IN SITU GENERATED DISPERSED SUBMICRON NI-CO-MO-BASED CATALYST FOR THE UPGRADING OF HEAVY CRUDE OIL

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ABSTRACT

A batch-reactor study for the upgrading of the heavy oil was conducted using an in-situ prepared, dispersed submicron trimetallic catalyst based on nickel, cobalt and molybdenum in the presence of hydrogen. Response surface methodology was used to design the experiments. The influence of reaction temperature, time and catalyst amount on the upgrading of the heavy oil was investigated. The results showed significant upgrading of the oil in terms of viscosity reduction (95%), API gravity increase (45%), sulfur removal (27wt %) and coke formed (0.05wt%) at temperature; 340ºC, time; 28hours, catalyst amount; 2500ppm. Reaction temperature proved to be the most influential with highest impact of all the reaction parameters investigated. Further characterization of liquid and gaseous products from selected experimental runs showed catalytic hydrocracking playing a significant role in the upgrading process. XRD and SEM-EDS analyses of solid recovered confirmed the in-situ generation of submicron catalyst based on nickel, cobalt and molybdenum.

Keywords: trimetallic catalyst, response surface methodology, viscosity reduction, sulfur removal, coke, hydrocracking

1. INTRODUCTION

Unconventional hydrocarbon resources - heavy oil and bitumen - reserves account for over 70% of the total quantity of petroleum in the world (Herron 2000, Chen, He et al. 2010, Chao, Chen et al. 2012). Depleting reserves of conventional crude oil coupled with growing demands for high quality fuels and petrochemical feedstock led to more research in the area of exploration and exploitation of unconventional resources.

Thus, many enhanced oil recovery (EOR) techniques have been developed and adopted for exploiting heavy crudes (Al-Adasani and Bai , Gogarty 1983, Donaldson, Chilingarian et al. 1985, Green and Willhite 1998, S. Thomas 2001, Shah, Fishwick et al. 2010, Hart, Leeke et al. 2014). Catalysts have been used for decades in refineries to improve and extract the maximum value from each barrel of produced oil. The catalysts facilitate the conversion of some components of the oil to components that result in lower viscosity with high value. Based on this, in-situ catalytic upgrading and recovery of heavy crudes and bitumen has received considerable attention in recent times (Hashemi and Pereira-Almao 2011, Chao, Chen et al. 2012, Hashemi, Nassar et al. 2013, Hashemi, Nassar et al. 2013, Hashemi, Nassar et al. 2014). A series of chemical reactions such as, pyrolysis, hydrocracking, hydrotreating, aquathermolysis etc. is expected to take place within the porous media during the process (Weissman and Kessler 1996, Weissman, Kessler et al. 1996, Cavallaro, Galliano et al. 2005, Galarraga and Pereira-Almao 2010, Zamani, Maini et al. 2010, Shuwa, Al-Hajri et al. 2015). Near-well-bore catalytic upgrading has been demonstrated and shown to decrease sulphur content and increase API gravity (Weissman and Kessler 1996, Weissman, Kessler et al. 1996, Cavallaro, Galliano et al. 2005, Mohammad and Mamora 2008, Gallaraga 2011, Chao, Chen et al. 2012). Moore *et al* and Weissman *et al* were the first to propose the concept of in-situ catalytic upgrading of heavy oil during in-situ combustion(Weissman and Kessler 1996, Weissman, Kessler et al. 1996, Cavallaro, Galliano et al. 2005).

A number of researches have been conducted to investigate the performance of various catalysts in upgrading heavy crude oil and residua (Tian, Mohamed et al. 1998, Fan, Liu et al. 2001, Nares, Schacht-Hernandez et al. 2006, Wen, Zhao et al. 2007, Mohammad and Mamora 2008, Chen, Wang et al. 2009). In our previous study (Shuwa, Al-Hajri et al. 2015), we investigated the effect of dispersed catalysts based on molybdenum in upgrading the same heavy crude oil of Oman deposits. The batch-reactor study of the upgrading processes showed that the catalyst has the potentials to be used for in-situ upgrading and recovery of the heavy oil.

However, the low stability of the water-in-oil emulsion formed which was caused by the presence of the deep eutectic solvent and absence of surfactants, and the formation of solid precipitate of micronic scale are some of the drawbacks observed. Hence, the use of dispersed catalyst from stable water-in-oil emulsion may offer a better approach for upgrading the heavy oil. Very high levels of catalyst dispersion can be achieved by introducing finely divided powders, water-soluble or oil-soluble precursor compounds into the feed (Panariti, Del Bianco et al. 2000, Liu, Gao et al. 2009). In situ upgrading using dispersed catalysts of nanometric or sub-micronic scale is a promising alternatives from both economic and environmental perspectives (Galarraga and Pereira-Almao 2010, Almao 2012, Hashemi, Nassar et al. 2013). Such catalyst is expected to minimize the

formation damage problems caused by pore plugging in the reservoir (Zamani, Maini et al. 2010, Shokrlu and Babadagli 2011, Zamani, Maini et al. 2011, Shuwa, Jibril et al. 2015). Water-in-oil emulsion are particularly attractive reaction media for the preparation of solid catalyst particles of submicron dimension through a complex process (Eriksson, Nylén et al. 2004). They have been applied in producing catalysts based on transition metals for hydrogenation and hydrocracking reactions (Ng and Milad 2000, Thomson 2008, Galarraga and Pereira-Almao 2010). The formation of water-in-oil (w/o) emulsions is driven by strong hydrophilic interactions of the polar head of the surfactant (emulsifier) molecule (López-Quintela 2003, Capek 2004). Based on the foregoing, we found of interest to study the effect of dispersed catalysts in water-in-oil emulsion. Here we present results of the performance of a new trimetallic catalyst based on molybdenum, nickel and cobalt in upgrading heavy crude oil. The catalyst was prepared in-situ.

2. EXPERIMENTAL
2.1 Materials
Heavy crude oil sample from an Omani oilfield used for the upgrading experiments (properties given in Table 1). All chemicals were used without further treatment.

Table 1: Properties of the Heavy crude oil

Property	Value
Density (30°C), g/cm3	0.9660
API gravity, °	14.31
Viscosity (30°C), cP	3951
Sulfur, wt%	3.67
Asphaltenes, wt%	4.0

2.2 Preparation of catalytic emulsion
Prior to the upgrading experiment, water-in-oil emulsion was formulated by mixing the water phase containing the metal catalyst precursors with the organic phase containing the surfactants (Eriksson, Nylén et al. 2004, Nassar and Husein 2007, Husein, Patruyo et al. 2010). The water phase which contains the metal precursor solutions was prepared in order to get the final loading of the metals to satisfy the atomic ratio: $Ni/(Ni + Co +$

$Mo) = 0.3$ and $Mo/Co = 3$ (Gallaraga, Scott et al. 2009). The water-in-oil emulsion was formulated by mixing the water phase containing the metal catalyst precursors with the organic phase containing the surfactants. The two surfactants polyethylene sorbitan monoleate (TWEEN 80[TM], HLB = 14) and sorbitan monoleate (SPAN 80, HLB = 4.5) were mixed in combination to give a surfactant with HLB of 8 (Galarraga and Pereira-Almao 2010). The mixing was conducted with ultrasound mixer at 40°C for 30mins at a mixer speed of 4000rpm. Fig.1 shows the schematic representation of the process.

2.3 Upgrading Experiment
Upgrading experiments of the heavy crude oil was carried out using a 300mL capacity batch-type laboratory reactor (4560 series, Parr Instrument Company). The following constant reaction conditions were utilized: 40bar initial hydrogen pressure and 750rpm stirring speed. Detailed experimental method was reported elsewhere (Shuwa et al., 2015)

Response Surface Method (RSM) was used to design the experiments to study the impact of variables; reaction temperature, reaction time and catalysts amounts on viscosity reduction, API increase, sulfur reduction, hydrogen pressure reduction and coke formed from the upgrading experiments. The independent design variables and their levels are presented in Table S1 (supporting Information). Table S2 presents actual and coded levels of variables with corresponding values of all the responses evaluated. At the end of the reaction time, the reactor was cooled to room temperature. Samples of the reactor contents were taken and analyzed for GC, sulfur content, asphaltene content, coke, FTIR, XRD, SEM-EDS, viscosity, density and API gravity. Refer to Table S3 for the results of these measurements.

3. RESULTS AND DISCUSSION
3.1 Preliminary Investigation
Three experimental runs were conducted to investigate the performance of the catalysts in upgrading the heavy crude oil based on conditions as indicated in Table S3.
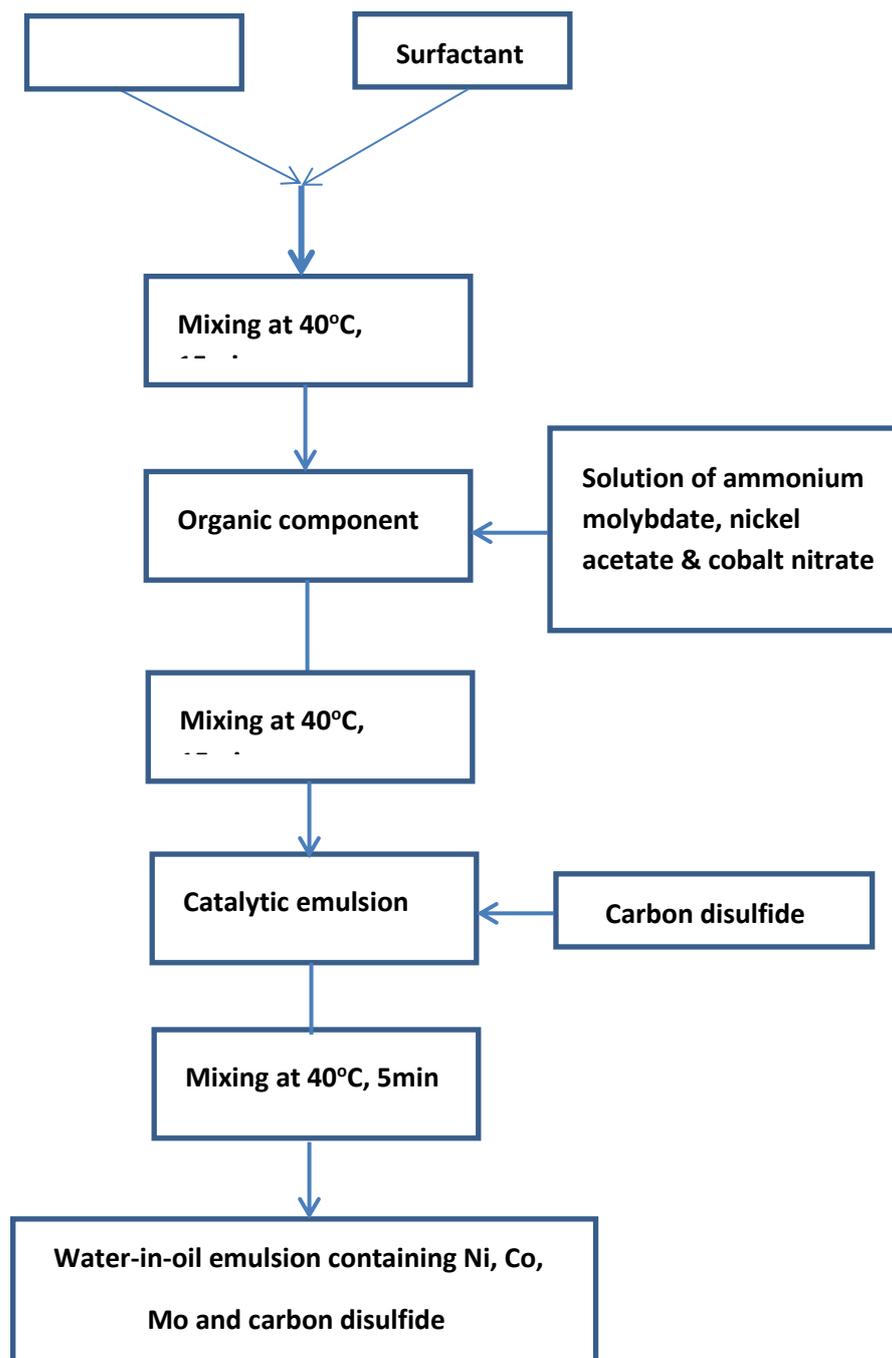
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│              │        │   Surfactant     │
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        │  Mixing at 40ºC,        │
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        ┌─────────────────────────┐      ┌──────────────────────────┐
        │  Organic component      │ ◄─── │ Solution of ammonium     │
        └─────────────────────────┘      │ molybdate, nickel        │
                    ↓                     │ acetate & cobalt nitrate │
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        │  Catalytic emulsion     │ ◄─── │   Carbon disulfide       │
        └─────────────────────────┘      └──────────────────────────┘
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        │  Mixing at 40ºC, 5min   │
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    ┌───────────────────────────────────┐
    │ Water-in-oil emulsion containing  │
    │ Ni, Co,                           │
    │                                   │
    │ Mo and carbon disulfide           │
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Fig.1: Schematic diagram for the preparation of the water-in-oil catalytic emulsion

The following conditions were kept constant during the runs: temperature of 300ºC, initial hydrogen pressure of 40bar, reaction time of 24hours and catalyst amounts of 2000ppm (0.2wt%). About 29% reduction in viscosity was observed when only water was added to the oil after 24hours of reaction at 300^0C as shown in Fig.2 (in P1).

Further reduction to about 48% (as in P2) and 58% (in P3) was recorded when the surfactants and surfactants containing catalysts respectively were added to the oil sample. This shows the catalysts and surfactants are effective in reducing the viscosity of the heavy oil at the given conditions. Similar trend could be observed with API gravity increase for the three runs. catalyst's activity in desulfurizing the heavy crude oil samples. The catalyst proved to adding catalysts and surfactants to the oil (as in P3) led to further sulfur reduction (16% in P3) compared to when there was no catalysts (about 10% for both P1 and P2). This demonstrates its effectiveness in upgrading the oil by reducing viscosity and sulfur and increasing API gravity. Having established that the catalyst is effective in upgrading the

heavy crude oil, the runs were designed and implemented. The study evaluates the solid, liquid and gaseous products of the reaction in order to be able to assess the performance of the catalyst in upgrading the heavy crude oil. To achieve that, some selected runs (conditions given in Table 2) out of the total 17 runs (results given in Table S2 and S3 of supporting material) were selected and reported here to aid the discussion of result.
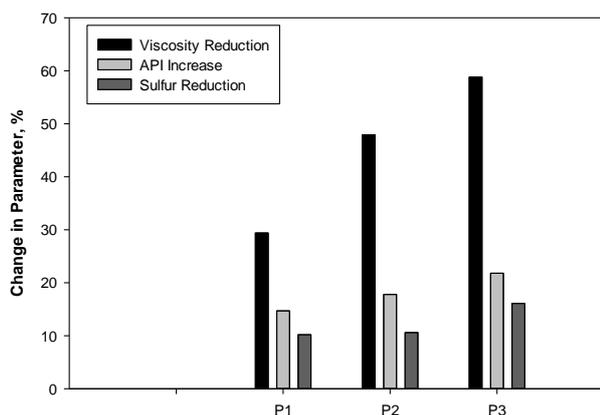

Fig. 2: Results from the preliminary runs; P1 = oil + H$_2$O, P2 = oil + H$_2$O + surfactant, P3 = oil + H$_2$O + surfactant + catalyst

Table 2: Operating conditions of four selected runs

Run number	Reaction temperature, ^{o}C	Reaction time, hours	Catalyst amounts, ppm
R10	340	28	2500
R11	340	28	500
R12	300	28	1500
R16	260	8	1500

3.2 physical properties of the heavy oil after reaction

Viscosity and API gravity are the two most important physical properties of heavy crudes; hence the heavy crude oil was analyzed to see changes in these properties after reaction. The results are shown in Table 3. Results of oil samples from other runs is shown in Table S3 (supporting material). The change in viscosity and API gravity was calculated according to the following equation:

$$\Delta M = \frac{Mo - M}{Mo} \: X \: 100\%$$

Where ΔM is the change in property [viscosity (mPas, 30°C)] or API gravity (@ 15 ^{o}C)], Mo is the initial property (viscosity or API gravity), M is the property of the sample after reaction.

Table 3: viscosity and API gravity of reacted oil samples

Oil sample	Viscosity, cP	API gravity, ^{o}	Viscosity reduction, %	API gravity increase, %
Fresh oil	3951	14.31	NA	NA
R10	182	20.61	95.4	43.9
R11	194	20.5	95.1	43.3
R12	1768	17.5	55.3	22
R16	3695	16.1	6.5	12.6

The upgrading reaction achieved a viscosity reduction of over 95% at the maximum reaction temperature of 340°C as shown in Table 3 for oils analyzed from runs R10 and R11. However, despite the difference in amounts of catalyst used between R10 and R11, there was no significant difference in viscosity reduction between the two runs. This shows that temperature plays a significant and influential role in reducing the viscosity of heavy crudes. The temperature effect is even more pronounced at high temperatures than the amounts of catalyst. A substantial reduction in viscosity of about 55% was also recorded at a moderate temperature of 300°C. However, and insignificant reduction in viscosity (6.5%) was observed at 260°C and 1500ppm of catalysts. This could be attributed to low operating conditions evidenced by the low temperature and reaction time. Furthermore, it could be as a result of inability of the catalyst to accelerate the chemical reactions that normally results into transformation of heavier components to lighter ones. The catalyst may not have been activated at that operating conditions since sulfiding of the precursor compounds and hydrocarbon decomposition normally take place at around 300°C (Thomson 2008). Table 3 also evidences that API gravity increases with the operating temperature, an indication of progressive transformation of heavy crude oil to lighter oil. Both viscosity and API gravity showed similar trend. This does not mean that they are directly correlated as oils varying widely in viscosity may have similar API gravity. This is not surprising because different factors are involved in determining the values of viscosity and API gravity (Ancheyta, Rana et al. 2005, Hinkle, Shin et al. 2008).

3.3 Sulfur content of the heavy oil after reaction

The sulfur content and the percent desulfurization of the fresh and reacted heavy oil samples from five selected runs are given in Table 4.. Refer to Table S3 for the results of all runs with experimental error of measurements. The maximum desulfurization (among the four selected runs) of about 24wt% was recorded for sample obtained from run R10. Whereas oil sample recovered from run R11 achieved only 14.5wt% sulfur removal in spite of the fact that both runs were subjected to same operating conditions with an only difference in amounts of catalyst used. This shows that unlike in viscosity and API gravity, the catalyst amount plays a significant role in reducing the sulfur contents of the reacted oil samples as demonstrated in the difference in

desulfurization values between runs R10 and R11. Comparing sulfur contents of oil recovered from runs R12 and R16 shows the significance of reaction temperature and time to the desulfurization process. It could be possible that the 1.7wt% sulfur removal achieved was due to the effect of thermal processes. This can be explained with the fact that the aquathermolysis process (thermal effect in the presence of water) involves breaking of the weak C-S bond which results into sulfur reduction (Fan, Liu et al. 2001, Wen, Zhao et al. 2007, Chen, Wang et al. 2009, Maity, Ancheyta et al. 2010, Chao, Chen et al. 2012). The catalyst's desulfurization performance increases with temperature and time as shown by the reduction in hydrogen partial pressure after reaction (Table 4). Hydrogen is required for reactions to progress and its enhanced consumption indicates catalyst's activity. It is evident in Table 4 and Table S3 that hydrogen pressure reduces with reaction temperature whenever the catalyst was used. In other words hydrogen consumption increases with temperature in the presence of the catalyst. This can be linked to ability of the catalyst to make the hydrocarbons consumed more hydrogen at high temperature due to catalyst's high activity at such temperatures.

Table 4: Chemical Properties of oil samples obtained from selected runs

Run	Sulfur content, wt %	Desulfurization, %	Coke, wt %	Asphaltene content, wt%	Reduction in H$_2$ pressure, bar
Fresh oil	3.67	NA	NA	4.0	NA
R10	2.86	24.2	0.05	0.9	13
R11	3.14	14.5	0.15	1.6	10
R12	3.14	14.5	0.2	1.1	7
R16	3.60	1.7	0.49	2.9	3

3.4 Coke content of the heavy oil after reaction

The coke contents of the fresh heavy oil and reacted oil samples from the four selected runs are shown in Table 4. In in-situ upgrading processes for recovering heavy crudes, coke formation is not desired because of its capacity to deactivate the catalyst (Dehkissia, Larachi et al. 2004, Ortiz-Moreno, Ramírez et al. 2012) and block pores of reservoir matrix which is responsible for pore plugging that causes damage to the formation. Formation of coke after upgrading reactions also leads to reduction of yield of liquid products commonly desired in hydroprocessing operations (Speigth 1999, Ancheyta, Rana et al. 2005, Eom, Lee et al. 2014).

The highest amounts of coke were recorded for R16 while the least amount of coke formed was observed for run R10. The coke formed by run R16 is even higher than that formed by run P1 (0.42wt%, Table S3) which is a preliminary run (base run) conducted without catalyst at 300ºC for 24hours. Also, run R17 (Table S3)

which was conducted at the same temperature with R16 but at a longer reaction time (28hours) and higher amounts of catalyst (2500ppm) recorded 0.44wt% coke, which is still lower than that of R16.

All this demonstrate that temperature, reaction time and catalyst amount play a significant role in determining the amounts of coke formed after reaction. It can be interpreted from the results that increasing all the three parameters within the range tested leads to effective reduction of coke after reactions. Similar trend was observed with the reduction in hydrogen pressure. The least the amount of coke formed, the higher the consumption of hydrogen. This clearly reveals that it is the increase in catalyst activity that leads to low amount of coke formed.

Since thermal and catalytic reactions are known to proceed via free radical chain reactions, a higher proportion of free radicals are expected to form, which subsequently lead to formation of higher amount of coke. However, when an effective catalyst coupled with high partial pressure of hydrogen are present, the free radicals will be stabilized and such reactions that lead to formation of coke suppressed. It is expected that catalytic thermal decomposition would result in less amount of coke because catalyst can create new pathways in the reaction schemes (Hashemi, Nassar et al. 2014).

3.5 FTIR and GC analyses of produced oil samples

FTIR spectra of liquid samples recovered from some selected few runs were acquired and presented in Fig.3. The transmission bands at 2925 and 2852cm-1 assigned to C-H stretching vibration (Pecsok, Shields et al. 1976, Chen, Wang et al. 2009, Chen, Yang et al. 2010, Chao, Chen et al. 2012) found in saturated hydrocarbons became much stronger after reactions (in R10, R11,R12 and R16) as demonstrated by the increase in intensity of their respective spectrum. Also, the absorption bands at 1460 and 1376cm^{-1} attributed to C-H bending vibrations (Pecsok, Shields et al. 1976, Chen, Wang et al. 2009) found in alkanes became stronger after reactions as shown in the spectra for all the runs compared to fresh oil sample.
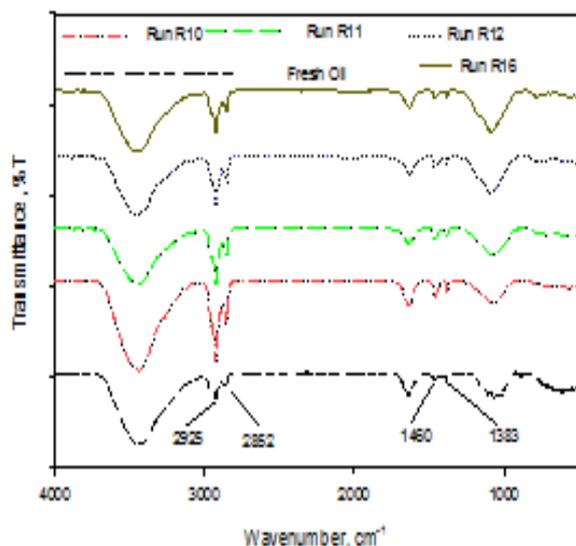
Fig. 3: FTIR Spectra of oil recovered from runs: fresh heavy oil, R10; 340ºC, 28h, 2500ppm catalysts R11; 340ºC, 28h, 500ppm catalyst, R12; 300ºC, 28h, 2500ppm catalyst, R16; 260ºC, 28h, 1500ppm

All these point to production of more saturates from the unsaturates presents in the initial fresh raw oil. This may be attributed to the conversion of unsaturated compounds in the other fractions of the oil such as resins and asphaltenes to saturates (Chen, Yang et al. 2010).

This was also confirmed by the reduction in asphaltene content of the oil after upgrading reactions as shown in Table 4. About 76% reduction in asphaltene content was observed for run R10 alone, which was conducted at 340ºC, 2500ppm of catalyst for 24hours. Even run R12 which was conducted at a lower temperature compared to R10 achieved 73% reduction in asphaltenes content. However run R11 which was carried out at 40ºC higher temperature than R12 but 2000ppm, lower catalyst amounts achieved only 60% reduction in asphaltene content. This shows how catalyst amounts plays a significant role in converting asphaltenes to other fractions of the oil. Just like sulfur and coke contents, asphaltene content has parallel behavior with temperature, catalyst concentration and reaction time.

The GC chromatograms of saturated hydrocarbons from these selected oil samples from the runs showed similar observations when compared with fresh heavy oil sample. There was increase in intensity of peaks of saturated hydrocarbons from the four selected runs when compared with that of fresh heavy oil. See the GC chromatograms of these oil samples as shown in Figs.S4 to S8 in supporting material document.

Table 5 presents the results of gases identified from selected four runs in terms of product distribution. Analysis of the gaseous products revealed the presence of C1-C6 hydrocarbons and substantial amounts of

hydrogen sulfide in some of the runs analyzed. The amounts of CH_4 decreases with temperature and increase with amounts of catalysts as s shown in Table 5. Similar trend was observed for the desulfurization behavior of the oils from the selected runs as shown in the H_2S weight (Table 5). This shows that operating at high temperatures for longer reaction time with high amounts of catalysts (within the range tested) gives better upgrading conditions. Since the results of sulfur, coke, asphaltene and hydrogen consumption revealed that the catalyst is only active at high temperatures (300-340ºC), it is logical to link the preferential generation of light hydrocarbon liquids to the high activity of the catalyst at such temperatures.

Table 5: Gaseous products distributions from selected runs after upgrading reactions

Identified gases	Weight %			
	Run R10	Run R11	Run R12	Run R16
CH_4	1.7	13.29	8.74	27.74
C_2H_4	7.67	9.63	8.34	13.47
H_2S	11.01	6.20	5.70	ND
C_3H_8	0.21	6.65	6.78	8.45
$i-C_4H_8$	ND	4.11	2.34	ND
$n-C_4H_{10}$	0.51	ND	1.21	0.53
$i-C_5H_{10}$	ND	ND	ND	4.69
$n-C_5H_{12}$	ND	60.11	ND	ND
$n-C_6H_{14}$	78.9	ND	66.89	45.13
Total	**100**	**100**	**100**	**100**

The presence of the catalyst at such temperatures enhances the hydrocracking reactions. This is expected in hydrocracking process as it leads to production of liquid distillate fractions at the expense of gaseous and solid products (Dehkissia, Larachi et al. 2004, Speight 2006).

3.6 Characteristics of solids recovered after reactions
XRD and SEM-EDS analyses were performed on recovered solids from some of the runs. The solids, a non-soluble filter cake from the filtration process, consist of the catalytic particles generated in situ and were characterized.
3.6.1 X-Ray diffraction
The XRD diffractograms of solids recovered from runs R10 and R12 are presented in Figs 4 and 5 respectively. The XRD patterns of the solids recovered from run R10, which was carried out at 240ºC, 28hours with 2500ppm of catalyst indicated the presence of highly crystalline materials as demonstrated by the resolution and intensity of the peaks recorded. The peak at $2\Theta = 26.6$ is attributed to the presence of β-$NiMoO_4$ (Jeon, Na et al. 2011). This diffraction peak was found out in both samples (R10 &R12) an indication of low sulfidation state of the catalyst precursor compounds. This diffraction peak is more pronounced in solid from run R12 than R10, which can be attributed to the poor sulfidation behavior in R12 compared to R10 at low temperature. In addition to that ,the sulfidation state of

such compounds are found to be low and very sensitive to water (Fixari, Peureux et al. 1994). In spite of the presence of this peak, a diffraction pattern similar to that of molybdenite (MoS_2), an active form of molybdenum hydrocracking catalyst was observed. The diffraction peaks at 2Θ = 14, 33, 34 and 44 were observed in the XRD patterns of the solids from the two runs (R10 and R12) and are due to the presence of the active form of the catalyst (Fixari, Peureux et al. 1994, McFariane, Hawkins et al. 1998, Panariti, Del Bianco et al. 2000, Gallaraga 2011).

The XRD pattern of solids from run R10 showed a crystallize as sulfides with a pyrrhotite-like structure. These are characteristics of sulfides derived from other metals (Ni, Co ,Fe etc.) and generally form a three-dimensional pyrrhotite-like crystalline structure (Panariti, Del Bianco et al. 2000). This shows the formation of the sulfides of Ni and Co which were used as promoters in this work.
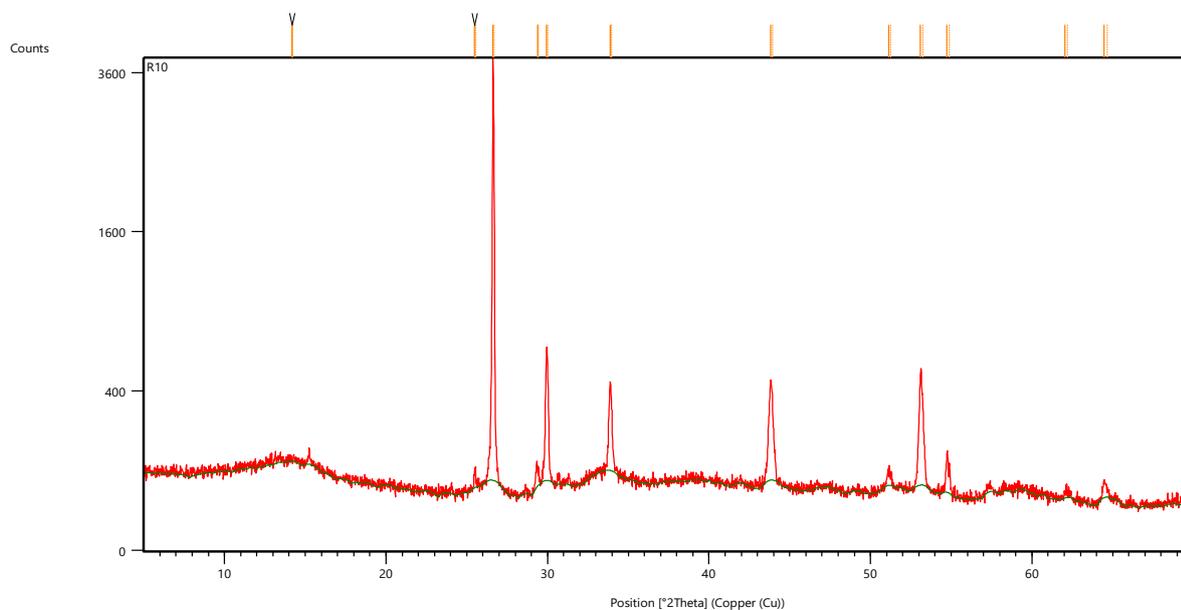
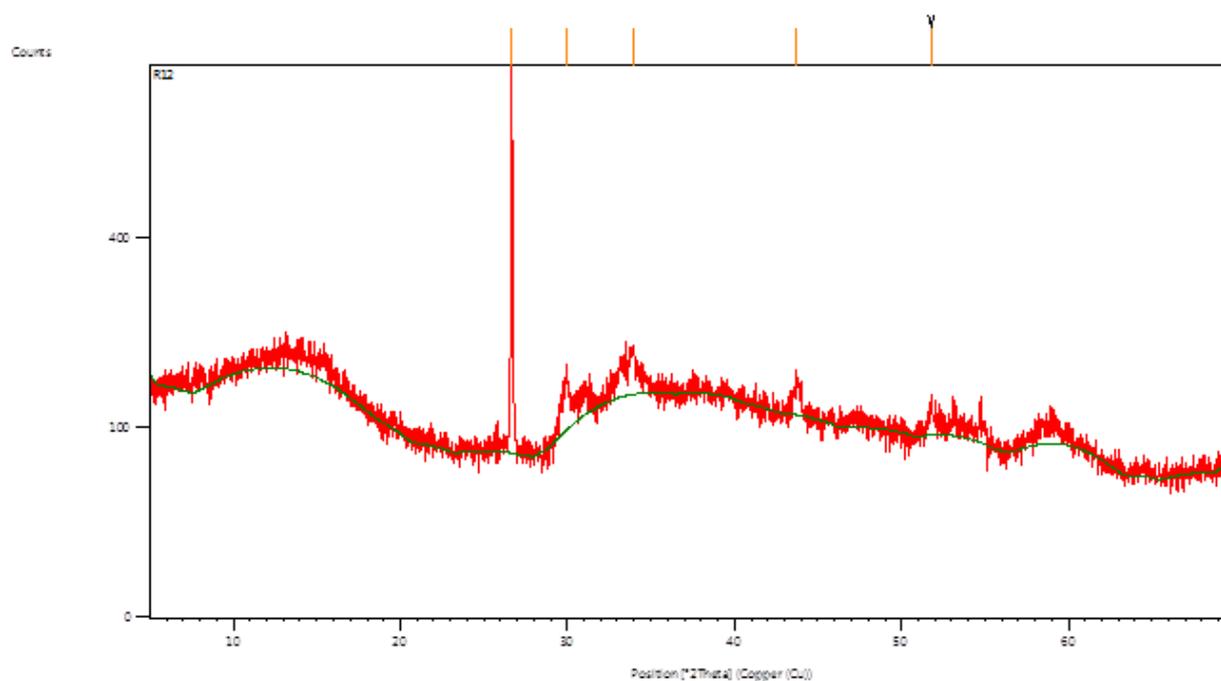**Fig.4: X-ray Diffractogram of solid recovered from run R10 at 340ºC, 28h, 2500ppm catalyst**

Fig.5: X-ray Diffractogram of solid recovered from run R12 at 300ºC, 28h, 2500ppm catalyst

3.6.2 SEM-EDS analysis

Figs.6 and 7 show the SEM microphotographs of the solid recovered from runs R10 and R12 respectively. Two types of morphologies could be observed from the SEM images as shown in the figures; the needle-like type with the small particle size (approximately 240nm on the average as shown in Fig.6) and the near round particle with a both small and a bit larger particle size (1.43-2.6µm shown in Fig.6 and 7). EDS analysis of this near-round particles revealed they composed principally of the catalytic metals used. The main structure of similar molybdenum and nickel catalyst aggregates and agglomerates are reported to have similar morphologies (Thomson 2008, Hashemi, Nassar et al. 2014). In contrast to the sizes of the catalytic particles obtained in R10, an approximate particle size of 400nm was found for run R12 as shown in Fig.7. The difference between this run and run R10 is the reaction temperature; R10 was carried out at 340ºC whereas R12 was conducted at 300ºC. This shows that the higher the temperature the larger the size of the catalyst particles. Similar observation of increase in particle size with decomposition temperature was made by Wang (Wang 2004).
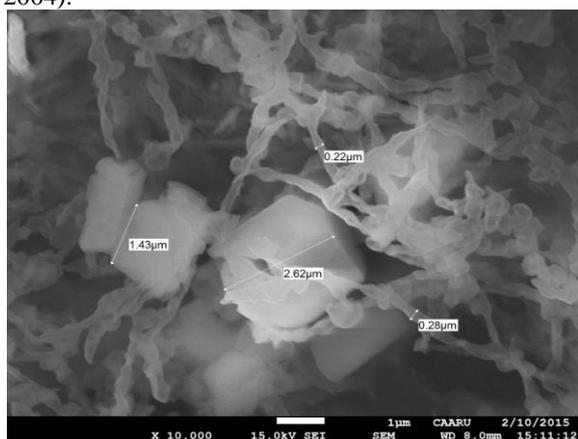

Fig.6: SEM image of filtered solid recovered from run R10 obtained at 340ºC, 2500ppm of catalyst for 28h
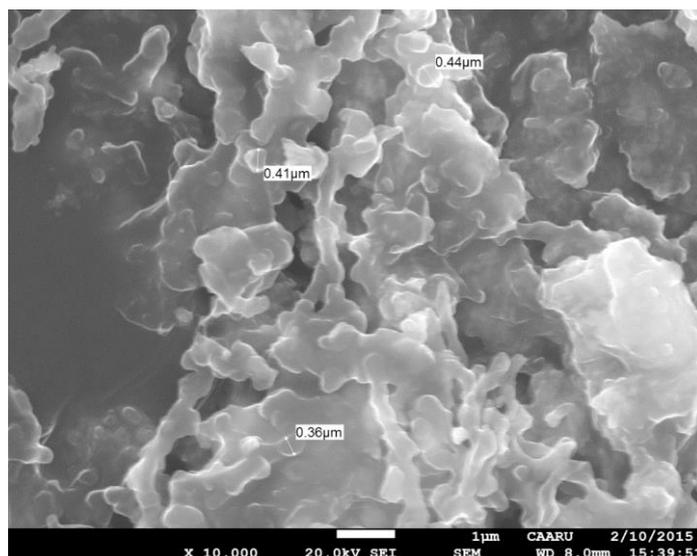

Fig.7: SEM image of filtered solid recovered from run R12 obtained at 300ºC, 2500ppm, 28h

Figs.8 and 9 show the EDS spectra and the quantification results of the elemental analysis of the two runs (R10 and R12). The results of the EDS analysis were presented on right hand side of the figures while SEM images of the zones used for the EDS were presented on the left hand side. The EDS analysis in Fig.8 was for spectrum 2 and spectrum 15 was chosen in Fig.9 as shown in SEM images in the figures.

The samples in the selected spectra 2 and 15 are composed mainly of O, Mo, S, Ni, Co and N as shown in the EDS elemental result. This is expected as the oil originally composed of heteroatoms in form O, N and S while Mo, Ni and Co from the catalyst particles used. Considering the three metals used for the formulation of the catalysts, Ni, Co and Mo, their amounts in the selected spectrum 2 were 11, 4.5 and 28.1%wt respectively. The equivalent amounts in atomic percent as shown in Table 6 is 5.3, 2.2 and 8.3% for Ni, Co and Mo respectively.
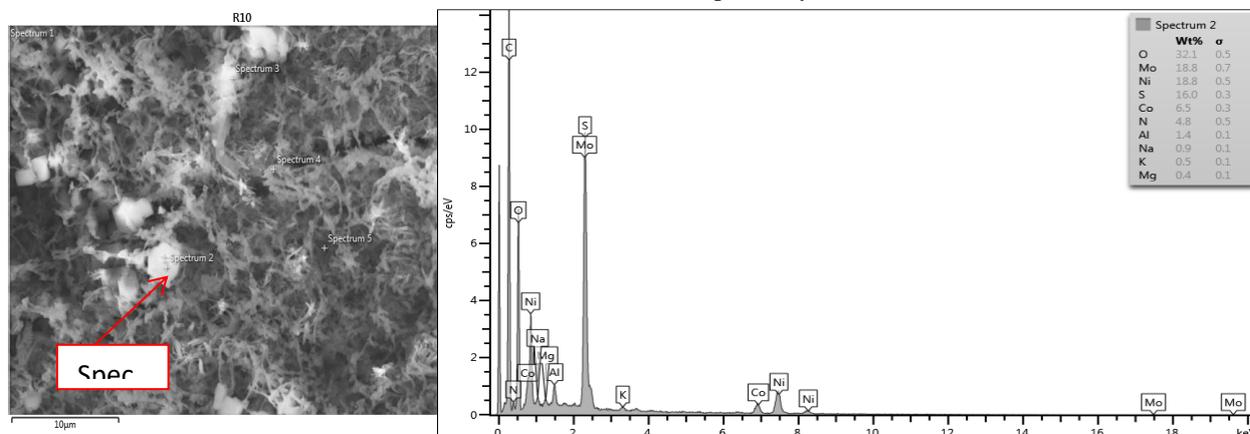

Fig.8: SEM image, EDS spectra and elemental result of solid recovered from run R10

This is close to the quantities introduced in to the reaction media. The ratio of Ni to the total metals [Ni/(Ni+Co+Mo)] or Ni/Me introduced to the reaction media through the catalytic emulsion was 0.3 and a value of 0.33 was found from the elemental analysis of the recovered solid

The ratio Mo/Co was 3 as introduced into the reaction media and a ratio of 3.77 was found from the elemental analysis. Contrary to that, there is a deviation in quantities of the metals introduced with the EDS elemental quantification results for solids recovered from R12 as shown in Table 6. This could be attributed to inhomogeneous distribution of the catalyst particles in the solids after the reaction
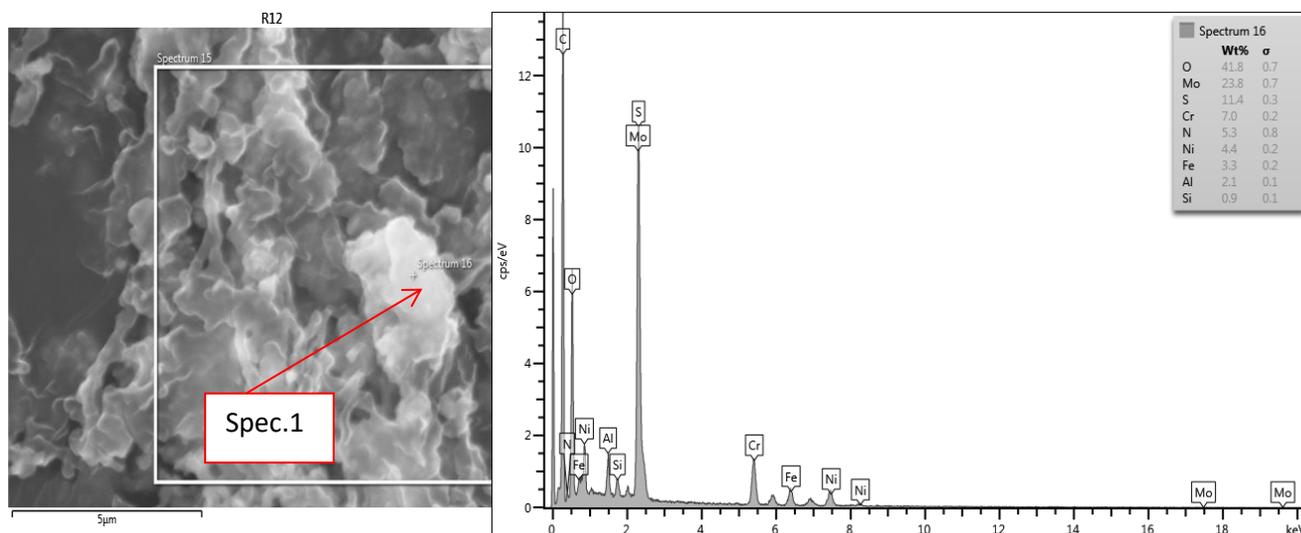

Fig.9: SEM image, EDS spectra and elemental result of solid recovered from run R12

Table 6: Chemical composition results of selected spots of solids recovered from runs R10 and R12

Element	Spectrum 2, R10		Spectrum 15, R12	
	Weight %	Atomic %	Weight %	Atomic %
Mo	28.1	8.3	32.3	9.3
Ni	11.0	5.3	5.6	2.7
Co	4.5	2.2	3.8	2.1
O	32.1	56.9	31.1	53.9
S	16.0	14.2	15.0	13.0
N	4.8	9.7	7.6	15.1
Al	1.4	1.5	1.7	1.8
Na	0.9	1.1	1.0	1.2
K	0.5	0.4	1.8(Fe)	0.9
Mg	0.4	0.4	ND	_
Ni/Me		0.33		0.19
Mo/Co		3.77		4.42

4. CONCLUSION

Preliminary evaluation showed the catalyst to be very effective in upgrading the heavy crude oil. Results showed that the catalyst can be used in upgrading the heavy crude oil as significant improvement in qualities of the oil after reaction was achieved. After analyzing the results from the heavy crude oil upgrading reactions in the presence of the catalyst at varying operating conditions, the following specific conclusions can be drawn:

1. While the presence of the catalyst appeared to have improved on API gravity and viscosity of the heavy oil after reaction based on preliminary investigation conducted; however, there was no significant change in these properties when the catalyst amount was varied from 500 to 2500ppm.

2. Varying the catalyst concentration from 500 to 2500ppm showed to have significant impact on the sulfur, asphaltenes and coke contents of the heavy oil after reaction. This indicates that the catalyst

have impacted more on the chemical properties of the heavy oil than on physical properties.

3. Sulfur, asphaltene and coke contents of the heavy oil after reaction have parallel behavior with temperature. In other words, raising temperature led to a significant reduction in the quantities.

4. XRD and SEM-EDS analyses of the recovered solids from some of the runs after reaction confirmed the in-situ formation of the dispersed submicron catalytic particles based on Nickel, cobalt and molybdenum.

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SUPLEMENTARY DATA

Table S1: Amounts and levels of the experimental independent design variables

Variable	Unit	lower level (-1)	center point (0)	higher level (+1)
Reaction temperature(X1)	^0C	260	300	340
Catalyst amounts (X2)	ppm	500	1500	2500
Reaction time (X3)	hour	8	28	48

Table S2: Coded and actual levels of variables and corresponding responses

Run	\multicolumn{3}{Coded levels of variables}			Actual levels of variables			Responses				
	X1	X2	X3	X1	X2	X3	Viscosity, cP	Sulfur, wt%	API incr.	H_2 P,bar	coke, %wt
1	0	0	0	300	1500	28	1798	14.1	19.2	7	0.22
2	1	0	1	340	1500	48	272	27	38.6	12	0.12
3	0	-1	-1	300	500	8	3212	8.5	17	3	0.33
4	0	1	-1	300	2500	8	2510	11.2	19.4	4	0.39
5	-1	0	1	260	1500	48	4545	6.2	6.2	5	0.41
6	0	0	0	300	1500	28	1765	13.7	22	6	0.21
7	-1	1	0	260	2500	28	4285	6.9	14.2	5	0.49
8	0	0	0	300	1500	28	1828	14	18.9	6	0.21
9	0	1	1	300	2500	48	2208	10.3	17.8	8	0.18
10	1	1	0	340	2500	28	182	24.2	43.9	13	0.05
11	1	-1	0	340	500	28	194	14.5	43.3	10	0.15
12	0	0	0	300	1500	28	1768	14.5	22	7	0.20
13	1	0	-1	340	1500	8	852	13.1	26.2	5	0.11
14	0	0	0	300	1500	28	1768	13.7	22	6	0.24
15	0	-1	1	300	500	48	1424	10.5	23.1	7	0.28
16	-1	0	-1	260	1500	8	3695	1.7	12.6	3	0.49
17	-1	-1	0	260	500	28	3992	1.9	4.8	3	0.44

Table S3: Results with experimental errors for all the 20runs conducted

| Run No.	Density, g/cm3	Viscosity, cP	API Gravity, ^{0}	Sulfur, wt%	Coke, wt%	H_2 P red., bar
Fresh Oil	0.9591 ± 0.003	3951 ± 3	14.32 ± 0.01	3.67 ± 0.124	-	-
P1	0.9459 ± 0.00005	2790 ± 10	16.42 ± 0.02	3.30 ± 0.005	0.42	2
P2	0.9432 ± 0.00006	2060 ± 0	16.87 ± 0.003	3.28 ± 0.002	0.41	2
P3	0.9394 ± 0.0004	1628 ± 5	$17.44 \pm 6x10^{-6}$	3.08 ± 0.006	0.19	7
R1	0.9419 ± 0	1798 ± 5	17.07 ± 0	3.16 ± 0.02	0.22	7
R2	0.9240 ± 0.0005	272 ± 3	19.85 ± 0.07	2.67 ± 0.009	0.12	12
R3	0.9438 ± 0.0002	3212 ± 3	16.76 ± 0.02	3.36 ± 0.02	0.33	3
R4	0.9418 ± 0.00008	2510 ± 5	17.1 ± 0.06	3.26 ± 0.03	0.39	4
R5	0.9540 ± 0.0002	4545 ± 6	16.49 ± 0.003	3.45 ± 0.02	0.41	5
R6	0.9391 ± 0.0008	1765 ± 5	17.47 ± 0.09	3.17 ± 0.04	0.21	6
R7	0.9462 ± 0.001	4285 ± 5	16.36 ± 0.1	3.42 ± 0.03	0.49	5
R8	0.9420 ± 0.0009	1828 ± 8	17.02 ± 0.09	3.13 ± 0.008	0.21	6
R9	0.9437 ± 0.0004	2208 ± 3	16.87 ± 0.2	3.29 ± 0.009	0.18	8
R10	0.9189 ± 0.0003	182 ± 3	20.61 ± 0.007	2.86 ± 0.02	0.05	13
R11	0.9196 ± 0.001	194 ± 2	20.52 ± 0.1	3.14 ± 0.02	0.15	10
R12	0.9391 ± 0.0004	1768 ± 3	17.47 ± 0.09	3.14 ± 0.04	0.20	7
R13	0.9353 ± 0.003	852 ± 3	18.07 ± 0.5	3.19 ± 0.02	0.11	5
R14	0.9391 ± 0.0008	1768 ± 3	17.47 ± 0.09	3.17 ± 0.04	0.24	6
R15	0.9378 ± 0.0002	1424 ± 7	17.63 ± 0.05	3.29 ± 0.03	0.28	7
R16	0.9481 ± 0	3695 ± 4	16.13 ± 0.06	3.60 ± 0.1	0.49	3
R17	0.9515 ± 0	3992 ± 8	15.01 ± 0.2	3.61 ± 0.1	0.44	3
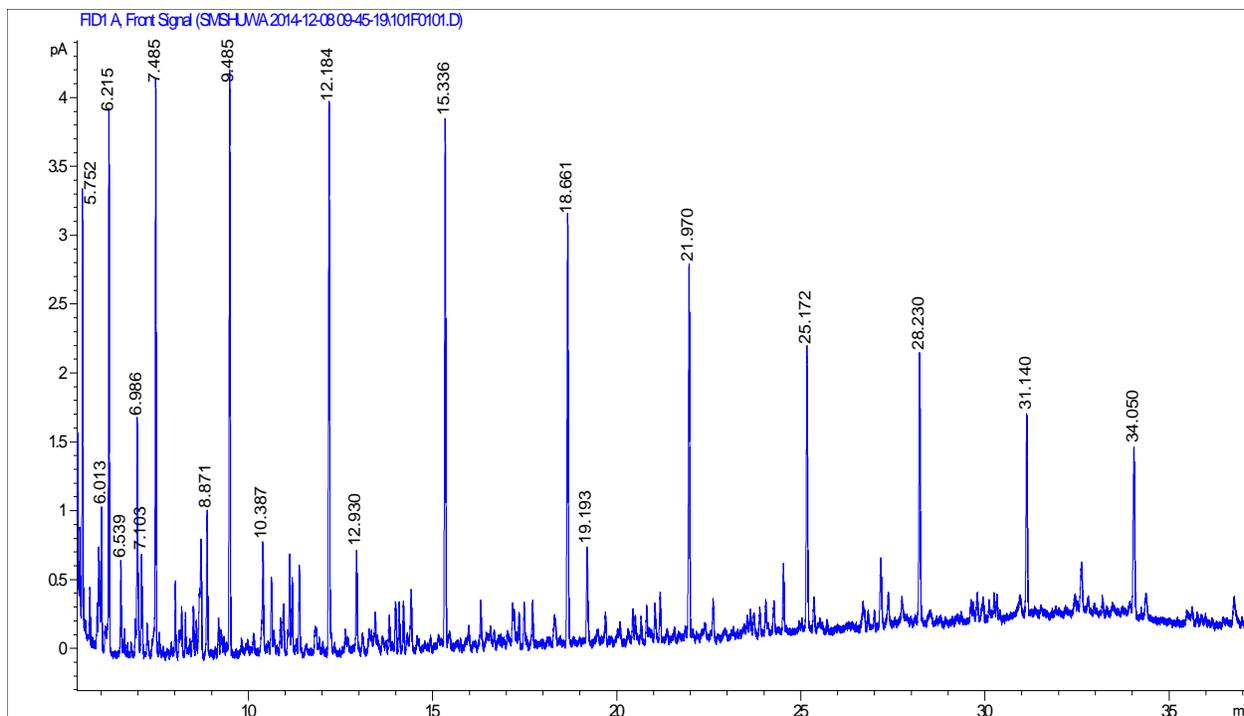
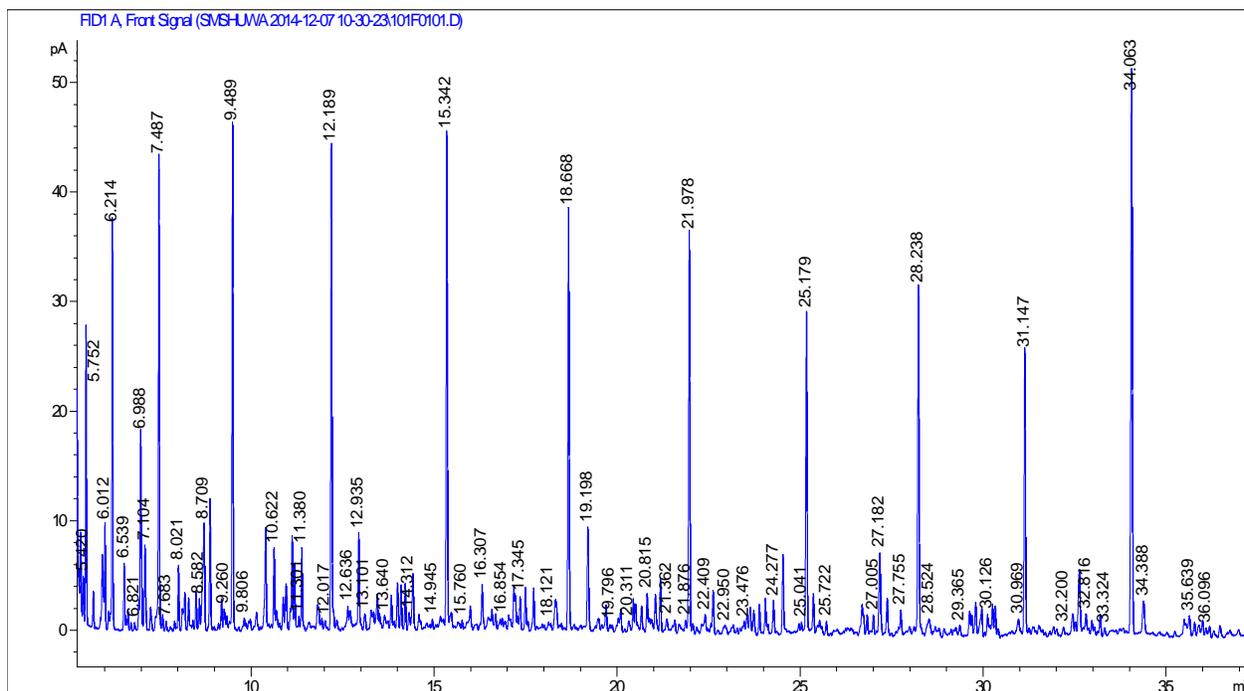**Figure S4: GC chromatogram of oil fresh Amal West heavy crude oil sample**

Figure S5: GC chromatogram of oil recovered from run R10 conducted at 340°C, 28h and 2500ppm catalyst amounts
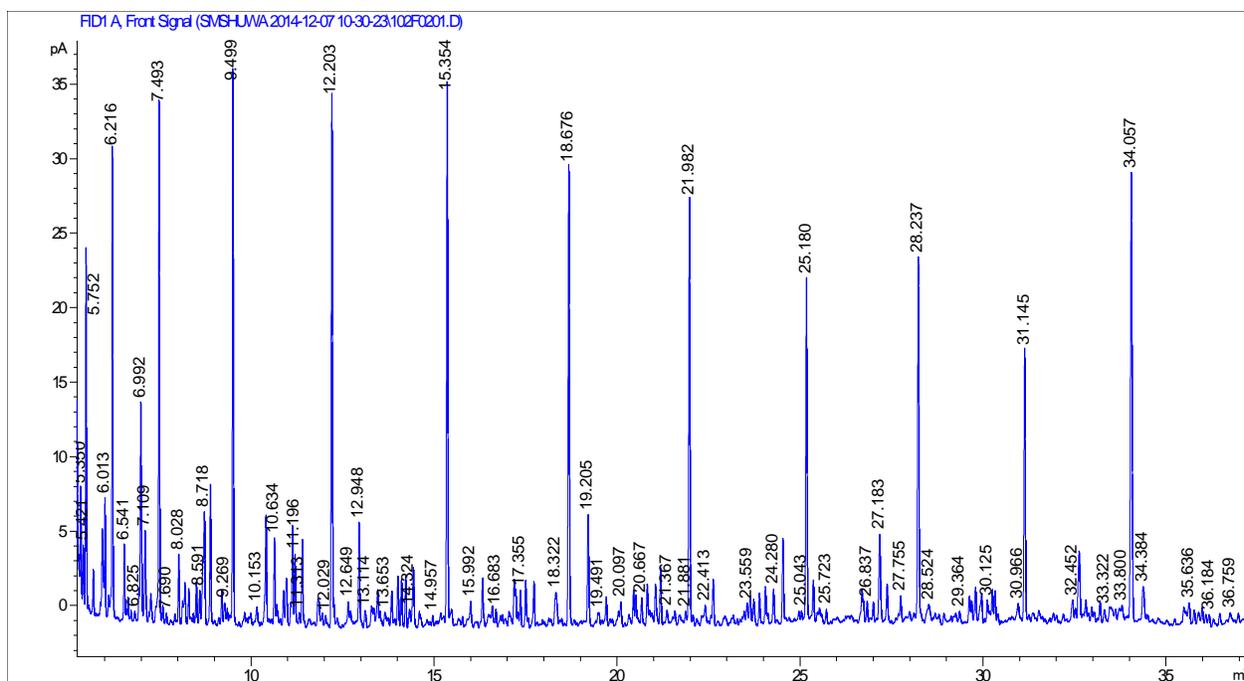
Figure S6: GC chromatogram of oil recovered from run R11 conducted at 340oC, 28h and 500ppm catalyst amounts
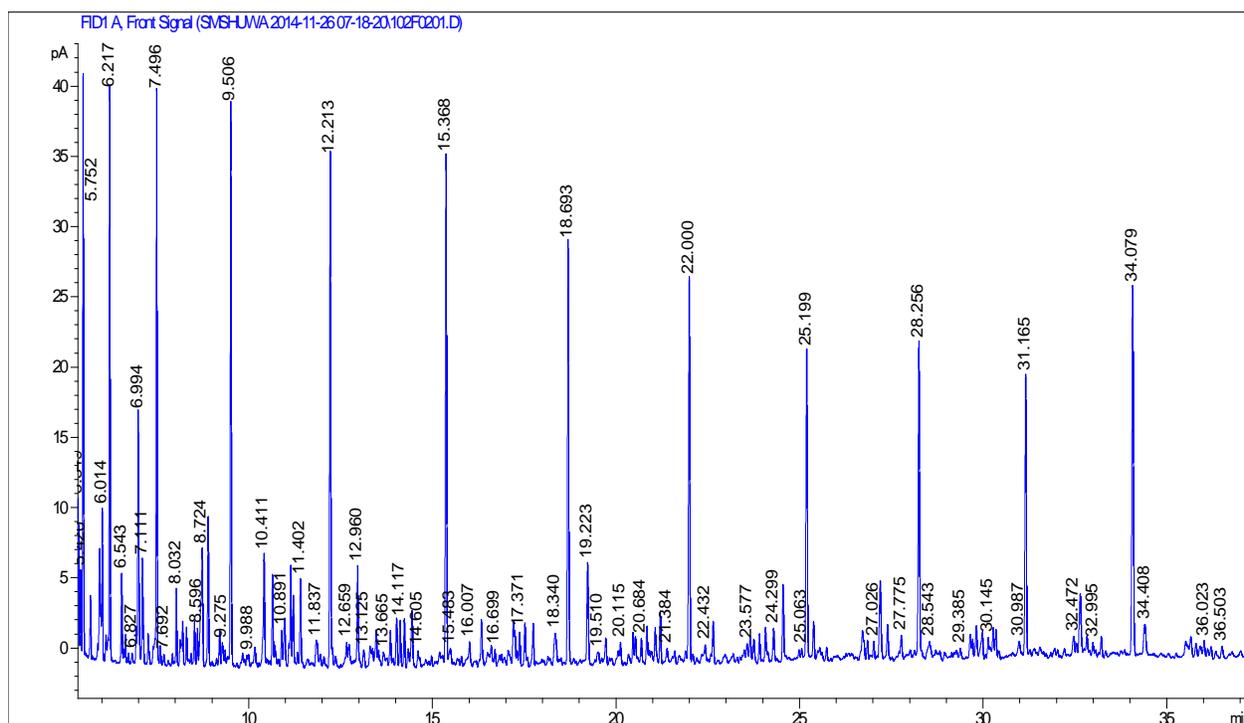

Figure S7: GC chromatogram of oil recovered from run R12 conducted at 300oC, 28h and 2500ppm catalyst amounts
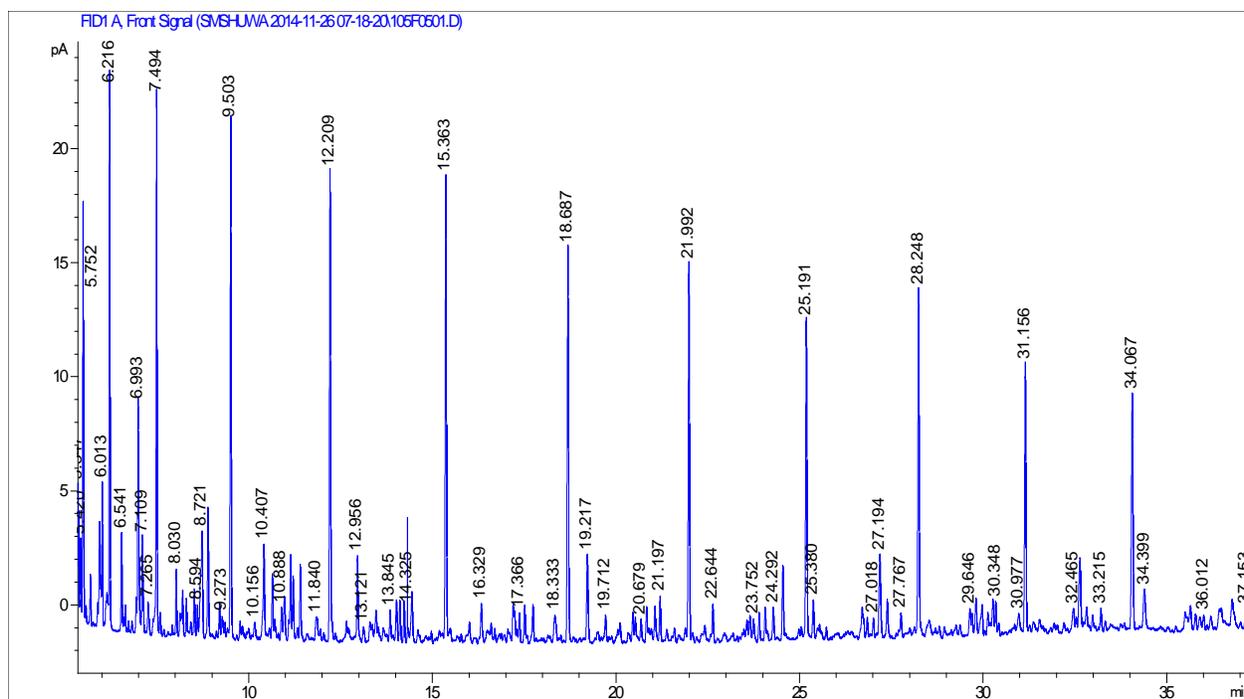
Figure S8: GC chromatogram of oil recovered from run R16 conducted at 260oC, 8h and 1500ppm catalyst amounts