Catalytic Aquathermolysis of Egyptian Heavy Crude Oil

S. Desouky, A. Al sabagh , M. Betiha, A. Badawi, A. Ghanem, and S. Khalil

Abstract—Two Amphiphilic catalysts, iron (III) dodecylbenzene sulfonate and nickel (II) dodecylbenzene sulfonate, were synthesized and used in the catalytic aquathermolysis of heavy crude oil to reduce its viscosity. The prepared catalysts exhibited good performance in the aquathermolysis and the viscosity is reduced by ~78.9% for Egyptian heavy crude oil. The chemical and physical properties of heavy oil both before and after reaction were investigated by FT-IR, dynamic viscosity, molecular weight and SARA analysis. The results indicated that the content of resin, asphaltene, average molecular weight and sulfur content of heavy oil is reduced after the catalytic aquathermolysis.

Keywords—Amphiphilic catalyst, Aquathermolysis, Heavy oil, Viscosity reduction.

I. INTRODUCTION

HEAVY crude oil exploitation is an interesting topic deal with the shortage of energy in the world. Heavy oil reserves are abundant in the world, which account for 70% of the total quantity of petroleum. However, extremely high viscosity and abundant amount of heteroatoms (S, O and N) in the structure of heavy oil molecules are examples of the challenges in their exploitation, transportation and processing. Thus, many techniques such as thermal recovery, chemical recovery, microbial recovery, Toe to Heel Air Injection (THAI), Steam Assisted Gravity Drainage (SAGD), in-situ combustion and cyclic steam stimulation (CSS) etc., have been developed and adopted for heavy oil exploitation [1]-[9].

For example, the situ combustion technique is heat generation via exothermic oxidation reactions of oil, which produce coke as the combustion fuel. These exothermic reactions provide energy required to partial upgrading of oil, which yield carbon–hydrogen bond breakage, water and carbon dioxide. The drawback of this process is oxygenated hydrocarbons such as carboxylic acids and sulfones [5], [7], [10], [11], which increase the viscosity of oil and affect the displacement efficiency and recovery factor [7].

Steam stimulation, a type of thermal recovery, is widely used to recover ordinary heavy oil. The steam was used as the heat carrier to raise the temperature of viscous oil; therefore it could reduce the flow resistance of heavy oil in the reservoir. In fact, there are chemical reactions between steam and heavy oil. The drawbacks of this technique are the cost and free radicals that may be generated during breaking of the large bonds. Sometimes, these free radicals participate in polymerization reactions and form bigger molecules. It leads to production of more viscous oil instead of reducing the viscosity. Different catalysts should be used to inhibit this kind of free radical formation and enhance the reduction of viscosity [12]. So that, researchers need, more studies, to achieve appropriate catalysts, which have the ability to inhibit radicals during the process.

Catalytic aquathermolysis [12], [13], a type of thermal-chemical recovery, is one of the most effective methods to reduce the viscosity of heavy oil [13]-[18]. It can break the C−S bond, increase the amount of saturates and aromatics, and decrease resins and asphaltenes in heavy oil, which leads to improve flow characteristics of heavy crude oil.

Clark [19] found that when aqueous metal species added into the process, the viscosity of heavy oil was further reduced in comparison with steam-only processes.

Fan [20] reported that the catalytic aquathermolysis reduce the viscosity of crude oil using oil soluble naphthenate catalyst. However, the catalytic effect is limited because of the selectivity of the catalyst to oil phase.

Many scientists have conducted researches on dispersed catalysts and its effect on heavy crude oil using aquathermolysis process. In this research area we have been synthesized two different catalysts, iron (III) dodecylbenzene sulfonate and nickel (II) dodecylbenzene sulfonate, in order to investigate their catalytic behavior on viscosity reduction of Egyptian heavy crude oil. The prepared catalysts were characterized by CMC, FT-IR, UV-Raman spectroscopy, TGA-DSC and XRD analyses. The resultant heavy crude oil also was characterized by SARA analysis and percentage of viscosity reduction in view of characterization of the prepared catalysts.

II. EXPERIMENTAL

A. Preparation of Iron (Iii) Dodecylbenzene Sulfonate and Nickel (Ii) Dodecylbenzene Sulfonate (SF & SN)

Commercial aromatic sulfonic acid (95%; Sigma Aldrich) was pretreated at 50°C for 30min before use to liberate water content. Portion of $FeCl_3$ or $NiCl_2$ (0.33 mmol, Sigma Aldrich) was added into 50-ml two-necked round-bottom flask, equipped with a condenser containing aromatic sulfonic acid (0.76mmol) under constant stirring by a magnetic agitator for 30min under N_2 atmosphere. Then, the mixture was undergone the interaction with each other under stirring at 85°C for 5h. The resultant product was filtered off, dried under vacuum at 80°C for 12h.

S. Desouky is with the Egyptian Petroleum Research Institute (e-mail: usdesouky@yahoo.com).

B. Properties of Heavy Oil Sample

The viscosity of the heavy oil sample is 28.6 mPa·s. is shown in Table I. It is recorded by a BROOKFIELD DV-III programmable Viscometer at 70°C. Density, API° gravity, Average molecular weight and Sulfur Content are also reported in Table I, before and after catalytic aquathermolysis.

TABLE I
PETROPHYSICAL PROPERTIES OF CRUDE OIL BEFORE AND AFTER USING THE CATALYSTS

samples	^{a}S	^{b}D	^{c}A	^{d}DV	^{e}VM
Crude oil	22400	0.9293	20.6	28.6	324.6
Aquathermolysis	22138	0.9249	21.3	20.8	309.2
SF	18931	0.9047	24.7	6.1	227.6
SN	18246	0.9058	24.5	7.7	241.1

^{a}Sulfur Content in ppm unit ,^{b}Density in g/cc, ^{c}API° gravity, ^{d}Dynamic Viscosity in mPa·s at 70 °C ,^{e}Average MWt

III. RESULTS AND DISCUSSIONS

A. Critical Micelle Concentration (CMC)

Fig. 1 represents the relation between surface tension and log concentration of dodecylbenzensulsulfonic acid surfactant and its catalysts (Ni^{2+} and Fe^{3+}) at 25°C. It's clear that the dodecylbenzensulsulfonic acid surfactant exhibits higher CMC values than the two catalysts. Decreasing the CMC value indicates the higher surface activity of the compound in the bulk of the solution. Comparing between the dodecylbenzensulsulfonic acid surfactant and its catalysts at the interface was performed throughout extracting the two parameters; γ cmc and π cmc listed in Table II. Indeed, the depression in surface tension of the dodecylbenzensulsulfonic acid surfactant and its catalysts solution near the CMC value indicates that SN catalyst is the most surface active compound at the interface. However, SF catalyst showed moderate surface activity and the lowest surface activity is dodecylbenzensulsulfonic acid.

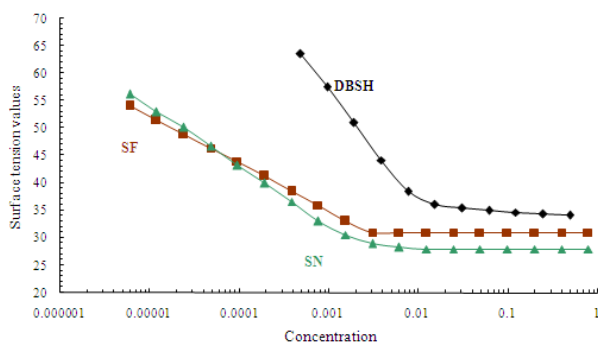Fig. 1 Surface tension values vs. log concentration for DBSH,SF and SN compounds

The high surface activity of the two catalysts than their parent surfactant is revealed to the high hydrophobicity and stereo chemical structure of the catalysts. The Ni^{2+} and Fe^{3+} are attached to two and three sulfonic molecules, respectively. That decreases the interaction between the metal-surfactant

molecules and the aqueous phase. Consequently, the interaction between the surfactant molecules and the aqueous phase pumps them into the oil-water interface and also enhance the micelization at lower concentration.

The interfacial tension values at the dodecylbenzensulsulfonic acid surfactant, SF and SN are also listed in Table II. It is clear that the values are very low in the range of 3-5 mN/m, which indicate their high efficiency at the interface. While, the lowest value is at 3 mN/m corresponds to SN because of its highest adsorption tendency at the water –oil interface. That is in a good agreement with the air-water interface data in the surface tension and effectiveness.

TABLE II
SURFACE AND INTERFACIAL TENSION DATA OF DBSH, SF AND SN CATALYSTS

Compound	IT, m N/m	γ CMC	π CMC	CMC
DBSH	5	36	36	1×10^{-2}
(DBS)$_3$ Fe	4	31	41	2.57×10^{-3}
(DBS)$_2$ Ni	3	28	44	1.99×10^{-3}

B. FT-IR Spectra of Dodecylbenzene Sulfonic Acid, SN and SF

The FT-IR spectra for dodecylbenzene sulfonic acid, SF and SN are shown in Fig. 2. The bands at 2927, 2858 and 1457cm^{-1} are the characteristic absorption bands of methyl and methylene group. The weak bands at 3100 and 3070cm^{-1} are due to C–H aromatic stretching vibrations, which have overtones in the 1980–1650cm^{-1} range. The bands at 748 and 682cm^{-1} are assigned to out-of-plane C–H bending vibrations of the hydrogen atoms remaining on the aromatic ring. The sulfonic (–S=O) stretching band is observed at 1170, 1037 and 1006cm^{-1} and a peak due to C–H p-substituted aromatic out-of-plane bending appears at 800cm^{-1}. However, the sulfonic bands have a notable blue shift to ~1178, 1142, and 1010cm^{-1} for catalysts 1 indicates that the sulfonic acid group has chelated with the iron and nickel. In addition, DBSA shows the characteristic S0$_3$H band at ca. 900cm^{-1}. In the reaction product, no such band is observed, indicating that there remains essentially no amount of un-reacted sulfonic acid.
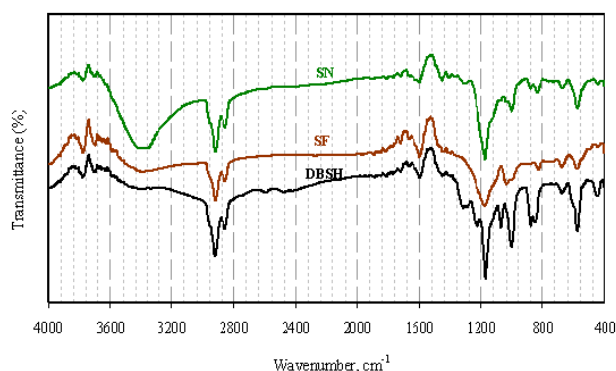

Fig. 2 Measurement of FT-IR spectra for DBSH, SN and SF compounds

C. UV-vis Spectroscopy

Diffuse-reflectance UV-vis spectroscopy is a sensitive tool that is widely used to detect the presence of framework and extraframework metal species. Two characteristic bands have been resolved for metal-containing materials in the UV-vis spectra (Fig. 3). A band with a maximum at about 200-220 nm is attributed to a ligand-to-metal charge-transfer transition in isolated metal units [21]. It is generally believed to connect directly with the framework M^{4+} (M= metal) in tetrahedral coordination and is usually used as direct proof that metal atoms have been incorporated into the substrate function group [22], [23]. The SF catalyst has three intense absorptions around 200, 222 and 238nm. The molecular orbital compositions showed that the intensive adsorption band near 200 nm is corresponding to the electronic transfer from the sulfonic group to the Fe atom. While for SN catalyst, the adsorption peaks were 200, 208, 214, 220, 248 and 254nm. The absence of absorption above 290nm is due to the nanometric scale of metallosurfactant. In addition, Barja reported that the UV–Vis spectra absorbance band at 293nm arising from the charge transfer bands of $Fe(OH)^{3+}$, $Ni(OH)^{2+}$ [24]. This spectra absorbance band is absence and a new one at 254nm when dodecylbenzene sulfonic acid is added. This new and more intense band confirms the formation of SF and SN catalysts in aqueous solution.
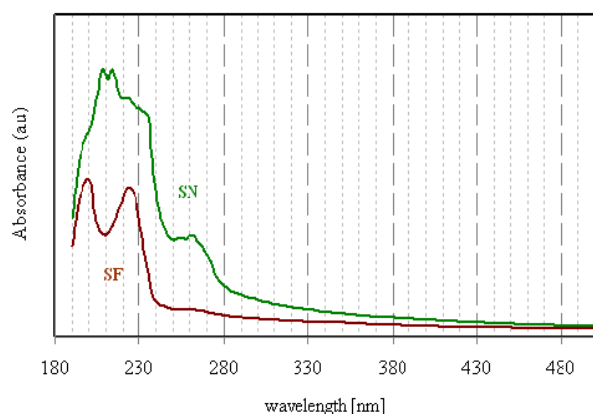

Fig. 3 Measurement of UV vs. spectra of SN and SF compounds

D. TGA & DSC Analysis

The thermal analysis of SF or SN was performed to determine the thermal stability of the catalysts and the concentration of metal species in metallosurfactant. The thermograms of the two catalysts are shown in Figs. 4 and 5. The thermograms indicate three major stages of weight loss, which are attributed to different causes. The first weight loss below temperature near 135°C results from moisture evaporation, the second weight loss at higher temperature between 135 and 245°C arises from degradation of aliphatic-DBSH molecule, and third one is attributed to the structural decomposition of iron and nickel catalysts associated with liberation of aromatic groups. From the thermogram, it was observed that total weight loss of SF and SN is of 91 and 80%,

respectively. Consequently, the metal incorporated dodecylbenzene sulfonic acid is about 9% and 20%for SF and SN catalysts, respectively.
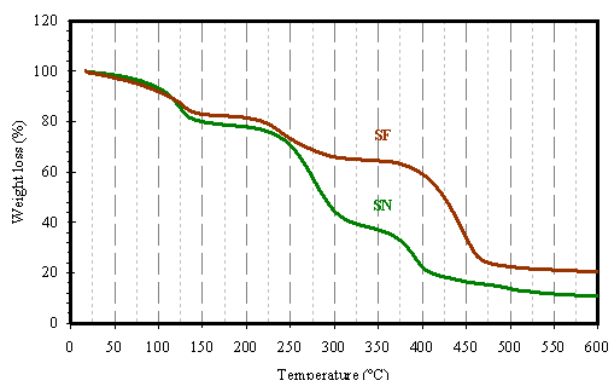
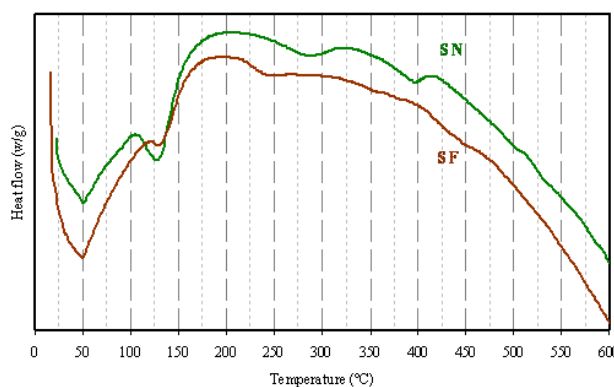

Fig. 4 TGA analysis of SN and SF compounds

Fig. 5 DSC heat flow of SN and SF compounds

The DSC curves for SF and SN catalysts show a sharp melting point at 51 and 55°C, respectively, and water vaporization at 132°C. This is consistent with previous DSC results for the pure ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [25], [26]. In addition, the absence of two-enthalpy overshoot reappears at ≈283 and 396°C resulted from degradation of complexes.

E. Catalytic Activity

1. Effect of Temperature on Viscosity Reduction

Fig. 6 shows that the SF and SN compounds used have a diverse effect on viscosity. The major general trend is that with increasing the temperature there is an increase in the measured viscosity reduction of heavy crude oil due to increase in homogeneity. The SF shows abnormal behavior at temperature range of 150-175°C. The SF may be break down the asphaltene agglomerates, but still have an attractive binding force throughout the mixture, which in turn binds the molecules together and hence increases viscosity. The viscosity reduction however may not just be related to the breakdown of the asphaltene agglomerates. According to

Eyring's theory [27], it must be conducted that the molar volumes, molecular weight of the compounds and the mixtures for SN catalyst has about 30% high molecular weight than SF catalyst that gives opposite effect on viscosity reduction.
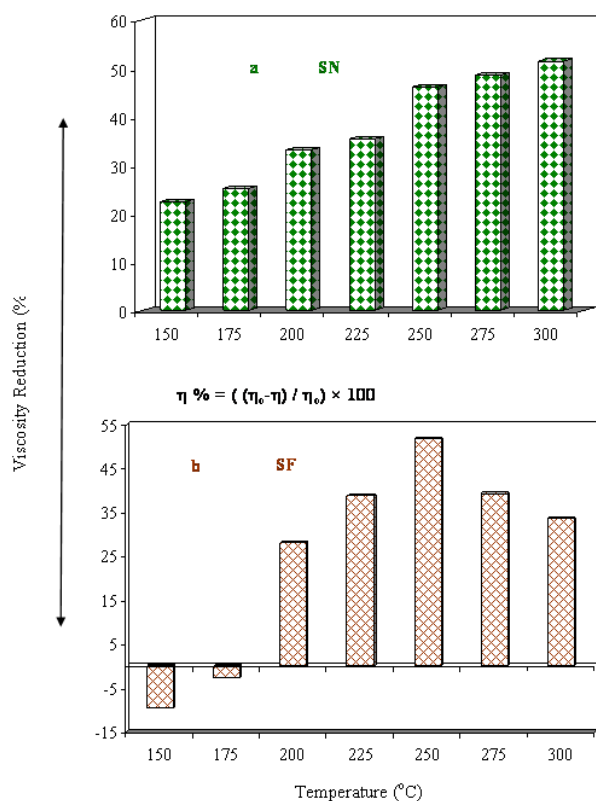

$$\eta \% = ((\eta_o-\eta) / \eta_o) \times 100$$

Fig. 6 Effect of temperature on viscosity reduction of heavy crude oil using (a) SN (b) SF catalysts where, η is the viscosity after using the catalyst η_o is the initial viscosity of crude oil

2. Effect of Catalyst Ratio on Viscosity Reduction

The viscosity reduction of crude oil using different catalyst concentrations at optimum temperature of SF (250°C) and SN (300°C) is shown in Fig. 7. It is clear that the 0.25 wt% of both catalysts is the best. At low concentration, 0.10-0.15 wt%, the viscosity reduction is mainly depend on catalysts concentration tell reach 0.25 wt%. Above 0.25wt% concentration, partial solubility is occurred causing a lower than expected viscosity measurement will be recorded. This is because when phase separation occurs, a low dispersity phase is occurred, i.e. the more additive compound, may tend to aggregate around the crude oil, and thus lower apparent viscosity.
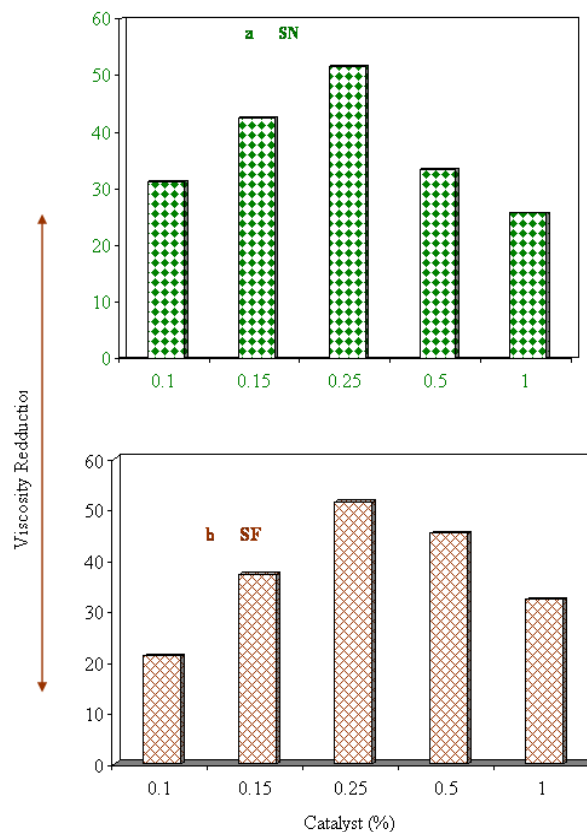

Fig. 7 Effect of catalyst loading on viscosity reduction using (a) SN at 300°C (b) SF at 250°C,

Assuming that the catalysts are dispersed in the heavy crude oil, then molecular size of the additive compound may have an important role in viscosity reduction. Smaller molecules or molecules with the correct physical and chemical characteristics to fit into the gaps between the asphaltene agglomerates can reduce the viscosity to a greater extent. This is caused by deeper penetration, which induces greater breakup of the asphaltene agglomerates.

3. Effect of Water Percent on Viscosity Reduction

The effect of water percent (aquathermolysis) on viscosity reduction is shown in Fig. 8. The SF catalyst shows viscosity reduction percent of 51.5, 55.1, 79.1 and 31.7 at water content of zero, 20, 30 and 40 wt%, respectively at 250°C. While SN catalyst shows 54.9, 58.2, 73.8 and 49.3 at water content of zero, 20, 30 and 40 wt%, respectively at 300°C. The high viscosity reduction of SF and SN catalysts at water % of 20-30 wt % may be resulted from more stability of microemulsion [28], while with increasing of water content an opposite result is obtained. This behavior resulted from separate phase formation in the oil/water microemulsion because of an increase in the water content makes the emulsion more susceptible to separating into two phases, thereby lowering the emulsion stability.
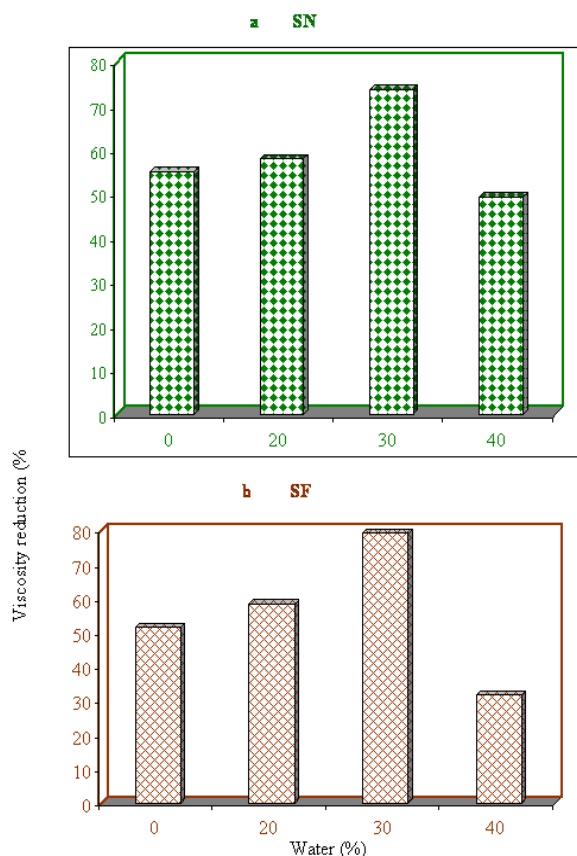
Fig. 8 Effect of water loading on viscosity reduction using 0.25wt % of (a) SN at 300°C ;(b) SF at 250°C

Fig. 9 Effect of time on viscosity reduction using (a) SN and (b) SF at optimum conditions

4. Effect of Time on Viscosity Reduction

The effect of time on aquathermolysis reaction is shown in Fig. 9. The viscosity reduction is increased with increasing time to 24h, and then decreased. Hyne stated that aquathermolysis is a thermal process and free radicals may be generated during breaking of the large bonds. With increasing time, these free radicals participate in polymerization reactions and form heavy molecules. It leads to production of more viscous materials instead of reducing the viscosity [13].
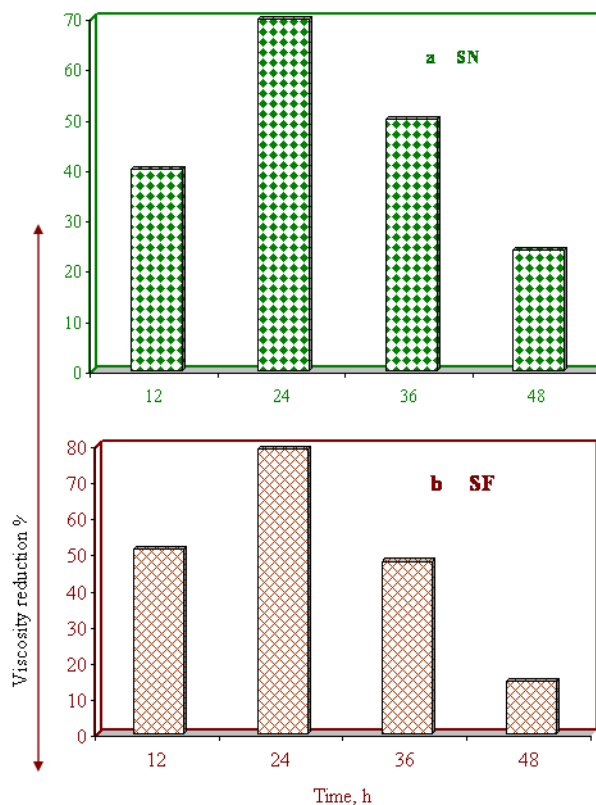
5. SARA Analysis

Four groups of compounds such as asphaltene, resin, saturated and aromatic hydrocarbons were separated from Issran heavy oil by using the column chromatography-based SARA method according to D2007ASTM.

Table III indicates the SF and SN catalysts can promote the pyrolysis; heavy resin and asphaltene are converted into lighter saturated and aromatic hydrocarbons and the viscosity of heavy oil is reduced by ~79% after the catalytic aquathermolysis.

It can be seen from Table III that the catalysts have reduced the viscosity of heavy oil by 79, 73 and 28% after reaction with SF and SN catalysts and also with only aquathermolysis, respectively, with conversion of heavy content to light content by 19.7, 16.9 and 5.5%, respectively.

TABLE III
SARA ANALYSIS OF CRUDE OIL BEFORE AND AFTER USING THE CATALYSTS

Samples	Content wt%				
	[1]VR%	[2]As	[3]R	[4]A	[5]S
Crude oil	....	12.34	28.1	32.8	26.7
Aquathermolysis	28	11.4	26.8	34.2	27.6
SF	79	8.97	23.7	38.6	28.73
SN	73	9.2	24.4	37.2	29.2

[1]ViscosityReduction,[2]Asphaltenes,[3]Resins ,[4]Aromatics ,[5]Saturates

IV. CONCLUSION

Two catalysts have been prepared, iron(III) dodecylbenzene sulfonate (SF) and nickel(II) dodecylbenzene sulfonate (SN) and used to reduce the viscosity of heavy crude oil by catalytic aquathermolysis technique, which was applied to laboratory study of Egyptian heavy crude oil (API^o gravity of 20.6). The prepared catalysts were characterized by surface tension, critical micelle concentration, FT-IR, Raman and UV-vis spectroscopy and Thermal analysis (TGA/DSC). A set of controlled experiments has shown that these catalysts have good catalytic efficiency for the aquathermolysis of heavy crude oil. The rate of viscosity reduction was 73 and 79 % for SN and SF catalysts, respectively.

REFERENCES

[1] Thomas S. and S. M. Farouq Ali, "Status and Assessment of Chemical Oil Recovery Methods", Energy Sources, 21,1999, 177–189

[2] Hitzman D. O., G. T. Sperl, "A New Microbial Technology for Enhanced Oil Recovery and Sulfide Prevention and Reduction" 1994, 171-179,SPE/DOE ninth Symposium on Improved Oil Recovery, Tulsa, OK, USA,.

[3] Xia T.X., M. Greaves, Upgrading Athabasca tar sand using toe□to□heel air injection, Journal of Canadian Petroleum Technology, 41 (2002) ,51–57.

[4] Pineda–Perez L.A., L. Carbognani, R.J. Spencer, B. Maini, P. Pereira□Almao, "Hydrocarbon depletion of Athabasca core at near steam□assisted gravity drainage (SAGD) conditions", Energy & Fuels 24 (2010) 5947–5954.

[5] Lee DG and Noureldin A. "Effect of water on the low-temperature oxidation of heavy oil", Energy & Fuels 3(6),1989; 713-715.

[6] Bagci S., M.V. Kok, In-situ combustion laboratory studies of Turkish heavy oil reservoirs, Fuel Processing Technology 74 (2001) 65–79.

[7] Shokrlu Y. H., Y. Maham, X. Tan , T. Babadagli, M. Gray, "Enhancement of the efficiency of in situ combustion technique for heavy-oil recovery by application of nickel ions", Fuel 105 (2013) 397–407.

[8] Hu CZ. 'Heavy oil exploitation technology". Beijing: Petroleum Industry Publishing Inc.; 1998.

[9] Lu LH, Li MH, Su YL. "The overview of the heavy oil" AOSTRA J Res., 29(3): 269-272.

[10] Dabbous M, Fulton PF. Low-temperature-oxidation reaction kinetics and effects on the in situ combustion process. SPEJ 14(3):1974; 53–62.

[11] He B, Chen Q, Castanier LM, Kovscek AR. Improved in situ combustion performance with metallic salt additives. 2005,In: SPE 93901, SPE western regional meeting, Irvine, CA, USA.

[12] Maity, S. K., Ancheyta, J., and Marroquı́n, G., Catalytic Aquathermolysis Used for Viscosity Reduction of Heavy Crude Oils: A Review, Energy & Fuels 24, (2010), 2809–2816

[13] Hyne J B, Clark PD. Studies on the chemical reactions of heavy oils under steam stimulation condition. AOSTRAJ Res, 6(1): 1990, 29-39

[14] Clark P D, Hyne J B. Steam-oil chemical reactions: mechanism for the aquathermolysis of heavy oil. AOSTRA J Res, 1(1): 1984, 15−20 .

[15] Clark P D, Hyne J B, Tyrer J D. Chemistry of organosulfur compound types occurring in heavy oil sands: 1 High temperature hydrolysis and thermolysis of tetrahydrothiophene in relation to steam stimulation processes. Fuel, 62(8):1983, 959-962

[16] Clark P D, Hyne J B, Tyrer J D. Chemistry of organosulfur compound types occurring in heavy oil sands:2 Influence of PH on the high temperature hydrolysis of tetrathiophene and thiophene. Fuel, 63(1): 1984, 125-128

[17] Fan H F, Liu Y J, Zhao X F. Study on composition changes of heavy oils under steam treatment. Journal of Fuel Chemistry and Technology, 29(3): 2001, 269−272.

[18] Fan H F, Liu Y J, Zhao X F. A study on heavy oil recovery by in-situ catalytic aquathermal cracking. Oilfield Chemistry, 18(1): 2001, 13−16.

[19] Clark P D, Clarke R A, Hyne J B, Lesage K L. Studies on the effect of metal species on oil sands undergoing steam treatments. AOSTRA J Res, 6(1):1990, 53−64.

[20] Fan Z X, Zhao F L, Wang J X, Gong Y G. Upgrading and viscosity reduction of super heavy oil by aquathermolysis with hydrogen donor. Journal of Fuel Chemistry and Technology, 34(3):2006, 315−318.

[21] Vayssilov, G. N. "Structural and Physicochemical Features of Titanium SilicalitesCatal. Rev.sSci. Eng. 39, 1997, 209.

[22] A. Budnyk , A. Damin, S. Bordiga, A. Zecchina, "Synthesis and Characterization of High-Surface-Area Silica–Titania Monoliths" J. Phys. Chem. C, 116 (18), 2012, pp 10064–10072.

[23] Zhang, W.-H.; Lu, J.; Han, B.; Li, M.; Xiu, J.; Ying, P.; Li, C. " Direct Synthesis and Characterization of Titanium-Substituted Mesoporous Molecular Sieve SBA-15 Chem. Mater". 14, 2002, 3413−3421.

[24] B.C. Barja, J. Herszage and M. dos Santos Afonso, "Upgrading and viscosity reduction of super heavy oil by aquathermolysis" Polyhedron 20 (2001) 1821–1830

[25] Susan, M. A.; Kaneko, T.; Noda, A. and Watanabe, M. "Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes" J. Am. Chem. Soc. 127,2005, 4976–4983.

[26] Seki, S.; Susan, A. B. H.; Kaneko, T.; Tokuda, H.; Noda, A.; Watanabe, M. " Distinct Difference in Ionic Transport Behavior in Polymer Electrolytes Depending on Matrix Polymers and Incorporated Salts" J. Phys. Chem. B 109, 2005, 3886–3892.

[27] Glasstone, S., Laidler, K.J., Eyring, H., in "The Theory of Rate Processes - The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena" McGraw-Hill, New York. 1941.

[28] LI Wei, ZHU Jian-hua, QI Jian-hua, "Application of nano-nickel catalyst in the viscosity reduction of Liaohe extra-heavy oil by aquathermolysis" J Fuel Chem Technol, 35, 2007, 176−180.