



Catalytic Influences of Dispersed copper Complex ion on Aquathermolysis of Heavy Crude Oil

M., Usman^{1*}, A., Galadima^{2,3}, U. Z., Faruq¹ and B. Y., Jibril⁴

¹Usmanu Danfodiyo University, Sokoto, Nigeria.

²Center of NanoTechnology, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

³Federal University, Gusau, Nigeria

⁴Ahmadu Bello University, Zaria, Nigeria

*Corresponding author: Tel.: +2348069603439, E-mail: hammeduss@yahoo.com

Received: November 2015

Revised and Accepted: January 2016

Abstract

Copper based catalyst Cu^{2+} was synthesized and characterised by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). Various concentrations of this catalyst was used to catalyse aquathermolysis of medium heavy crude oil (API gravity = 29.40°) at temperature of 200°C for three hours (3h). The oil sample(s) were characterised before and after aquathermolysis reaction using FT-IR. SARA analysis was carried out using column chromatography and the sulphur content, kinematic viscosity, density and API gravity were also determined. The original viscosity of the fresh crude oil was 9.8799 m²/s, after the reaction without catalyst; the viscosity was reduced to 8.8125 m²/s (10.80% reduction). When Cu^{2+} was used at optimum concentration, it was further reduced to 7.7339 m²/s (21.61% reduction). The catalyst reduced the sulphur content by 4.37% and it was reduced by 2.77% when no catalyst was used. Also, API gravity was increased by 1.02% without catalyst while it was reduced by 2.72% when the catalyst was used. The results indicate that the percentage by weight of asphaltenes and resins were reduced due to cleavage on carbon to heteroatom bonds while that of aromatics and saturates were increased. The compared results with previous researches strongly confirmed that this catalyst possessed good catalytic activity owing to its strong viscosity reduction properties.

Keywords: Aquathermolysis catalyst; SARA; heavy crude oil; viscosity; sulphur reduction.

1.0 INTRODUCTION

The world oil demand is expected to increase by more than 40% by 2025 (US Department of Energy, 2005). As the world's conventional light crude oil production approaches its peak, exploitation of massive deposits of heavy oil and bitumen remains one of the options to balance for the increase in demand (Hirsch *et al.*, 2006). Heavy oil reserves are abundant in the world and

it accounts for 70% of the total quantity of petroleum. Heavy crude oil exploitation is an emerging special area that deals with energy shortage in the world (Hu, 1998; Thomas and Farouq, 1999; Pineda-Perez *et al.*, 2010). However, the high contents of heavy components such as resins, asphaltenes as well as the high viscosity, density of the heavy crude

oil and bitumen make its exploitation and utilisation very complicated (Lee and Noureldin, 1989; Yufeng *et al.*, 2009; Yousef *et al.*, 2014). Several advancements have been made regard to effective exploration and utilization of heavy crude oil aiming to curtail over dependent on conventional light crude which is almost at peak. However, this advancements 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., are associated with some problems like formation of oxygenated hydrocarbon and free radicals formation (Hu, 1998; Bagci and Kok, 2001; Oskouei *et al.*, 2012; Desouky *et al.*, 2013). These free radicals can aggregate to form more complex molecules of high viscosity. These setbacks led to the development of more advanced technology known as catalytic aquathermolysis (Al-Bahlani and Babadagli, 2011; Fatemi and Kharrat, 2011; Desouky *et al.*, 2013).

The term aquathermolysis describes chemical reactions first discovered during steam stimulation of heavy oil reservoirs. The objective of the steam stimulation was to effect temporary change which would enable the heavy oil to flow effectively from the producing well but to the surprise of Hyne and Co-worker, a permanent change was observed in the physical properties of the heavy oil (Desouky *et al.*, 2013; Muraza and Galadima, 2015). Therefore, aquathermolysis can be described as a series of chemical reactions among heavy oil, water and reservoir matrix which result to the viscosity reduction of the crude oil. It involves the cleavage of carbon to hetero-atoms bonds such as carbon-sulphur (C-S), carbon-nitrogen (C-N) and carbon-oxygen (C-O) in asphaltenic and resin components of the heavy oil/bitumen which lead to viscosity reduction (Hashemi *et*

2.0 EXPERIMENTAL

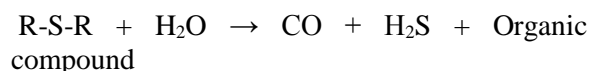
The medium heavy crude oil used was obtained from Kaduna Refinery and Petrochemical Company (KRPC), Kaduna State, Nigeria.

al., 2012; Fabian, 2013; Muraza and Galadima, 2015).

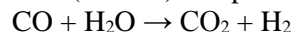
In catalytic aquathermolysis, suitable catalysts are used to enhance the reactions and also repress formation of free radicals which can cause repolymerisation. Attention is rapidly shifting to water soluble catalysts owing to their low cost of production especially for industrial scale

Equation of aquathermolysis (Wassmuth *et al.*, 2009; Shokrlu *et al.*, 2013).

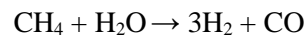
During the reaction, water molecule reacts with the oil to release carbon monoxide



The produced CO takes part in the water gas shift reaction (WGSR) and produces hydrogen.



Hydrogen is also generated from the reaction between methane and water under the influence of catalyst as shown below:



The produced hydrogen molecules attack the unstable and unsaturated molecule of oil and produce lighter and saturated molecules via hydrogenation and hydrogenolysis (Needham and Doe, 1987; Shokrlu and Babadagli, 2014). Researches have been conducted on water soluble or disperse catalysts and their influences on viscosity reduction of heavy oil through aquathermolysis processes. In this research, tetraamine copper sulphate monohydrate was synthesized with the aim of determining its catalytic effect on viscosity reduction of medium heavy crude oil. The prepared catalyst was characterized using basic techniques; X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). The oil sample was characterized before and after aquathermolysis by FT-IR. Also, the SARA analysis was carried out before and after the reaction.

2.1 Preparation and Characterisation of the Catalyst

Copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$, Sigma Aldrich, 95%) was weighed (15.0 g) into a 250.0 ml beaker. 20.0 ml of water was added to the solid and then, in a fume cupboard, 30.0

ml of 15 M NH₄OH (Sigma Aldrich, 95%) was added and was gently heated by placing beaker on a heating mantle in a cupboard at a temperature of 60°C. This was to ensure complete dissolution. The solution was swirled to obtain homogeneous species and then allowed to cool to room temperature by placing it in an ice bath. In a slow, drop-wise manner and with continual swirling, 20.0 ml of 95% ethanol (LOBA Chemie) was added to the resulting mixture. The ammine complex salt was precipitated as deep purple-blue crystals (Emmanuel *et al.*, 2012). The mixture was cooled in an ice water bath for about 15 minutes. 30.0 ml solution was prepared from 15.0 ml of concentrated ammonia solution and 15.0 ml of 95% ethanol. This was properly mixed and set aside. The resulting solution was filtered using vacuum filtration apparatus and was allowed to dry. The dried product was calcined at 385°C for 4h in muffle furnace (Emmanuel *et al.*, 2012).

The calcined product was characterized by FT-IR (Shimadzu, MB3000) and X-ray Diffraction (Shimadzu, XRD-6000).

2.2 Experiments on Catalytic

Aquathermolysis

All the experiments were carried out by mixing a mass (0.051, 0.026, 0.013 and 0.007g) of the catalysts (Cu²⁺) with 7.0 g of distilled water and stirred with glass rod gently until a homogenous solution was formed. The solution was heated

slightly at the temperature of 40°C to ensure complete dissolution. 15.0 g of the oil sample was then added to this solution (oil/water ratio = 2:1), in a steel reactor. The temperature of the furnace was programmed to 200°C for 3 hours. After the heating period, the reactor was cooled down slowly to room temperature to allow condensation. Water and oil were separated using separating funnel (Shokrlu and Babadagli, 2014; Jian *et al.*, 2013).

The viscosity of the oil sample before and after aquathermolysis was carried out using Oswald viscometer at 40°C and the viscosity reduction rate was evaluated by $\Delta\eta$ (%) = $((\eta_0 - \eta)/\eta_0) \times 100\%$, where η_0 (m²/s) and η (m²/s) represent the viscosity of oil sample before and after reaction, respectively and $\Delta\eta$ is change in viscosity (Jian *et al.*, 2013).

2.3 SARA Analysis

The SARA (Saturate Aromatic Resin Asphaltene) analysis was carried out using column chromatography before and after the reaction. The SARA fractions were quantified gravimetrically.

2.4 Density, API gravity and Sulphur Content

The density and API gravity studies were carried out using portable density meter (DMA 35, Anton Paar). And the sulphur content was determined using X-ray Fluorescence Sulphur-in-oil Analyzer (Horiba SLFA-60).

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

The FT-IR spectra of the catalyst before and after calcination are shown in Figure 1.

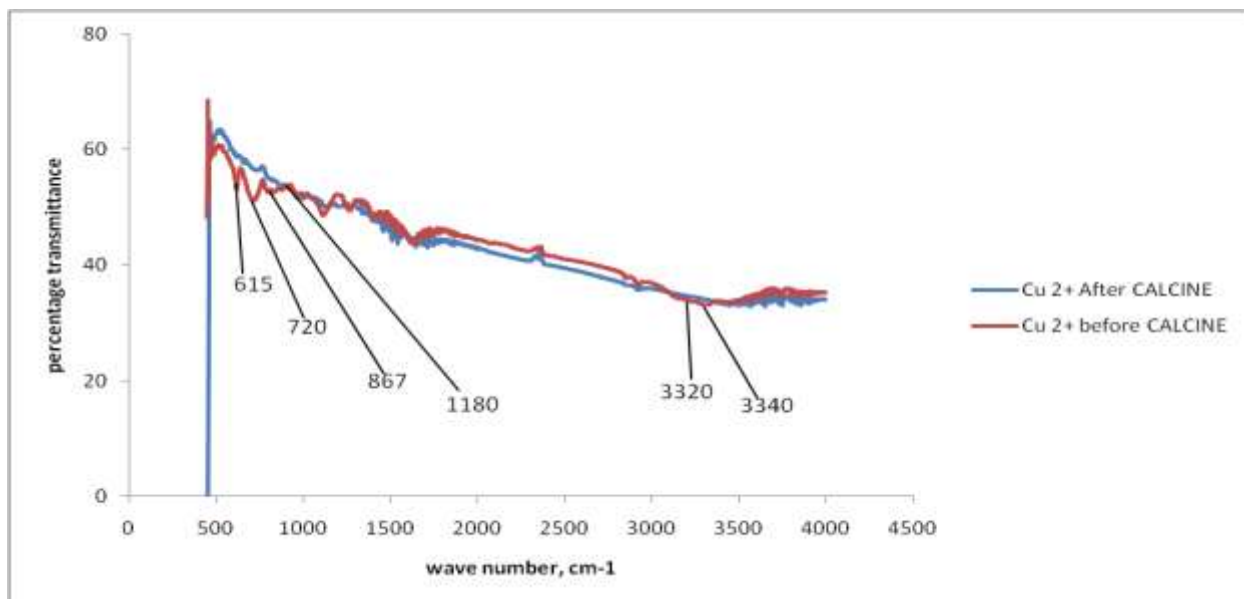


Figure 1. Superimposed FT-IR Spectra of prepared copper complex before and after Calcination.

After calcinations of the prepared $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ at 385°C as shown in figure 1, there is shift from 867 to 879 cm^{-1} and from 720 to 740 cm^{-1} . This indicates change in the coordination of the catalyst. vibration mode of metal ion Cu^{2+} may be observed at Cu-O-H and Cu-O vibration are assigned to 867 and 720 cm^{-1} respectively as observed by Anne *et al.* (2015). Absorption band at 3320 cm^{-1} assigned to ammonia, disappeared showing that ammonia has been released (Jacos and Thompson, 2005). Absorption bands 3340 cm^{-1} and 2120 cm^{-1}

corresponding to vibration of water also disappeared confirming that water has been given out in the form of steam (Jacos and Thompson, 2005). Absorption band 1180 cm^{-1} corresponding to vibration of sulphate got diminished due to the heat. This clearly showed that CuSO_4 was formed.

3.2 X-ray Diffraction (XRD)

Figure 2 shows peaks for x-ray diffraction analysis. It was used to determine the crystallinity of the catalyst.

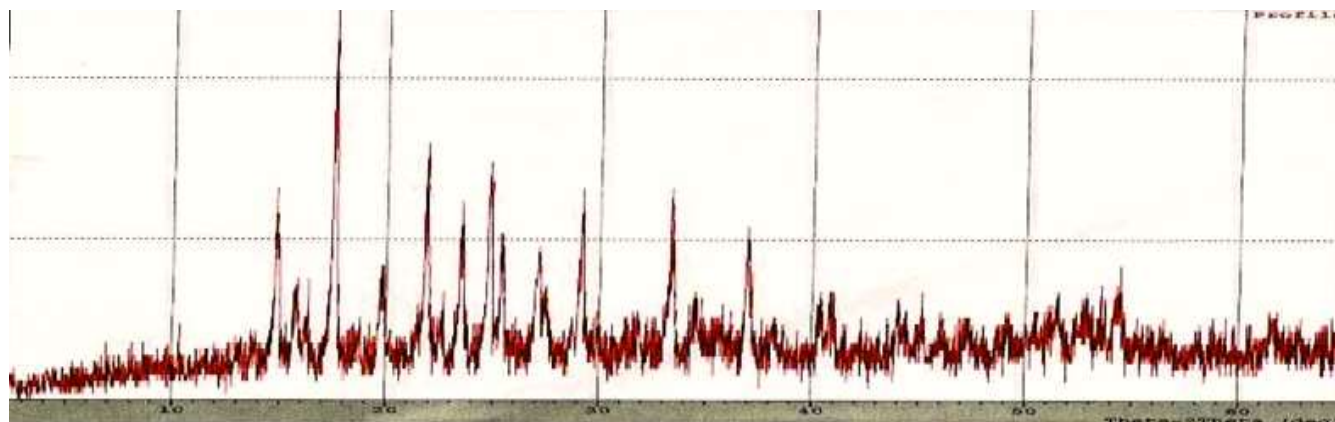


Figure 2. X-ray diffraction pattern of the catalyst after calcination.

The XRD results showed several diffraction peaks corresponding to angle of diffractions, 2θ . For proper overview of these peaks, three of the most intense peaks were considered from each of the catalyst for the analysis. The diffraction peaks demonstrated a narrow strong reflection corresponding to the miller indices, hkl; (110), (111) and (200) crystal plane (Miller indices hkl, shows the dimension of unit cell in the crystal) corresponding to CuSO_4 . This implied that the catalyst is cubic in shape. The three peaks at 2θ

values of 17.5342° , 21.8657° and 24.8166° were observed corresponding to the sizes; 36.0, 38.3 and 34.6 nm respectively. This is consistent with the standard powder diffraction card of JCPDS, file No. 72-1248 (Godo *et al.*, 2006).

3.3 FT-IR Spectra of the Oil Samples Before and After the Reaction

Figure 3 shows the FT-IR spectrum of the fresh oil sample. It was aimed to determine the functional group in the oil sample before the reaction.

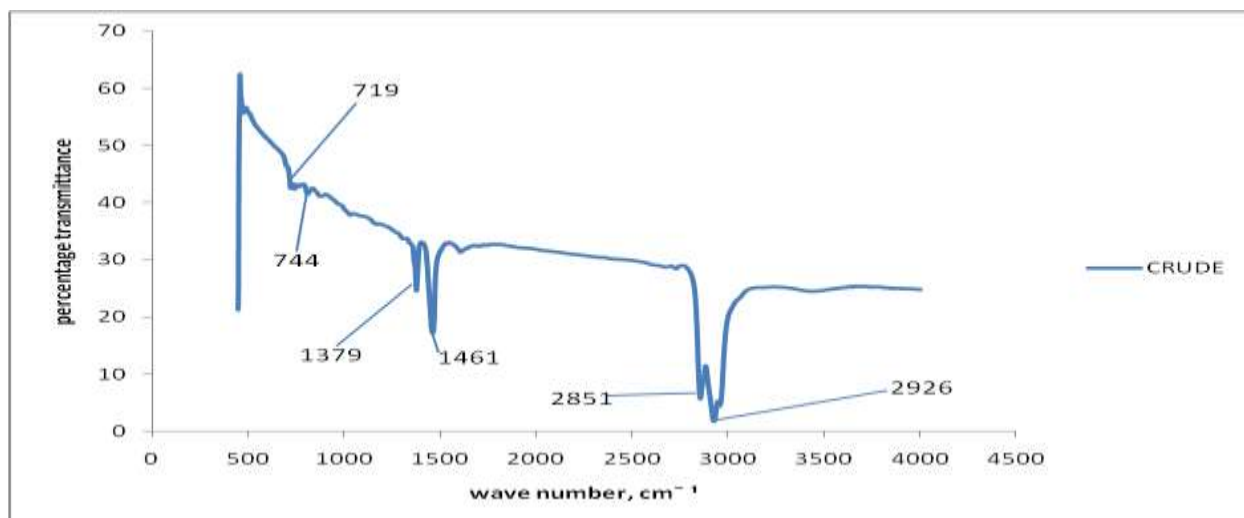


Figure 3. Spectrum of Fresh Crude Oil Sample before Aquathermolysis.

From Figure 3, the spectrum showed strong absorbance at 2940 cm^{-1} , 2926 cm^{-1} and 2851 cm^{-1} which correspond to C-H stretch in CH_3 , CH_2 , CH , typical of alkanes (saturates) and also strong absorbance at 1461 cm^{-1} and 1379 cm^{-1} which correspond to C-H stretch in alkyl group and C-H bend in methyl respectively as reported by Adebisi and Omole (2006). The weak absorption band at 1620 cm^{-1} showed the presence of C=C stretch in alkene, while the weak peak 1697 cm^{-1} could be due to carbonyl

stretch C=O in ketones, amides, aldehydes or carboxylic. The weak absorption band at 719 cm^{-1} is typical of C-S stretching vibrations (Adebisi and Omole, 2006).

Figure 4 below shows the FT-IR spectra of the oil sample before and after aquathermolysis. It was meant to comparing the functional groups after the reactions using various concentrations of the catalyst.

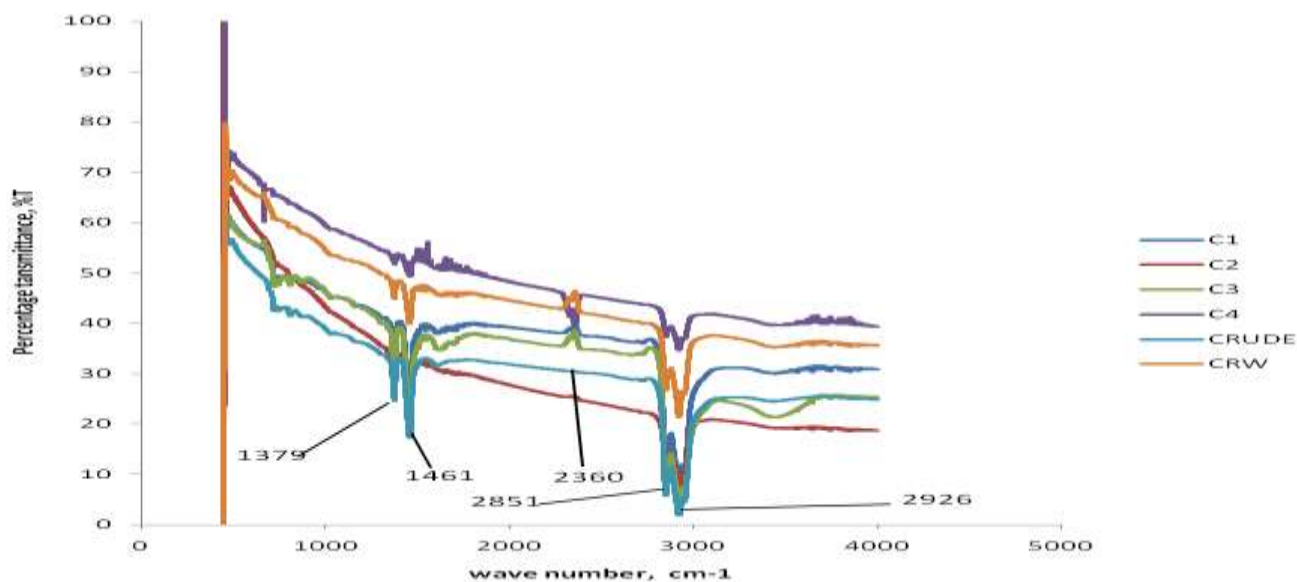


Figure 4. Superimposed FT-IR Spectra of Crude, CRW, C1, C2, C3 and C4.

Key: CRW=sample without catalyst, C1= sample + catalyst ($\text{Cu}^{2+} = 0.051\text{g}$), C2=sample + catalyst ($\text{Cu}^{2+} = 0.026\text{g}$), C3= sample + catalyst ($\text{Cu}^{2+} = 0.013\text{g}$), C4= sample + catalyst ($\text{Cu}^{2+} = 0.007\text{g}$).

From Figure 4, the narrow bands at 2940 cm^{-1} , 2926 cm^{-1} and 2851 cm^{-1} in crude sample clearly lost intensity and become shortened in CRW, C2, C3 and C4. This may be due to cracking of heavy molecular weight of alkanes to lighter ones. In C1, the bands gained intensity to become stronger and longer. This shows that the saturate content becomes increased due to hydrogenation of unsaturated content and perhaps, pyrolysis of the long chain alkanes

which is in line with the observation of Shuwa *et al.* (2014).

From the Figure, it is clearly shown that the strong absorbance at 1461 cm^{-1} and 1379 cm^{-1} in the crude lost intensity and become shortened in C1, C3 and even more weaker in CRW, C2 and C4. This may be due to cracking owing to activity of various concentrations of the catalysts (Jian *et al.*, 2013).

3.4 Physical Properties of the Oil Samples

Table 1 below shows some physical properties of the oil sample before and after the reaction

Table 1: Physical Properties of the Oil Sample before and after Aquathermolysis.

Sample	Viscosity (at 40°C) (m^2/s)	VRR (%)	Density (15°C) (g/cm^3)	API gravity (deg)	IAPI (%)	Sulphur Content (%)	SCR (%)
Fresh Oil	9.8799	-	0.880	29.40	-	1.2359 ± 0.0015	-
CRW	8.8125	10.80	0.864	29.70	1.02	1.2017 ± 0.0028	2.77
C1	7.7339	21.61	0.837	30.20	2.72	1.1819 ± 0.0040	4.37
C2	7.7564	21.49	0.839	30.05	2.22	1.1964 ± 0.0040	3.20
C3	7.7676	21.37	0.841	29.83	1.46	1.2001 ± 0.0023	2.90
C4	7.7901	21.15	0.843	29.73	1.12	1.2011 ± 0.0023	2.82

Where VRR = Viscosity reduction rate, IAPI = Increase in API gravity, SCR = sulphur content reduction, - = decrease, + = increase.

Table 1 shows the oil sample properties before aquathermolysis experiment. From the table, the API gravity of the crude oil is found to be 29.56°. This indicates that the sample is a medium heavy crude oil.

3.5 Viscosity Reduction and Density

From the table, it can be observed that the viscosity of the oil sample was reduced from 9.8799 to 8.8125 m²/s without catalyst. It can also be seen that there was further reduction of viscosity when the catalyst was used. The highest reduction was obtained at oil/catalyst in the ratio of 294:1 wt/wt (optimum concentration) and the lowest reduction was obtained at oil/catalyst ratio of 2143:1 wt/wt. However, the least viscosity reduction obtained when low concentration of the catalyst was used is still higher than the reduction that was observed when no catalyst was used. It is clear that the best concentration for effective reduction is at oil/catalyst ratio of 294:1 wt/wt. Jian *et al.* (Jian *et al.*, 2013) used Cu²⁺ and Fe³⁺ to catalyse aquathermolysis and found that Cu²⁺ has more catalytic activity than Fe³⁺. They concluded that Cu²⁺ (0.203g of Cu²⁺ to 100g of oil) mainly caused depolymerisation of the heavy components. Similarly, the viscosity reduction rate (VRR) follows the same pattern in this work. The highest VRR (21.61%) was obtained at optimum concentration (oil/catalyst =294:1 wt/wt) and the lowest (21.15%) was obtained at concentration of 2143:1 wt/wt oil/catalyst ratio which is higher than VRR (10.80%) obtained without catalyst. This is similar to the observation of Desouky *et al.* (2013). Though, Jian *et al.* (2013) achieved 95% viscosity reduction rate (VRR) with Cu²⁺. This may be due to the residence time (24h) as against 3h that was used in this research. If there observation is to be viewed hourly, it means they achieved 3.95% reduction per hour where as 7.20% per hour was achieved in this research. This high per hour viscosity reduction is apparently due to the high concentration of the reactant at the beginning of the reaction. Therefore, it can be inferred that the same 95%

3.7 SARA Fractions

Table 2 below shows SARA analysis results of the sample.

reduction or more could be achieved had the reaction continued for 24h. Conversely, Shokrlu and Babadagli (2014) used copper particles and achieved 9.5% at 300°C for 24h which is even lower than that of Jian *et al.* (2013). It can be concluded that the viscosity reduction is proportional to the concentrations of the catalyst used. This characteristic is also observed in the density.

3.6 Sulphur content and API gravity

Table 1 shows the results of sulphur content determination and API gravity after aquathermolysis. The original sulphur content and API gravity before the reaction were 1.2359% and 29.40 (Table 3.3) respectively. After aquathermolysis, the amounts of sulphur content have reduced, indicating that part of C-S bonds in the heavy component of the oil sample has been cleaved. The removal of sulphur demonstrates that hydrodesulphurisation process had occurred (Chao *et al.*, 2012). From Table 1, it can be seen that the sulphur content decreased from 1.2359% (Original sulphur content of the fresh sample) to 1.2017% (2.77% reduction) when no catalyst was used during the reaction. It further decreased to 1.1819% (4.37% reduction) when the catalyst was used at optimum concentration. From the Table, the decrease in sulphur content is proportional to viscosity reduction. This infers that viscosity reduction is largely dependent on cleavage of C-S bonds in the heavy components as reported by Chen *et al.* (2009). Desouky *et al.* (2013) achieved 18.54% reduction using amphiphilic catalysts at 200°C for 24h. This implies that tentatively, 0.77% reduction was achieved per hour.

Table 1 also reported the result of API gravity. From the table, API gravity of the fresh oil was increased from 29.40 to 29.70° during aquathermolysis when no catalyst was used. The Table also showed that API was increased further to 30.20° when catalyst (Cu²⁺) was used at optimum concentration. It is observed that the least concentration of the catalyst increased the API more compared to when no catalyst was used. This shows that the catalyst was effective.

Table 2: Percentage SARA Fractions of the Samples before and after Aquathermolysis.

Sample	Asphaltenes (%)	RA (%)	Resins (%)	RR (%)	Aromatics (%)	IA (%)	Saturates (%)	IS (%)
Fresh Oil	6.7	-	11.94	-	29.56	-	50.80	-
CRW	6.35	5.22	9.80	17.92	30.20	2.17	51.17	0.73
C1	6.02	10.15	8.81	26.21	31.51	6.6	52.05	2.46
C2	6.13	8.51	8.93	25.21	31.51	6.6	51.70	1.77
C3	6.26	6.57	9.05	24.20	30.71	3.89	51.52	1.42
C4	6.32	5.67	9.20	22.95	30.59	3.50	51.38	1.14

Where RA= Reduction in Asphaltene, RR= Reduction in Resins, IA= Increase in Aromatics, IS=Increase in Saturates, + = increase.

From Table 2, the content of the asphaltenes, resins, saturates and aromatics before the reaction are 6.7, 11.94, 50.80 and 29.56 respectively. After the aquathermolysis without catalyst, the content of aromatics and saturate increased from the previous 29.56 and 50.80% to 30.20% (2.17% increment) and 51.17 (0.73% increment), respectively. After adding catalyst, the content of aromatic and saturate hydrocarbon further increased. The optimum concentration (C1) of the catalyst increased both aromatics and saturates from the original 29.56 and 50.80% to 31.51 (6.6% increment) and 52.05% (2.46% increment) respectively. This illustrates that

heavy component of the sample can be pyrolysed into light components more easily during aquathermolysis (Shokrlu and Babadagli, 2014). From the Table, it is easy to notice that all the concentrations of the catalyst have increased aromatics and saturate compared to when no catalyst was used. Furthermore, the contents of asphaltene decreased by 10.15, 8.51, 6.56, and 5.67% for C1, C2, C3, and C4 respectively compared to the oil sample before the reaction. In the same line, resins reduced by 26.6, 25.2, 24.2 and 22.9% for C1, C2, C3, and C4, respectively.

4.0 CONCLUSION

The activities of Cu^{2+} catalyst were studied using various concentrations for catalytic aquathermolysis. It was found that the optimum concentration of the catalyst is oil/catalyst ratio 294:1 for aquathermolysis of medium heavy crude oil. The decrease in asphaltenes and resins are largely due to cleavages along hetero-atoms to carbon bonds which in turn, increased the

saturate and aromatic contents. The catalyst at all concentrations demonstrated high activities when compared to the reaction without catalyst. Therefore, from the results, it can be concluded that the cleavages and the conversion of heavy molecular weight component to the lighter ones are function of catalyst concentrations.

5.0 REFERENCES

Adebisi, F. M. and Omode, A. A. (2007) Organic, Chemical and Elemental Characterization of Components of Nigerian Bituminous Sands Bitumen.

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 29(8), 669-676.

- Al-Bahlani, A. M. and Babadagli, T. (2011). Steam-over-solvent Injection in Fractured Reservoirs (SOS-FR) Technique as a new Approach for Heavy Oil and Bitumen Recovery: An Overview of the Method. *Energy Fuels*, 25, 4528–4539.
- Anne, M. M., Perumal, S. and Prabu, K. M. (2015). Growth, Structural and Optical Studies on Pure and 1-histidine Doped Single Crystals of Copper Sulphate. *International Journal of Research in Engineering and Technology*, 04, 07, 114-119.
- Bagci, S. and Kok, M. V. (2001). In-situ Combustion Laboratory Studies of Turkish Heavy Oil Reservoirs. *Fuel Process Technology*, 74, 65–79.
- Chao, K., Chen, Y., Liu, H., Zhang, X. and Li, J. (2012). Laboratory Experiments and Field Test of a Difunctional Catalyst for Catalytic Aquathermolysis of Heavy Oil. *Energy & Fuels*, 26, 1152–1159
- Chen, Y. L., Wang, Y. Q., Lu, J. Y. and Wu, C. (2009). The viscosity Reduction of Nano-keggin Mechanochemically synthesized nanocrystalline CuS. *Thermochemical Acta*, 440, 19–22
- Desouky, S., Al sabagh, A., Betiha, M., Badawi, A., Ghanem, A. and Khalil, S. (2013). Catalytic Aquathermolysis of Egyptian Heavy Crude Oil. *International Journal Chemical, Nuclear, Metallurgical and Materials Engineering*, 7, 8, 286-291.
- Emmanuel, S. A., Thomas, S. A., Idris, S. O. and Iyun, J. F. (2012). Syntheses and Spectra Studies of Copper II Sulphate Complex with Furancarbamide, Benzoic Acid Hydrazone and its Acetone Hydrazone derivative. *Der Pharma Chemica*, 4 (1):370-376
- Fabian, B. (2013). "Heavy Oil Production Technology Challenges and the Effect of Nano Sized Metals on the Viscosity of Heavy Oil" A Literature Review and an Experimental Study. MSc. Dissertation, Norwegian, University of Science and Technology, Norway.
- Fatemi, S. M. and Kharrat, R. (2011). Assessment of Vapor Extraction (VAPEX) Process Performance in Naturally Fractured Reservoirs. *Journal of Petroleum Science and Engineering*, 75, 260–273.
- Godo, E., 'ikov'a, 'c., Bal'a'z, P., Criado, J. M., Real, C. and Gock, E. (2006). Thermal behaviour of Heavy Oil Catalyzed by Two Different Catalytic Ions: Cu²⁺ and Fe³⁺ *Energy and fuel*, 27(5), 2555-2562
- Hashemi, R., Nassar, N. N. and Pereira-Almao, P. (2012). Transport behavior of Multimetallic Ultradispersed Nanoparticles in an Oil-sands-packed Bed Column at a High Temperature and Pressure. *Energy Fuels*, 26, 1645–1655.
- Hirsch, L. R., Bezdek, R. and Wendling, R. (2006). Peaking of World Oil Production and its Mitigation. *Perspective*, 52 (1), 2–8.
- Hu, C. Z. (1998). "Heavy oil Exploitation Technology". Beijing: Petroleum Industry Publishing Inc.
- Jacos, M. E. and Thompson, W. E. (2005) Infrared Spectrum of the NH₄⁺ cation in solid neon. *Journal of Physical Chemistry and Chemical Physics*, 7, 768-775
- Jian, L., Yanling, C., Huachao, L., Pujian W. and Feng, L. (2013). Influences on the Aquathermolysis of -K₃PMo₁₂O₄₀ in Catalytic Aquathermolysis of Heavy Oil. *Fuel*, 88, 1426–1434
- Lee, D. G and Noureldin, A. (1989). "Effect of Water on the Low-temperature

- Oxidation of Heavy Oil", *Energy & Fuels*, 3(6), 713-715.
- Muraza, O. and Galadima, A. (2015) Aquathermolysis of Heavy Oil: A Review and Perspective on Catalyst Development. *Fuel*, 157, 219–231
- Needham, R. and Doe, P. (1987). Polymer Flooding Review. *Journal of Petroleum Technology*, 39, 1503–1507.
- Oskouei, S. J. P., Maini, B., Moore, R. G. and Mehta, S. (2012). Effect of Initial Water Saturation on the Thermal Efficiency of the Steam-assisted Gravity-drainage Process. *Journal of Canadian Petroleum Technology*, 51, 351–361.
- Pineda–Perez, L. A., Carbognani, L., Spencer, R. J., Maini, B. and Pereira-Almao, P. (2010). "Hydrocarbon Depletion of Athabasca Core at Near Steam Assisted Gravity Drainage (SAGD) Conditions". *Energy & Fuels*, 24, 5947–5954.
- Shokrlu, Y. H. and Babadagli, T. (2014). Viscosity Reduction of Heavy Oil/Bitumen Using Micro-and Nano-metal particles During Aqueous and Non-aqueous Thermal Applications. *Journal of Petroleum Science and Engineering*, 119, 210–220
- Shokrlu, Y. H., Maham, Y., Tan, X., Babadagli, T. and Gray, M. (2013). "Enhancement of the efficiency of in situ combustion technique for heavy-oil recovery by application of nickel ions", *Fuel*, 105, 397–407.
- Shuwa, S. M., Al-Hajri, R. S., Jibril, B. Y. and Al-Waheibi, Y. M. (2014). Novel Deep Eutectic Solvent -Dissolved Molybdenum Oxide Catalyst for the Upgrading of Heavy Crude Oil. *Industrial & Engineering Chemistry Research, ACS Paragon Plus Environment*, 1-37.
- Thomas, S. and S. M. Farouq, A. (1999). "Status and Assessment of Chemical Oil Recovery Methods", *Energy Sources*, 21, 177–189
- US. Department of Energy, Energy Information Administration. (2005). *Int. Energy Outlook*; Washington, DC
- Wassmuth, F., Green, K., Arnold, W. and Cameron, N. (2009). Polymer Flood Application to Improve Heavy Oil Recovery at East Bodo. *Journal of Canadian Petroleum Technology*, 48, 55–61.
- Xia, T. X. and Greaves, M. (2002). Upgrading Athabasca Tar Sand using Toe to Heel Air Injection. *Journal of Canadian Petroleum Technology*, 41, 51–57.
- Yousef, H. S. and Tayfun, B. (2014). Viscosity Reduction of Heavy Oil/Bitumen using Micro- and Nano-Metal Particles during Aqueous and non-Aqueous Thermal Applications. *Journal of Petroleum Science and Engineering*, 119, 210–220
- Yufeng, Y., Shuyuan, L., Fuchen, D. and Hang, Y. (2009). Change of Asphaltene and Resin Properties after Catalytic Aquathermolysis. *Petroleum Science*, 6(2), 194–200.