it could only

deliver +300k bbls/d. which is around 40% less than what have been promised. The study models the recovery from 1 line drive pattern consisted of 2 producers and 1 WAG injector. The company idealized model gave a recovery of around 3.2 MM bbls represented by the blue with 10 pseudo components that is underestimating the heavy components Figure 49.

Idealized Horizontal Pattern Study

- 2 horizontal production wells and 1 horizontal injection well pattern
- PVT: 10 Components PR EOS (our study recommends using at least 16)
- $N_x * N_y * N_z$: 21 * 50 * 14 (14,700 cells)
- Average grid size between wells: 50 ft
- Grid size range along wells: 1000 ft
- Used to generate waterflood type curve for horizontal well pattern with different fluid properties

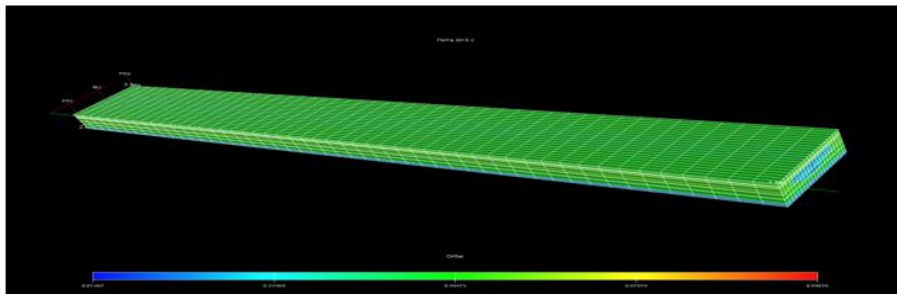


Figure 48 Conceptual Study

WAG Simulation

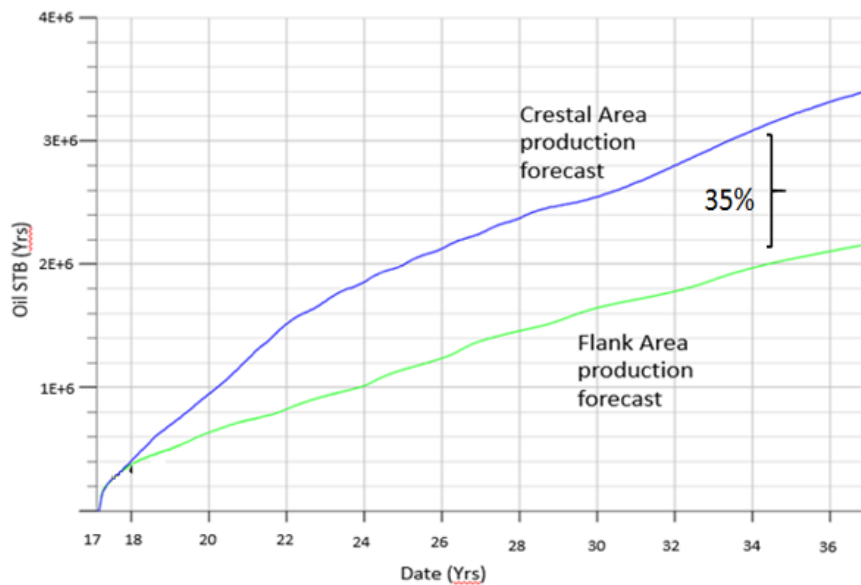


Figure 49 Oil Recovery

Business Impact of Incorrect Pseudo Component Composition

- MOQ model assumption of a near paraffinic behaviour based on crestal fluid samples lead to over estimating the production from the field even with API gravity extrapolated to flank areas (not actual oil properties).
- WAG is near miscible for crestal injection, but corrected model shows immiscible gas injection for WAG in flank.
- In 2009 Maersk Oil came to QP and announced that they could not deliver the 520K bopd and reduced the plateau oil rate to 300K bopd
- In 2016 Maersk Oil lost bid to Total for operation of block
- By 2018 Total still has not calibrated full field model to predict correct oil properties in flanks and as result the drilling program has not maintained plateau oil rate and total

production has declined to 250K bopd with a net loss of \$800 MM/yr.

Way Forward

- Developing the heavy oil (API < 28) flank with transition zone injection using produced near miscible gas to mobilize residual oil (WAG)
- Pseudo oil components will need to include at least one N, S, or O atoms for the calculating oil density, oil viscosity and surface tension.
- Pseudo asphalt/tar components will need to include at least two S or O atoms and S/O ring for the precipitation calculation and mobilization with injection of rich hydrocarbon or carbon dioxide gases
- Most physical properties of hetro-atom families do not exist and will have to be estimated.
- WinProp needs a pseudo component creator for heteroatoms and hydrogen number.

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