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The study of coprecipitation of heavy organics from crude oil

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ABSTRACT

Heavy organics exist in crude oil mixtures in various proportions . the separation of these four organics into four popular fractions; Saturates, Aromatics, Resins and Asphaltenes commonly referred to as SARA has been highlighted. Coprecipitation of heavy organics can occur due to the variation of factors such as temperature, pressure and composition in the oil fields. Such occurrence has been recognized to be the most problematic in the oil industriies as it causes the plugging of pipelines and reservoirs, fouling of production facilities and poisoning of refinery catalysts. The role of solvent precipitation as a solution technique to heavy organic coprecipitation and deposition has been highlighted. A modified version of ASTM D6560 laboratory test method has been described for small scale coprecipitation of heavy organics. Usage of n-pentane (C_5), n-octane (C_8) , and n-dodecane (C_{12}) as precipitating solvents showed that C_5, C_8, and C_{12} n-alkane solvents gave percentage precipitate yields of 9.11, 3.24 and1.28 respectively. The results showed that the quantity of precipitates decreased as the carbon number of the n-alkane solvents increased.

Keyword; Coprecipitation, Heavy organics, Crude oil, n-alkanes etc.

INTRODUCTION

Nigeria is a country naturally endowed with abundant reserves of crude oil. Crude oil is naturally occurring and consist of a complex mixture of hydrocarbons. The hydrocarbons are composed of light discrete components and a heavy end known as heavy organics (Abedi et al,1998). Crude oil has been the major source of energy, revenue, chemicals and foreign exchange for most countries including Nigeria. However, a major problem presently confronting the petroleum and natural gas industries is the untimely deposition or precipitation of solid organic compounds during production, transportation and storage of petroleum fluids. This deposition has resulted to complete clogging of flow lines and consequently leading to serious damages to storage vessels and processing equipment. The solution to many technological problems posed by such deposition lies on a good understanding of the multi-phase species which precipitate (Acevedo, et al 1995). The production or mining processes of petroleum products has become both financial and capital intensive due to the the attendant consequences of this precipitation in the petroleum sector. Coprecipitation is the process whereby a solute that would normally re main dissolved in a solution precipitates out on a carrier that forces out to bind together rather than remaining dispersed. Mansoori in 1996 reported that numerous challenges in the oil industry has been associated with heavy organic depositions, the recognition of arterial blockage in petroleum industry is due to the deposition of heavy organics in

petroleum fluid. Heavy organics such as paraffin wax, resins, asphalthenes, mercaptans and aromatics compounds may exist in crude oil solution due to various forces and on precipitation and deposition cause blockage in the oil reservoirs in the wells, pipelines and reservoir in the wells, pipelines and in production and processing facilities. Wang 2000 portends that asphaltenes flocculation leads to plugging of reservoirs, fouling of production facilities, poisonining of refinery catalysts and altering of wettability, as a result of reduction in pressure and increase in temperature of pipelines and reservoirs in the oil fields. Heavy organics (asphalthenes) in crude oil could be eliminated prior to transportation and processing by precipitation technique followed by filtration.(Vasquez, and Mansoori, 2000). Apart from changes in temperatures and pressure Kawanaka,et al1991, the addition of suitable organic solvents known as precipitants to the crude oil can also induce the precipitation of heavy organics. Such solvents disturb the composition of the liquid phase in which these are dispersed hence precipitate by using filtration techniques, the precipitated heavy organics can be removed as residue leaving behind a relatively heavy organics depleted crude oil filtrate, prior to transportation and processing Leontaritis, (1996 . Asphaltenes collected in the field are known to differ significantly from those generated in the laboratory using n-alkane solvent precipitant according to Becker,1997 It is believed that in the field conditions, saturates,aromatics and resins are probably co-precipitated with asphaltenes. The laboratory methods include redissolution in aromatics solvents (Andersen.1994) Filtration to remove insoluble waxes reprecipitation in order to obtain pure asphaltenes, without the precipitated aromatics and resins.

Materials and Methods

Coprecipitation of heavy organics in the laboratories

Precipitation of asphaltenes was carried out by precipitation experiments similar to those implemented by Kokal et al 1992 and Eduardo et al 2004 and modified version of the American Society for testing and Materials (ASTM) method (D6560).

Procedures

1.00g of crude oil was weighed out into a flask and 30ml of a chosen solvent added to it in the flask. The mixture was shaken vigorously for 30 minutes and allowed to stand for 24 hours after which the mixture was filtered using a pre-weighed filter paper with a 0.45 membrane filter connected to a vacuum pump in a Buchner funnel. The membrane filter with the precipitated material was dried in an oven for 2 hours and then cooled in a cooling vessel for 30-60 minutes and finally weighed to determine the heavy organic mass precipitates. Due to high susceptibility to oxidation, adherence to the procedure specified in the drying stage with respect temperature and time becomes important. The mass of heavy organics precipitated was obtained by the differences between the combined mass of filter paper and residual precipitates and the mass of the filter paper alone.

That is,

Mass of heavy organics precipitated = Mass of (filter paper + precipitate)- mass of filter paper alone. The percentage weight of heavy organics precipitated can be calculated by the formular;

$$\% \text{ heavy organics} = \frac{\text{weight of HO precipitated mg/L}}{\text{Weight of crude oil mg/L}} \times 100$$

Where HO represents heavy organics

RESULTS

Comparison of heavy organics precipitated single C_5, C_6 and C_{12} solvents.

n- alkane solvent	Weight of crude oil residue (g)	Weight of HO ppt	Weight % of HO ppt.
C_5	1.0185	0.0928	9.11
C_8	1.0109	0.0327	3.24
C_{12}	1.0293	0.0132	1.28

DISCUSSION

The result obtained showed that under the same conditions , single n-alkanes containing C_5, C_8 and C_{12} solvents yielded 9.11, 3.34 and 1.28 weight percents respectively. This shows that as the carbon number of the precipitating solvent increases , the weight percent of the precipitates decreases. The asphaltenes which are insoluble in n-alkane solvents containing C5-C8 carbon atoms co-precipitate with other heavy organics. (SARA). As the carbon number in the solvent increases, some precipitated asphaltenes re-dissolve. Hence, the quantity of the precipitate decrease. By applying similar techniques, the percentage of heavy organics precipitation by different by different organic solvents can be obtained. The asphaltenes generated in the different laboratories are different from those generated in the fields. This is because the laboratory methods include re-dissolution in aromatic solvents, filtration to remove insoluble waxes re-precipitation to produce purer asphaltenes without the precipitated resins and aromatics.

CONCLUSION

Heavy organics such as asphaltenes, resins, and wax present in crude oil coprecipitates at various stages of production, transportation and processing causing series of problems that lead to economic consequences in petroleum industries. Thus occurs due to variation in temperature, pressure and composition of petroleum fluids in the field, reservoirs and pipelines. Also by the application of suitable solvents to the crude at the onset prior to transportation and processing, these heavy organics can precipitate and be filtered off. The pattern of organics precipitation can be studied in the laboratories by using various suitable solvents or a mixture of solvents. Knowledge obtained from these studies can be applied on a large scale in oil industries to reduce the cost of production.

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