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AN ENVIRONMENTALLY FRIENDLY SOLVENT MIX FOR ASPHALTENE DEPOSIT REMOVAL

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ABSTRACT

Conventional benzene, toluene and xylene (BTX) solvents have been successfully applied for remediation of asphaltene problems during crude oil production and processing. However, BTX solvents have low flash point, high acute toxicity and low biodegradability, and therefore, considered non-environmentally friendly. Consequently, stringent environmental laws are continuously enacted to restrict the applications of such solvents. This paper investigates the utilization of environmentally benign solvents derived from natural and renewable precursors to dissolve and disperse asphaltene deposits. A composite mixture of methyl ester oleate and ethanol was examined in a solvent and co-solvent synergistic function to dissolve and disperse asphaltene. The solvent blend possesses favourable health, safety and environmentally friendly characteristics such as high flash point (78ºC) and high biodegradability (98%). Results show that the composite solvent gives better dissolution and dispersion of asphaltene deposits when compared with the respective performance of methyl ester oleate and aromatic xylene. Further adsorption studies was conducted and experimental data validated by Langmuir and Freundlich models, confirms a favourable adsorption of methyl ester oleate and methyl ester oleate/ethanol mix on asphaltene

Keywords: asphaltene adsorption, asphaltene dissolution, asphaltene dispersion, environmentally friendly solvent, methyl ester oleate.

INTRODUCTION

Asphaltene is defined as a solubility class of high molecular weight component of crude oil which is insoluble in n-alkanes but soluble in benzene, toluene and xylene (BTX). The structure of asphaltene has been identified as having poly-aromatic and poly-cyclic rings bearing alkyl side chains and heteroatoms such as nitrogen, oxygen and sulphur and traces of metals which include vanadium, nickel and iron (Speight, 1999). It is polar and possesses the highest molecular weight in the range of few hundreds to thousands gram per mole (Jamaluddin *et al.*, 1996; Alberto *et al*., 1997). The true state of asphaltene in the crude oil has been deliberated in literature. One school of thought opined that asphaltene is in true solution with the crude system (Hirschberg *et al*., 1984; Kawanaka *et al.*, 1988) while the other claimed that asphaltene is in a state of colloidal suspension with adsorbed resins providing a protective sheathe in the crude oil (Lichaa, 1977; Leontaritis, 1989). Meanwhile, the latter model has been adopted to explain the existence of asphaltene in crude oil.

Asphaltene precipitation occurs when there is destabilization of thermodynamic equilibrium that exist in crude oil. Changes in composition, temperature and pressure are the three main factors responsible for the thermodynamic equilibrium destabilization (Leontaritis, 1989). These phenomenon causes asphaltene to grow in size from nano-scale to micro-scale in a stage referred to as asphaltene precipitation. Flocculation occurs when the precipitated asphaltene begins to attract each other and aggregate thereby forming particles of larger sizes. The large sized asphaltene particles drop out as their weight could no longer be supported in the crude oil and therefore, deposit on metal surfaces or in the porous media.

Deposition of asphaltene in porous media leads to formation damage by plugging the pore throat thereby causing reduction in permeability. Asphaltene deposition can reverse reservoir wettability from water wet to oil wet which affects the formation relative permeability. Also, asphaltene precipitation increases oil viscosity which may promote water-in-crude oil emulsion (Leontaritis, 1996). Severe asphaltene problems near wellbore region have been reported. Asphaltene deposition in tubings reduces areas open to flow and disrupts proper operation of safety valves. In downstream, asphaltene deposits interfere with the operations of surface facilities and deactivate catalysts in refinery operations. Tremendous asphaltene problems have affected project economy in terms of cost of remediation and lost time due to shut in.

Sequel to this, different remediation methods have been employed to remove asphaltene deposits. Mansoori (2010) outlined different methods for asphaltene remediation which include mechanical, production scheme alteration, chemical method, external force field technique, and micro wave technique. However, chemical method has been widely and successfully employed to resolve asphaltene problems. Aromatic solvents such as benzene, toluene and xylene (BTX) are the commonly used solvents for asphaltene dissolution. For over two decades, industry operators have developed proprietary solvents with almost

equal or better solvency over the aromatics. Despite this development, aromatic solvents are still in use today.

Regardless of their strong solvency for asphaltene and other organic deposits, aromatic solvents have a downside due to concerns over flammability, acute toxicity and environmental issues (Samuelson, 1992). Lightford *et al* (2006) designed a less toxic solvent-water emulsion made up of high flash point heavy aromatic naptha and alkyl polyglucoside. The low toxicity solvent-water emulsion was tested in the laboratory for asphaltene solubility with great success and subsequently deployed to remedy asphaltene deposition problem in Southern Italy oilfield. Frost *et al* (2008) employed an emulsified solvent system (ESS) similar to the emulsion of Lightford and co-worker, to conduct asphaltene dissolution experiment. ESS was blended with surfactant to optimize its performance. The work of (Salgaonkar and Achala, 2012) utilized water/solvent emulsion system to treat asphaltene deposits problem. An aqueous acid was introduced into the formulation to dissolve inorganic deposits deposited together with asphaltene.

Effort are being directed towards utilizing solvent derived from natural and renewable sources with favourable Health, Safety and Environment (HSE) properties to remedy asphaltene deposition problems. Curtis (2003) employed naturally occurring terpene derived from orange peel and resinous pine sap. To improve its effectiveness, terpene was emulsified with an environmentally friendly surfactant. Berry *et al* (2007) utilized bio-solvent (methyl ester) derived from soybean and ethyl lactate from esterification of fermented carbohydrate feedstock. The resulting solvent exhibits good solvency for organic deposits with impressive environmentally friendly characteristics. Acunto (2008) patent claim reported a combination of terpene (d-limonene) and a commercial solvent (LPA-210) to dissolve wax and asphaltene. Rouet *et al* (2012) patent claim utilized chlorophyll extracted from green leaf treated with copper nitrate and synergized with methyl ester rich in oleic acid to disperse asphaltene. Okafor *et al* (2014) reviewed environmentally benign solvents for asphaltene remediation and their challenges.

Mechanism of asphaltene dissolution

Jamaluddin *et al* (1996) and Kelland (2009) proposed the mode of interaction between asphaltene dissolvers/dispersants and asphaltene molecules, which are: π-π interaction between unsaturated or aromatic groups, hydrogen bonding, acid-base interaction and dipole-dipole interaction. To this end, asphaltene dissolvers/dispersants must contain: functional groups, alkyl side chains and polarity to enable it interact with asphaltene molecules. (Becker, 1997) noted similar assertion of solvating specie for asphaltene should contain alkyl substituted aromatic or hetero-aromatic molecules. Asphaltene dissolvers dissolve asphaltene by surrounding themselves around the asphaltene molecules. Solvent interact between the asphaltene molecules and replaces the asphaltene-asphaltene connection with asphaltene-solvent π-π interactions, thus solubilizing the asphaltene (Kelland, 2009). A vivid explanation about the interaction of asphaltene molecule and solvent dissolvers/dispersant was presented by (Sara *et al*, 2012) (Sara and Abbas, 2012), according to their work, solvents containing polar head groups (heteroatoms) attach to the asphaltene polar surface thereby creating an asphaltene-solvent interaction. The alkyl end blocks or isolates the asphaltene molecules from further contact with another asphaltene molecule. This phenomenon was explained by the dissolution of asphaltene using dodecylbenzenesulphonic acids (DBSA).

Asphaltene dissolution solvent

Lasting treatment for asphaltene problems can be achieved by introducing a co-solvent that improves the main solvent in dissolving and dispersing asphaltene deposits. Co-solvents may not necessarily contribute to the solvency of the asphaltene deposits but can act to disperse, suspend or water wet the rock surfaces (Trbovich and King, 1991). Xylene, the popular aromatic solvent for asphaltene solubilization is recommended to be combined with a co-solvent with good water wetting characteristics and of moderate carbon chain length alcohol, to maintain restored productivity over a long period (Trbovich and King, 1991). Ethanol has been applied as a co-solvent to aromatic solvents due to its water wetting characteristics. Petra *et al* (2013) tested an array of hydrophobic pore surfaces with ethanol and concluded that ethanol was capable of facilitating wetting of all surfaces. Checco *et al* (2006) used Atomic Force Microscopy (AFM) to investigate wettability of ethanol on surfaces consisting of hydrophilic carboxyl-terminated and methyl-terminated lines. Results from images clearly demonstrate that ethanol completely wets the carboxyl-terminated lines and does not wet the methyl end. The earlier work of Triebe *et al* (1972) established contact angle measurement for water-wet wettability range of 0°-75° for sandstone and carbonate rock reservoirs. Contact angle of ethanol can be determined by various methods, commonly used is sessile drop method against a solid surface and found to be in the range of 21°-23° (Hanis Husin, 2010).

Merit of methyl ester oleate-ethanol solvent mix

Xylene is the commonly used aromatic solvent for asphaltene dissolution. Kelland (2009) reported that aromatic xylene requires more volume to dissolve asphaltene and xylene dissolves asphaltene at nearly 50% by weights. After asphaltene dissolution, xylene quickly reaches critical saturation and subsequently allowing asphaltene particles to re-aggregate, dropping out of solution to re-deposit. Therefore, continuous injection of xylene is required for a successful remedial job which can adversely affect the economics of the operation.

Zoviedavianpoor *et al* (2013) analyzed xylene solvent utilization for asphaltene problem remediation in 11 wells during a 7 years period located in Southern Iranian oilfield. The wells were reported to follow an increased xylene usage cumulatively over 3,700 barrels.

Methyl ester or bio-diesel is derived from trans-esterification of vegetable oil or more economically from waste cooking oil. Most importantly, the starting materials for methyl ester are abundant in nature and from renewable sources which are not in direct competition with food and pharmaceutical industry. Examples of such materials are rubber seed and jatropha. Economic production of methyl esters and cost-effective sensitivity analysis is presented by (Murugesan *et al* 2009, Shivom and Rangaiah, 2013). Ethanol has been brewed for centuries, materials for ethanol production are obtained from natural sources and processes of production are by natural fermentation followed by distillation. The economics and economic sensitivity analysis for ethanol production is presented by (Franceschin *et al*, 2008)

This work investigates the solvency potential of environmentally friendly methyl ester oleate and ethanol acting synergistically to dissolve and disperse asphaltene. Methyl ester oleate and ethanol are both polar substances derived from natural precursors. Ethanol contains heteroatom in its functional group (-OH) which supports the potency of methyl ester oleate in solubilizing asphaltene.

Experiment

Asphaltene was separated from a crude oil sample using ASTM D2007-80 standard procedure. Heptane was used as the precipitating solvent. Forty times as much crude oil volume of heptane was added to form a mixture and aged for 24 hours in a dark place. Precipitated asphaltene was filtered using 0.45µm filter paper in a filter assembly. The asphaltene deposit was collected, washed, and allowed to dry overnight at 50ºC. X-Ray fluorescence (XRF) test was conducted to determine the composition of the precipitated asphaltene. The results of the analysis are presented in Table-1.

Table-1. Results of the elemental analysis from XRF.

Element	**Quantity** (wt %)
Carbon	84.2
Hydrogen	8.70
Nitrogen	1.24
Oxygen	2.56
Sulphur	3.30
Vanadium (ppm)	114
Nickel (ppm)	74

Asphaltene dissolution

Asphaltene dissolution test was conducted by placing 0.1g of asphaltene into a test tube containing 10cc of methyl ester oleate solvent (90% purity). Several samples were prepared to determine asphaltene solubility in methyl ester oleate at different temperatures with time. The samples were incubated at different temperatures and at set durations in an oven. After incubation, the samples were allowed to cool to ambient temperature and then, filtered with 0.45µm filter to collect undissolved asphaltene. The percentage of solubilized asphaltene is calculated using equation 1. The solubility limit of asphaltene in methyl ester oleate was determined by increasing the mass of asphaltene. Complete dissolution was observed for 0.1, 0.2 and 0.3g while 0.4 and 0.5g were partially dissolved. Hence, 0.3g per 10cc is the solubility limit for asphaltene solubility in methyl ester oleate.

$$\% \text{ Solubilized Asphaltene} = \frac{M_2 - M_1}{M_1} \quad (1)$$

Where,
M_1= Initial mass of asphaltene, g
M_2 = Remaining mass, g

Ethanol (98% purity) was blended with methyl ester oleate on a volume-by-volume basis. Firstly, the capacity of ethanol to serve as asphaltene dispersing agent was investigated. The conventional asphaltene dispersant test (ADT) was conducted against a blank sample. Asphaltene precipitation tendency of the crude sample used for ADT experiment was assessed from its SARA fraction analysis and colloidal instability index (CII) (Table-2).

Asphaltene Dispersant Test (ADT)

Hundred micro-litre of ethanol was added to 10ml of n-heptane in a test tube and the mixture shaken vigorously. Five hundred micro-litre of crude oil sample was measured into a 15ml centrifuge tube. The heptane-ethanol mixture was added into the centrifuge tube and capped. The centrifuge tube was shaken and allowed to stand in a dark place for 24 hours. A blank sample was prepared for comparison. The volume of asphaltene deposited was compared to the blank case. Another method to infer and compare effective asphaltene dispersion is to collect an aliquot of suspended asphaltene from the supernatant above the basal deposit. Sample collected is transferred to a turbidity bottle and placed in a turbidity metre. The turbidity metre measures scattered and absorbed light at specific directions. The suspended asphaltene particles absorb the light passing through thereby preventing its transmittance. Portable HACH 2100Q model turbidity metre model turbidity metre was used for this experiment, ranged between 0-1000 NTU with light emitting diode (LED) at 860nm. A relatively high turbidity reading is indicative of an effective

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asphaltene dispersant while a low turbidity reading is indicative of ineffective or poor asphaltene dispersant.

UV-Vis spectroscopy can be utilized to investigate the effectiveness of asphaltene dispersion. The presence of asphaltene can be detected in the visible region (400-800nm). In this experiment, an aliquot of suspended asphaltene was collected in similar manner as the previous experiment and placed in a cuvette. The cuvette containing the sample is placed in the UV-Vis spectrophotometer and the absorbance was measured at two fixed wavelengths, 640nm and 720nm respectively. An effective asphaltene dispersant has a higher absorbance reading. Table-3 shows the result of deposit volume, turbidity test result and UV-Vis readings for blank and ethanol samples.

Dissolution test was conducted with methyl ester oleate and ethanol blends. Solid asphaltene was placed in a test tube containing 10ml of the blends at 1:100 (w/v). The ethanol volume was varied from 10 to 50vol%. Xylene and a mixture of xylene and DBSA were used as reference solvents. The same asphaltene weight per solvent volume measurement was used to conduct asphaltene dissolution tests. Previous asphaltene dissolution experiments were repeated with the new solvents. However, xylene and xylene/DBSA blend were maintained at ambient condition. Particle size of solubilized asphaltene was investigated to discern the effectiveness of the co-solvent in dispersing solubilized asphaltene. Mastersizer 2000 particle size analyzer was used with detectable particle size range of 0.02-2000µm.

Asphaltene adsorption isotherm

Asphaltene adsorption study was conducted by measuring different amount of asphaltene into seven flasks (20, 40, 60, 80, 100, 120, 140mg). Using the UV-Vis spectrophotometer, initial concentration of methyl ester oleate and the mix of 80 vol% methyl ester oleate and 20 vol% ethanol was measured. 25ml of the adsorbate was added to each flask for each case. The flasks was placed in a shaker at 25°C and agitated at a constant speed of 150rpm. An equilibrium period of 8 hours was allowed, after which the content of each flask was filtered and centrifuged for 10 minutes at 5000rpm. The supernatant from each centrifuge tube was placed in the UV-Vis spectrophotometer and measurement was taken at 420nm fixed wavelength. Equilibrium concentration measurement was taken three times and averaged. The amount of adsorbate adsorbed by asphaltene is given by the relationship:

$$q = \frac{(C_0 - C_e).V}{m} \quad (2)$$

Where C_o is the initial concentration (mg/L), C_e is the final concentration (mg/L), V is the solution volume (L), and m is the mass of the asphaltene (mg).

Properties and solvent blend biodegradability test

Biodegradability test on methyl ester oleate and ethanol blend was conducted according to APHA 5210B standard method for five days BOD using Nitrogen fixing bacteria (Nitrosomonas). Flash point test was performed on the blend using SETA Multiflash flash close cup apparatus. The viscosity and density of the mix were measured at ambient conditions after heating and allowing the temperature to cool down to ambient

RESULT AND DISCUSSIONS

Figure-1 shows asphaltene dissolution for varied soak time. Asphaltene solubility in methyl ester oleate at ambient condition increased with time. On application of heat, asphaltene solubility in methyl ester oleate increased and complete asphaltene dissolution was observed. Xylene which can effectively dissolve asphaltene was used to compare the performance of methyl ester oleate. Result shows that complete asphaltene dissolution in methyl ester oleate were observed at 80°C after three hours. Figure-2 shows the effect of temperature on asphaltene solubility profile. Temperatures ranging from ambient to 80°C and three soak durations (one, two and three hours) were investigated. Gradual asphaltene solubility was observed with temperature while complete asphaltene solubility was achieved at 80°C after three hours.

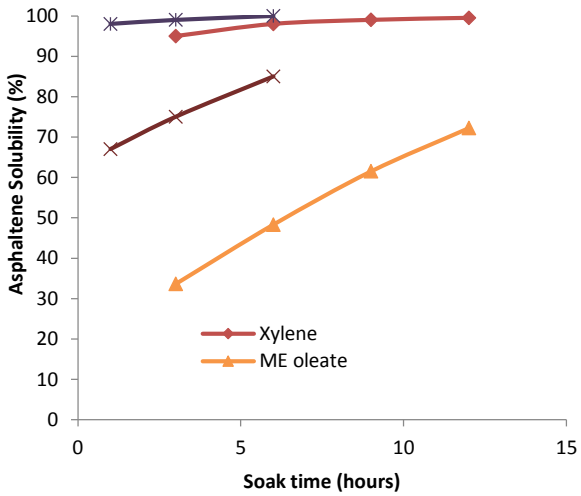

Figure-1. Asphaltene solubility in methyl ester oleate.

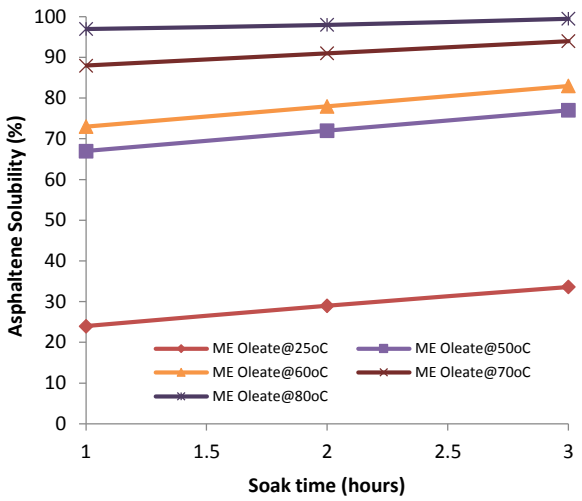

Figure-2. Asphaltene solubility in methyl ester oleate at various temperatures.

Two crude oil samples (A and B) with SARA contents shown in Table-2 were used in another asphaltene dissolution and dispersion tests. The crude oil samples have asphaltene precipitation potential due to their high Colloidal Instability Index (CII >0.9). Table-3 shows the result of ADT conducted on the samples using ethanol as the dispersant. Comparing the asphaltene basal deposit volume for blank case and ethanol, it is observed that ethanol was able to disperse 0.5 and 0.6ml of precipitated asphaltene from crude A and B respectively. The dispersed volume was suspended in the supernatant above the basal deposit. Turbidity reading is indicative of the effectiveness of the applied dispersant and in each case ethanol showed a higher reading than the blank case indicating the presence of more dispersed asphaltene particles. A high absorbance reading is indicative of suspended asphaltene of which ethanol had a higher asphaltene dispersion in the crude oil samples.

The ADT shows clearly that ethanol acts as asphaltene dispersant. Subsequently, various volumes of ethanol ranging from 10 to 50 volume percent were blended with methyl ester oleate and asphaltene solubility test was conducted. No complete asphaltene dissolution was observed above 50 volume percent of ethanol. After dissolution, an aliquot of the dissolved asphaltene in methyl ester oleate and ethanol blend was collected and absorbance was measured via a UV-Vis spectrophotometer. Measurement was taken at two fixed wavelength 640nm and 720nm and the maximum absorbance reading was recorded at 20 volume-percent ethanol and 80 volume-percent methyl ester oleate, as shown in Figure-3. Table-4 shows a comprehensive asphaltene solubility test and UV-Vis spectrophotometer test results. In each case of the solvent blend, complete asphaltene dissolution was recorded but xylene and 1000ppm DBSA (dodecylbenzenesulphonic acid) blend recorded the maximum absorbance indicating a greater dispersed asphaltene after dissolution. Overall methyl ester oleate blend with ethanol gave better performance against methyl ester oleate and xylene respectively.

Table-2. SARA fraction and Colloidal Instability Index (CII) of crude oil samples.

Crude	**Saturates** (wt %)	**Aromatics** (wt %)	**Resins** (wt %)	**Asphaltene** (wt %)	**CII**
A	58.42	20.41	20.83	0.34	1.42
B	51.36	38.16	7.15	3.33	1.21

Table-3. Asphaltene Dispersant Test (ADT) result.

	Deposit volume (ml)	**Turbidity** (NTU)	**640nm**	**720nm**
Crude sample A				
Blank	1.80	29.7	1.129	0.573
Ethanol	1.30	35.2	1.407	0.749
Crude sample B				
Blank	1.70	17.3	1.430	0.739
Ethanol	1.10	23.3	2.031	1.091

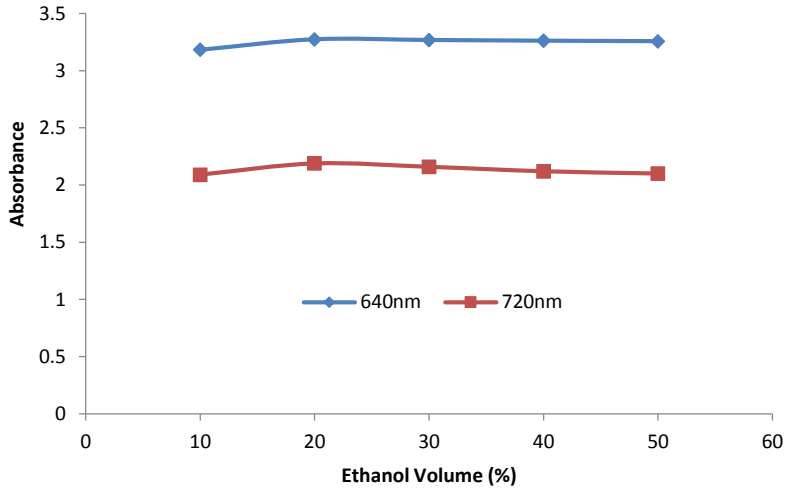

Figure-3. Result of ethanol as asphaltene dispersant at two wavelengths.

Further investigation was conducted to quantify the size distribution of dissolved and dispersed asphaltene particles. Figure-4 shows the dissolved asphaltene particle size distribution in xylene and the composite mixture of methyl ester oleate and ethanol. The distribution in xylene (the reference solvent) was predominantly 70 to 600µm but 50 to 400µm and 0.7 to 30µm in the composite mixture. The size distribution in methyl ester oleate alone ranges from 10.3 to 40µm and 40 to 450µm as shown in Figure-5. This indicates, as established previously, that the addition of ethanol further disperses the asphaltene by reducing the asphaltene particle size. Figure-6 compares the performance of the reference solvent (xylene) with the DBSA blend. DBSA is an effective asphaltene dispersant and when added to xylene, it aided asphaltene dissolution by greatly reducing the particle size to the range 0.25 to 40µm. Xylene and DBSA blend presents an effective solvent asphaltene dissolution and dispersion. Also, the more environmentally benign methyl ester oleate and ethanol mix performs the same functions and is more effective than xylene and methyl ester oleate respectively.

Table-4. Asphaltene solubility and dispersion performances of the selected solvents.

Solvent blend	Asphaltene solubility (%)	640nm	720nm
Methyl Ester Oleate	100	3.043	1.770
80vol% Methyl Ester Oleate + 20vol% Ethanol	100	3.274	2.190
Xylene	100	2.535	1.476
90vol% Xylene + 10vol% DBSA(1000ppm)	100	3.682	2.864

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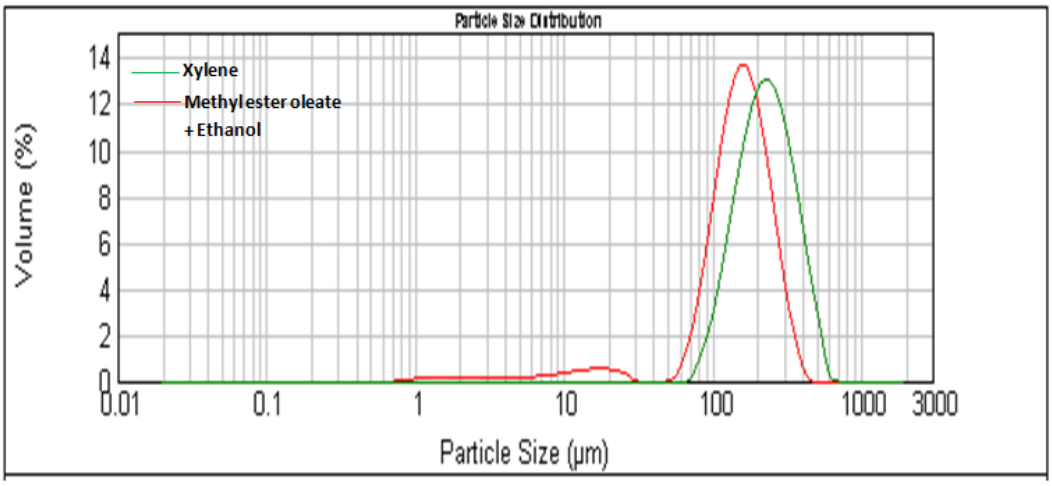

Figure-4. Particle size distribution of dissolved asphaltene in xylene vs. methyl ester oleate and ethanol blend.

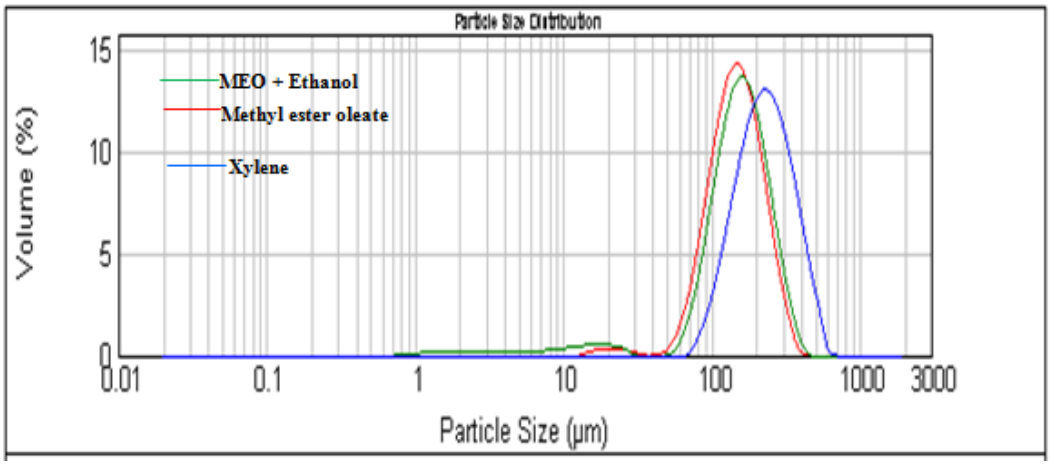

Figure-5. Particle size distribution of dissolved asphaltene in methyl ester oleate; methyl ester oleate and ethanol blend; and xylene.

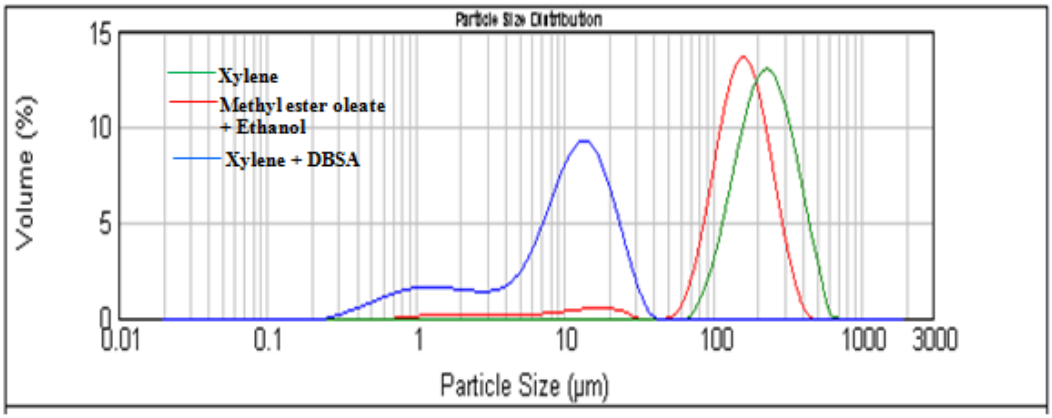

Figure-6. Particle size distribution of dissolved asphaltene in xylene; methyl ester oleate and ethanol blend; and xylene and DBSA blend.

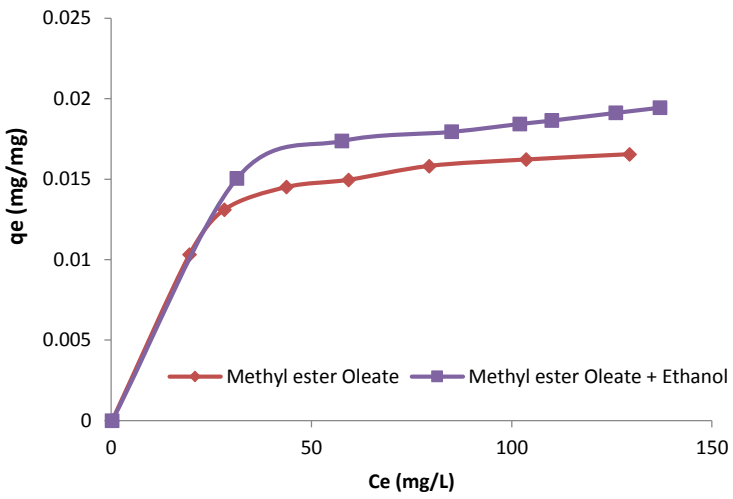

Figure-7. Adsorption isotherm of methyl ester oleate and methyl ester oleate/ethanol mix on asphaltene.

The adsorption isotherm of methyl ester oleate and methyl ester oleate-ethanol mix is shown in Figure-7. The shape of adsorption isotherm is indicative of type I adsorption isotherm usually characterized by Ce>>1. Langmuir and Freundlich models were applied to validate experimental data and explain the interaction between the adsorbate and asphaltene. The linear model of Langmuir is represented as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \cdot \frac{1}{C_e} \quad (3)$$

Where q_m is the amount of adsorbate required to form a single monolayer per unit mass of asphaltene (mg/g) and K_L is the adsorption equilibrium constant (L/mg). Essential features of Langmuir isotherm can be expressed in term of a dimensionless parameter, R_L, expressed in the form:

$$R_L = \frac{1}{1+K_L C_o} \quad (4)$$

Freundlich model is employed to describe adsorption phenomenon on heterogeneous surfaces. The Freundlich model and its linear form are expressed as:

$$q_e = K_F C_e^n \quad (5)$$

$$Log q_e = log K_F + n log C_e \quad (6)$$

R_L values are indicative of the adsorption nature, R_L is unfavourable when $R_L > 1.0$, linear when $R_L = 1.0$, irreversible when $R_L = 0$ and favourable when $0 < R_L < 1.0$. From Table-5, R_L values lies between 0 and 1.0 indicating a favourable adsorption and R^2 values for both cases also shows that the data fits well with the Langmuir isotherm model. K_F is indicates roughly the adsorption capacity and a larger value implies greater adsorption capacity while 1/n is indicative of stronger adsorption strength and values lower than 1.0 is indicative of favourable adsorption (Nashaat *et al*, 2011). R^2 values for Freundlich model data also shows a good fit, implying a favourable adsorption for methyl ester oleate and methyl ester oleate/ethanol mix on heterogeneous surface of asphaltene.

Methyl ester oleate generally is highly dense and viscous; blending it with 20 volume percent ethanol reduces the density and viscosity properties. Methyl ester oleate measured flash point is >130°C and the final flash point of the blend is 68°C which is still within the acceptable and recommended standard. Methyl ester oleate is very biodegradable with 95% 5-Day BOD test; addition of ethanol improves its biodegradability by additional 3% as shown in Table-6.

Table-5. Regression data and isotherm constants for Langmuir and Freundlich models.

	Langmuir				Freundlich		
Adsorbate	**q_m**	**K_L**	**R_L**	**R^2**	**1/n**	**K_F**	**R^2**
Methyl Ester Oleate	0.189	0.068	0.981	0.957	0.1269	0.0898	0.982
Methyl Ester Oleate + Ethanol	0.2081	0.083	0.980	0.985	0.1681	0.0849	0.995

Table-6. Properties of methyl ester oleate and ethanol blend.

Property	Methyl ester oleate	70vol% Methyl Ester Oleate + 30vol% Ethanol
Density (g/cm^3)	0.8787	0.8623
Viscosity (cp)	5.867	2.633
Flash point (ºC)	>130ºC	78ºC
Biodegradability	95% (5 days BOD)	98% (5 days BOD)

Table-7 shows the chemical properties of methyl ester oleate and ethanol that facilitate interactions with asphaltene molecule. Polarity of the individual solvent is as a result of the presence of heteroatoms which makes up the functional group. The functional group of methyl ester oleate is carboxyl (-$COOCH_3$) which is a precursor of carboxylic acid present in vegetable oil while ethanol contains hydroxyl (-OH) as present in alcohol family. Aliphatic alkyl present in methyl ester oleate is methyl while for ethanol is ethyl. Methyl ester oleate participate in hydrogen bonding predominantly as hydrogen bond donor while ethanol participate in hydrogen bonding by the interaction of hydrogen atom with electronegative heteroatoms present in asphaltene. There is no aromatic ring present in the two solvents. Esters are one of the few non-aromatic bearing solvents containing only heteroatoms capable of dissolving asphaltene.

Table-7. Features of methyl ester oleate and ethanol.

Property	Methyl Ester Oleate	Ethanol
Polarity	Yes	Yes
Aliphatic Alkyl	Yes	Yes
Functional group	Yes	Yes
Hydrogen bonding	Yes	Yes
Aromatic presence	No	No

CONCLUSIONS

Methyl ester oleate and ethanol are bio-solvent derived from natural and renewable resources abundant in nature. It has been established in this work that Methyl ester oleate has good solvency for asphaltene. It effectively dissolves asphaltene at 80ºC in three hours contact time. For improved effectiveness, ethanol was blended with the methyl ester oleate. Ethanol is a polar solvent with hydroxyl bearing functional group which functions by boosting asphaltene dispersion. Further investigation of the dissolved asphaltene in the blend shows that asphaltene dissolves better in the blend when compared to methyl ester oleate and aromatic xylene respectively. Adsorption experiment further proves that there is a favourable interaction between methyl ester oleate, methyl ester oleate/ethanol mix and asphaltene.

Physico-chemical properties of methyl ester oleate and ethanol mix reveal a homogenous mixture at 80ºC without observable phase boundary. Addition of ethanol leads to reduction in density, viscosity and flash point of the methyl ester oleate. The final flash point is due to the flammable nature of ethanol but meets the approved Environmental Protection Agency (EPA) standard of 5ºC above ambient temperature. Moreover, there is great improvement in the biodegradable nature of the mix which makes it more health, safety and environmentally friendly.

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