A REVIEW ON THE EFFECTS OF ASPHALTENES ON PETROLEUM PROCESSING

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Asphaltene is one of the constituents of crude oil that plays an important role in the physical behaviour of crude oil. It precipitates and deposits on the surface of equipments that are used to process crude oil and this is because asphaltene is the solid constituent of crude oil that contains a high percentage of Carbon, Nitrogen, Oxygen and Sulphur. The composition of asphaltene is yet to be fully explored due to the fact that it has a complex molecular structure. Several scholars have done research on the asphaltene content of crude oil, but this one concentrates on the effects that asphaltene has on the production and processing of petroleum.
In this research paper, we highlighted past and current works and findings on the effect of asphaltenes on petroleum processing.

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Introduction

Crude oil is a mixture of hydrocarbons that can exist in solid, liquid or gaseous form. In most cases, it is found in reservoir in liquid or gaseous form. It is also a naturally occurring brown to black flammable liquid.[2,20]Crude oil is formed when biodegradable organic materials settle at the bottom of a large body of water (sea or ocean) where there is insufficient amount of oxygen to aid decomposition. It was first discovered in the world at the ancient region of Mesopotamia where it formed pools on the surface of the earth.

As technology became more advanced, oil wells were dug in order to produce crude oil in large quantity that can sustain the economy of a nation. The first oil well was struck at Titusville in Pennsylvania by Colonel Drake in 1859 and this led to the production of the first combustion engine in 1897. This resulted to a very high demand in crude oil around the world.[17]

The countries of the world are divided into developed and underdeveloped economy. The developed countries are those that consume high amount of energy to sustain their development while the underdeveloped countries consume less energy for the same purpose. Therefore, these countries are either oil producers or consumers. For example, Saudi Arabia is the world's largest producer of crude oil and United States of America is the world's largest consumer of oil. The Chinese economy is one of the economies of the world that changed from being an oil producer to an oil importer because of their high energy consumption.[12]Crude oil is now the major source of energy in the world. The chart below shows the proved oil reserve in the world.

Crude oil is generally made up of hydrocarbons that exist as a mixture and they can be separated into different components that include naphtha, kerosene, diesel, bitumen, etc.[15,22] These components are made up of mainly carbon and hydrogen but there are also some traces of oxygen, nitrogen and sulphur that can also be found in crude oil. There are also aromatic constituent of crude oil and they include benzene, toluene and xylene which are also known as BTX.[4]

Basically, the presence of asphaltene in crude oil has more disadvantages than advantages. One of these disadvantages is the ability of asphaltene to block pipelines that are used to transport crude oil and also increase the viscosity of petroleum. Asphaltene content of crude oil is one of those factors that increase the time required to distill crude oil. The determination of sulphur content in Crude oil is important because the amount of sulphur indicates the type treatments required for the distillates.[20]Most of the crude oil found in different parts of the world have high sulphur content but the Nigerian crude oil is sulphur free and this is the reason why it is called sweet crude oil. Asphaltene has high concentration of sulphur in it. Therefore, it is a major determining factor of the sulphur content in crude oil.[18]

Hydrocarbons can be defined as alkanes, alkenes, alkynes and aromatics depending on the type of carbon to hydrogen bond present in the structure of the compound.[6] Crude oil can be paraffinic, if the amount of paraffinic hydrocarbons is high compared to aromatics and naphtenes. It is said to be naphthenic when the ratio of naphthenic and aromatic hydrocarbons are relatively higher than in paraffins. Asphaltic crude oil has large amount of polynuclear aromatics (a very high asphaltene content) and relatively less paraffins than paraffinic crude.[14,20]

Furthermore, crude oil is a very complex mixture that is composed of several compounds. These compounds can be divided into four major fractions which are saturates, aromatics, resins and asphaltenes. The asphaltene content of crude oil is normally extracted from the heaviest fraction which is bitumen. This is normally done with the use of n-pentane because asphaltene is insoluble in the solvent and the chart below shows how it is seperated into different components.

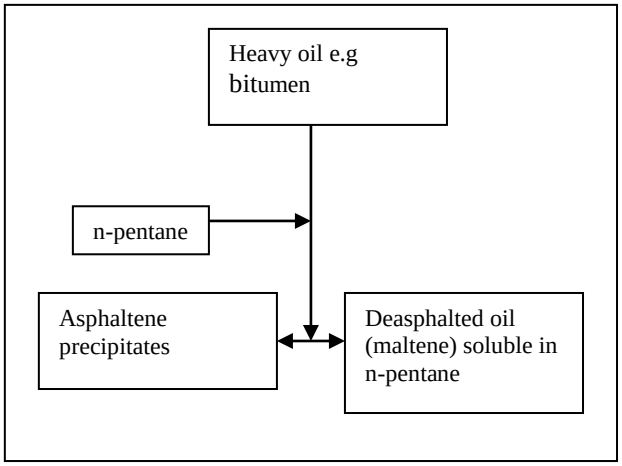

Figure 1. The chart above shows the separation of bitumen into asphaltene and maltene.[21]

The nature of the source material and regional variations in maturation conditions differentiate crude oil and hence, one asphaltene from another. The difference between asphaltene clearly shows the distinction between the relative functional molecular types and the structural type combination in the various asphaltenes. Also, exposing asphaltene to atmospheric oxygen can greatly affect the oxygen content. It has been reported that the asphaltene content of a crude oil sample increases as a result of the presence of high amount of sulphur content.[15]The molecular structures below are that of asphaltenes from two different sources.

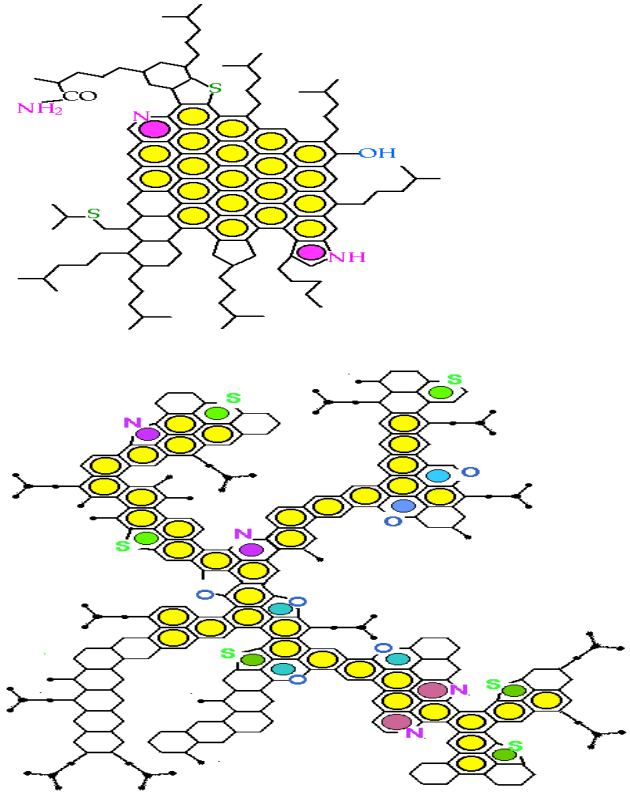

Figure 2. The molecular structures above are Asphaltenes.[3]

Most of the research carried out on the non-volatile component of petroleum concentrated on asphaltene fraction and this is because it contains the largest percentage of heteroatoms (O, N, S) and organometallics such as Ni, V and Fe in crude oil. The molar weight of asphaltene is estimated to be between 500 to 2000 g mol^{-1}.[1]

Since crude oil is made up of a mixture of hydrocarbons, it has to be seperated into different components in order to be useful to humanity. This necessitated the establishment of oil refinery which is saddled with the responsility of seperating crude oil into its various frations through a process known as fractional distillation. This is the most effective technique of seperating crude oil sample because it takes advantage of the boiling points of the various components in crude oil mixture in order to seperate them. On an industrial scale, a very large distillating column which has cooling plates, heat exchangers and other equipments that perform the operation. The crude oil sample is heated and sent into the fractionating column for seperation and then the products are carried through pipes to different collection points in the refinery.[22]The table below shows the different boiling points at which crude oil samples are seperated.

Table 1. The boiling points of fractions during fractional distillation.[4]

Crude oil fraction	Boiling Point (ºC)
Light naphtha	90
Heavy naphtha	170
Kerosene	240
Light gas	340
Heavy gas	425
Residue	425+

Uses of the various products of petroleum cannot be over emphasized because almost every device in world that produces energy today is powered by fuel which can either be kerosene, diesel, gasoline or gases. Kerosene can be used to serve as fuel for lamps and jet engine while gasoline is used to power vehicles and power plants. There are also vehicle that can use diesel to power their engines and this is because it takes less time for the fuel to burn in the combustion engine.

The deposition and precipitation of asphaltene produces a lot of problem in oil production, transportation and processing facilities. The precipitation is caused by several factors which include changes in pressure, temperature, chemical composition of the crude oil and mixing of crude oil with diluent or acids during processing. The precipitated asphaltene can also reduce the permeability of a reservoir near the wellbore region which can lead to the plunging of the wellbore and the tubings. As processing of petroleum is done continously, asphaltene gradually accumulates on equipments and lead to operational problems, safety hazards and an overall decrease in production efficiency which results in increasing production cost. Asphaltene deposition can be removed by either mechanical, chemical cleaning or reserviour manipulation.[11]

Asphaltenes and Petroleum Processing

Asphaltene is not a major constituent of crude oil but plays a significant role in the behavoir of crude oil. Eric in his paper titled *Petroleum Asphaltene-Properties, Characterisation and Issues*, asserted that asphaltene is considered an important factor that causes hinderance in many petroleum operations such as production, transportation, refining, wax crystallisation, crude oil emulsification and de-emulsification. He went further to state that asphaltenes can be categorised in to macroscopic and microscopic scale. The microscopic characterisation of asphaltene according to him, aims to understand molecular properties of asphaltenes, both chemically and physically, and to also deal with the hinderance it may cause during refining operation. He also accounted that asphaltene also poison catalyst which speeds up reactions in refining processes, more especially at a very high temperature and pressure where asphaltenes is expected to exist in a molecular form. He also made clear that it is important to characterise asphaltene macroscopically to enable field engineers perform operational decisions and optimization of production. It was also discussed in the paper that macroscopic characteristics of asphaltene is still the main area of focus, because data obtained from it has be used to study complex fluids.[25]In another paper, Mahdi *et al* stated that asphaltenes precipitation is one of the problems affecting crude oil production and refining processes. They highlighted that the changes in temperature, pressure and composition of crude oil are the main factors causing asphaltenes instability and consequent precipitation. They also stated that precipitated asphaltenes particles will lead to its deposition during production and transportation through pipeline which will lead to operational problems.[13] Moreover, Karman *et al* in their research paper titled *Problematic but Rich in Potential*, commented that the only advantage asphaltenes exhibit is when it does not form deposits on surfaces. However, they discovered that asphaltenes like other hydrocarbon components have the potential to reveal important characteristics about the resservoir's fluid, history and connectivity. They went further to reveal that asphaltenes also causes other challenge to fluid flow; not only does it affect fluid viscosity and density but they also stabilize oil-water emulsion. Asphaltenes are also important factor in determining the formation wettability. They also stated that changes in wettability can occur when a very small amount of asphaltene is adsorbed to the formation grains and also asphaltenes exist as monomers in bulk crude oil and as an aggregates in an associated state in the precipitate phase.[9]Miadonye *et al* studied the effect that temperature has on the viscosity of crude oil and they discovered that light crude oil were better diluents for the production and transportation of heavier petroleum.[16]

Furthermore, Joseph *et al* in their research on the *Effect of Asphaltene Solvency on Stability of Water in Crude Oil Emulsion*, accounts that the lack of understanding of the molecular origin of emulsion stabilization and full range of factors that govern emulsion stabillity have slowed down the approach to develop demulsification. They also understood that asphaltenes are not soluble in the distillate part of crude oil but they do dissolve to varying extent when associated with resins. It has also been determined that asphaltenes stabilize water-in-oil only if they are near or above boiling point at which colloids start to form. They also found out that resins and asphaltenes in crude oil are known to contain both acidic and basic groups, where as the pH of the water in the emulsion can be expected to affect both the quantities and the types of materials constituting the interfacial film. They also discussed that the pH of the water was also found to affect the physical properties of the adsorbed asphaltenes and these properties include rigidity and mobility.[8] Further research made by Irena *et al* explored the chemical structure of asphaltene which changes upon hydrotreatment which leads to the reduction of product stability and as result asphaltene might precipitate, causing coke deposition on catalyst and refinery equipments. This is the main reason that leads to the limitation of conversion and possible reduction in product yield.[7]The structure of asphaltene gives it the ability to block off molecules such as biomakers. The reminant in an oil reservoir is considered as biomaker and asphaltenes could hinder its secondary alteration. Asphaltenes obtained from crude oil were put under oxidative treatment to disrupt their structure and this leads to the release the trapped oil. They also stated that oil collected from the released hydrocarbon was collected and compared with original crude oil to evaluate the level of alteration as a result of biodegradation. The crude oil are found to be depleted in n-alkane which is an effect attributed to biodegradation. However, they also claimed that the products obtained from asphaltenes have n-alkane distribution ranging from C_{15}-C_{35}, this indicates protection from biodegradation due to the encapsulation provided by the asphaltene network.[24]

Even further, in another article Srisvastava *et al* revealed that asphaltene deposition problems are not limited to miscible flooding after the initial waterflooding but they are also encountered during natural gas depletion, gas-lift operations, caustic flooding and matric acidizing. Asphaltenes is believed to exist either dissolved in oil or finely dispersed in the oil stabilized by the resins adsorbed on the surface. They continued their research by stating that the asphaltene to resin ratio and high or low molecular weight determine which crude oil can precipitate asphaltenes and the application of mechanical, chemical or electrical forces can alter these ratios and destabilize resins and asphaltenes; fine particles of destabilised asphaltene coalesce and cause flocculation. The flocculated asphaltene contain some amount of oil which inhibits deposition. They also confirmed that asphaltene precipitation occur when flocculated asphaltene seperate from oil phase. However, precipitated asphaltene can return to the solution if the asphaltenes to resins ratio of the precipitated phase is the same as that of the original oil. They also explained that in carbon dioxide or hydrocarbon flooding, asphaltenes to resins of crude oil is altered which leads to asphaltene precipitation and deposition and the role of resins in stabilizing asphaltenes is well understood but asphaltene precipitation is not clear uptil today. The need to access the likelihood of asphaltene precipitation and consequent oil recovery and monetary losses are some of the problems that confront reservoir and production engineers' cosidering a miscible carbon dioxide flood for a well.[19]

Even though, the precipitation of asphaltenes is a complex situation that involves resins and asphaltenes. Speight in his book *Chemistry and Technology of Petroleum*, proved it by dissolving bitumen in solvents such as n-pentane, n-hexane or n-hepatane but n-pentane is the most desirable of them because it provides maximum asphaltenes yield. He went further to state that asphaltenes can also be the fraction of crude oil or petroleum product that can be seperated by adding n-pentane. Resins are the fraction of deasphalted oil that can be adsorbed by alumina or silica and only be removed from such surfaces by a mixture of toluene and methanol or pyridine. He also highlighted that asphaltenes and resins are aromatic heterocompounds with aliphatic substitution and they serve as the major constituent of the polar fraction of crude oil. Since petroleum is a complex mixture that is not only difficult to analyze the recovered materials but also the original oil in place, the incompatibility of crude oil constituents with each other and the suspension of organic solids during oil recovery are issues that require tremendous attention. Therfore, Speight in his article the *Chemical and Physical Structure of Petroleum: Effects on Recovery Operation*, revealed that the problem can also reduce the efficiency of various processes in the petroleum industry. A more detailed knowledge of composition and reactivity of asphaltene will help in understanding the recovery processes.[21]Consequently, solvents such as natural gas liquids; liquified natural gas, natural gas and carbon dioxide are used during enhanced oil recovery and can lead to asphaltene deposition and flocculation. He went further to state that the quantity of asphaltene deposited during this operation is not known and depressuring an oil reservoir is also another factor that leads the deposition of asphaltenes.[22] It was further discussed by Leontaritis *et al* that the organic formation damage can result from flocculated asphaltenes causing permeability problems by plugging the pore throat and wettability alterations by adsorbing negative mineral sites such as clay and silicas. When efficient oil production is required, water-wet reservoir rocks permits it owing to the favourable relative permeability to the hydrocarbon fluids. But, oil flows through throats and pore channels that are more oil-wet than water-wet. This makes water to flow through larger pore throat and by-pass some of the oil.[10]

CONCLUSION

After reviewing several literatures, we came to a final assumption that asphaltenes are one of the constituents of crude oil and they also cause problems during petroleum processing. The effects of asphaltenes on petroleum processing cannot be over emphasized because of the detrimental impacts it has on the oil industry. The structures of asphaltenes were also studied, even though they do differ from one reservoir to another. Asphaltenes do affect catalyst during refining processes and also hinder petroleum operations such as transportation, production, wax crystallization, etc. The flocculation and deposition of asphaltenes are governed by alot of factors such as reservoir wettabilty and solvent injection. They can also be determined by the temperature, pressure and composition of the crude oil in a given reservoir. Asphaltenes are basically the storage place for heavy metals and other elements found in crude oil. As a result, it easily solidifies when isolated from crude oil. Asphaltenes deposition can be remediated using either mechanical or chemical methods. Mechanical cleaning method can be done using coiled tubing, wireline cutting or pigging while chemical cleaning is done by injecting xylene into the wellbore.

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