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Viscosity reduction of extra-heavy crude oil using nanocatalysts

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Abstract−Exploiting extra-heavy crude oil and converting it to operational products is considered a challenging process in the industry due to the difficulty in processing this kind of crude oil. So, in the present study, viscosity reduction of extra-heavy crude oil is inquired using nanocatalysts. This is the first study that investigates and juxtaposes the results of viscosity reduction of extra-heavy crude oil based on direct heating and microwave radiation as the indirect heating source at the presence of ZSM-5 catalyst as well as silica, clay, and synthesized nickel oxide nanocatalysts in order to facilitate the process of extra-heavy crude oil upgrading. The results illustrate that nanocatalysts have a fundamental impact on the viscosity reduction of extra-heavy crude oil. According to the findings, nanosilica represents the best efficiency among others as it makes a 98.3% reduction in the extra-heavy crude oil viscosity. Besides, the application of microwave radiation in the upgrading of extra-heavy crude oil leads to an incredible reaction duration reduction as approximately 60% of sample oil viscosity is reduced in just 90 seconds. Analysis of upgraded oil reveals that adding excess nanocatalyst to the extra-heavy crude oil actuates an efficiency reduction due to the agglomeration of nanoparticles. Finally, the findings offer appealing information for the enhancement of upgrading processes in the industry.

Keywords: Extra-heavy Crude Oil, Viscosity Reduction, Nanocatalyst, Nickel Oxide, Microwave Radiation

INTRODUCTION

Global crude oil consumption has increased in recent years, and from 2004 to 2010 more than 3% change was observed in the annual average consumption [1]. Reports have declared that about 70% of extractable deposits of crude oil over the world oil reservoirs are associated with heavy and extra-heavy crude oil as well as bitumen [2], while within the next two decades 80% of the global energy consumptions will be supplied through oil production [3]. The application of heavy and extra-heavy crude oil in the industry has some difficulties, especially in extraction and transportation due to their high viscosity as well as high sulfur, nitrogen, and heavy metals content. Therefore, there must be efficient processes to reduce heavy and extra-heavy crude oil viscosity and molecular weight.

A simple and suitable method for investigating the results of cracking reactions and heavy crude oil upgrading is viscosity measurement [4]. The main process in reducing heavy and extra-heavy crude oil viscosity is cracking heavy compounds to produce light ones. For this, several methods could be adopted in very high temperatures, like visbreaking, thermal cracking, aquathermolysis, cocking, and catalytic cracking. Following investigations on the catalytic aquathermolysis methods, Chuan et al. [5] reduced crude oil viscosity by 95.5% using aromatic sulfonic copper at 200 °C for 24 hours. Hydrocarbon cracking in the presence of catalysts enables producing light hydrocarbons with lower temperature and higher selectivity. Catalysts with high stability and mechanical strength could decrease operational costs and raise process efficiency [6]. Clark et al. [7] investigated the effect of catalysts on the enhancement of distillation residue quality in the presence of water at 375-415 °C and reported that the reaction rate could be raised in the presence of metals substantially. Ovalles et al. [8] upgraded Hamaka extra-heavy crude oil using iron catalyst. They reported a 99.8% viscosity reduction for compounds that require temperature higher than 500 K. Selectivity and activity of the catalyst is strongly related to size, shape, and structure. Jia et al. [9,10] applied special types of clay to inspect their catalytic impact on the viscosity of heavy crude oil. Smectite, a kind of clay, plays a positive role in catalyzing effects for oil oxidation. Also, illite, chlorite, and kaolinite are the catalysts by which the activation energy of crude oil oxidation could be decreased. Jia et al. [11] used these catalysts for the upgrading of heavy crude oil through the oxidation method. They maintained that temperature, oil composition, and internal molecular structures are the substantial factors influencing oil flowability.

Among types of catalysts, recently, nanocatalysts have gained the most attention due to the high surface area to unit volume and mass, controllable size and shape, higher efficiency and selectivity in comparison to bulky catalysts [12]. Compared to micron size, nanocatalysts demonstrated higher activity and considerable strength [13]. In recent years, the application of nanosized catalysts for the upgrading of heavy and extra-heavy crude oil has been enhanced and they need to be scrutinized more.

Wei et al. [14] applied 6.3 nanometric nickel nanocatalysts, synthesized through the microemulsion method, in an aquathermolysis process at 553 K. Results showed that sulfur content was reduced to 0.23% and the amount of resins and asphaltene was decreased by 15.83% and 15.33%, respectively. Detailed investigation on the catalytic aquathermolysis divulged that changes in oxygen compounds could offer a remarkable viscosity reduction [15]. Abu Tarboush and Husein [16] studied the adsorption of asphaltene from heavy crude oil by adopting in-situ prepared NiO nanocatalysts.

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Eventually, 2.8 grams asphaltene reduction per mass unit of NiO nanocatalyst was reported. In addition, the reduction of heavy crude oil viscosity by nanocatalysts during a thermal cracking method could be achieved on the basis of catalyst type and nanoparticle size. In another study, Liu et al. [17] decreased the viscosity of heavy crude oil from 184 to 42 Pa·s (a 77.17% reduction) by use of silica-supported nanoFe/Ni alloy in anaquathermolysis process at temperature 150 °C. They determined that using SiO_2/Fe/Ni catalyst for reducing the viscosity of heavy crude oil in the aquathermolysis process represents a better efficiency than unsupported Fe/Ni nanoparticles. Li et al. [18] investigated the efficiency of the process of heavy crude oil viscosity reduction using carbon nanocatalysts boosting with microwave radiation and observed a 96% viscosity reduction. Their finding indicated that nanocatalyst particle size could affect the process efficiency.

Some molecules, like solvents, are capable of absorbing microwave energy and transforming it to kinematic energy. These molecules can rotate due to electromagnetic radiation, leading to generating heat as a result of molecules collision [20]. Greff et al. [21] investigated the effects of microwave radiation, using a standard 2.45 GHz emitter, on heavy crude oil viscosity reduction. Different nanocatalysts (Fe, Fe (III) Oxide, and Cu) were utilized in concentration ranging from 0.1% to 1% weight and a significant reduction in heavy crude oil viscosity was reported. In another research, silicon carbide was applied as the ray absorbent and nickel as well as molybdenum nanopowders were applied as the nanocatalysts. The process was heated by a 2,450 MHz emitter. Results showed that adding molybdenum nanocatalysts increased reaction efficiency and °API to 72% and 21, respectively [22]. Also, da Silva et al. [23] investigated distillation gasoil residue catalytic cracking through Y-zeolite and microwaves at 1,500 W power and 2,450 MHz frequency and reported a 57% reduction in sulfuric compounds. Besides, in-situ heavy crude oil recovery using Ni, Fe, and Fe_2O_3 nanocatalysts under electromagnetic heating pointed out that the best performance was for Ni nanocatalysts at the power of 800 W. Also, findings disclosed that the efficiency of Ni was higher than Fe [24]. In another study, Bera and Babadagli [25] recovered heavy oil by adopting electromagnetic heating (frequency of 2.45 GHz and 2 kW) and reported a reduction in the mass fraction of heavy crude oil. They also intensified the process efficiency by adding metal nanoparticles like Ni and Fe. Reports suggested that Ni nanoparticles were more beneficial in upgrading heavy crude oil.

Despite numerous advantages that former studies offered to tackle the challenges in upgrading extra-heavy crude oil, there are still some obstacles. Studies reveal that some issues refer to the presence of some troublesome compounds, such as water vapor, hydrogen, and methane. On top of that, some challenges directly involve operational costs. High temperature and long reaction duration are the most indispensable factors that are less highlighted. In addition, there is a pressing need for unprecedented catalyst types with satisfactory price and availability. Accordingly, the main objective of this study was to investigate the viscosity reduction of extra-heavy crude oil using nanocatalysts in the absence of hydrogen and water vapor. The effect of temperature enhancement using microwave radiation was also studied. To the best of our knowledge, based on detailed literature reviews, this is the first study that analyzes and compares results of viscosity reduction based on direct heating and microwave radiation as the indirect heating source in the presence of nanocatalyst. In this study, nickel oxide nanoparticles synthesized through the precipitation method, clay nanoparticles due to their low cost and plentifulness, and silicon dioxide due to its suitable sustainability were applied as the nanocatalysts, and ZSM-5 was also used as a catalyst for the witness test owing to its high application in upgrading processes. Then, the system was heated through an external source to investigate the reduction of extra-heavy crude oil viscosity. Microwave radiation was used as the indirect heating in hope of mitigating difficulties, such as operating temperature and pressure as well as reaction elapsed time.

MATERIALS AND METHODS

1. Catalysts

In this study, three types of nanoparticles including silica, nickel oxide, and clay were adopted. Silica nanocatalyst was received from US Nano, nickel oxide nanocatalyst was synthesized through the precipitation method, and clay nanoparticles were purchased from Sigma-Aldrich. ZSM-5 was applied for the witness experiments due to its high application in refinery and petrochemical processes; it was received from Zeolyst. Table 1 represents the properties of applied catalysts.

NiO nanocatalyst was synthesized by the reaction of 5.8 grams nickel (II) nitrate hexahydrate with adding ammonium hydroxide rendering pH to 10. Then, it was heated continuously for about 20 hours at 373 K and precipitated using centrifugal force. Further, the precipitated compound was calcined at 573 K for about 3 hours. The final nickel oxide was investigated using XRD and SEM.

2. Extra-heavy Crude Oil

In this study, extra-heavy crude oil with 14.3 °API and 724 g/mol molecular weight was used. The crude oil viscosity at 25 °C was 35,000 cP and relative density at 25 °C and initial boiling point were 0.97 and 130 °C, respectively.

3. Experimental Setup

3-1. Direct Heating

All the experiments were performed on a mantel stirrer with a

Table 1. Physical properties of nanocatalysts

Catalyst	Type	Particle size (nm)	Pore size (Å)	Surface area (m^2/g)
ZSM-5	MFI with ratio of Al/Si=50	-	5.4-5.6	425
Silica	Silicon oxide 99%	11-13	-	600-785
Clay	Montmorillonite	1-2	60	500-750
NiO	Synthesized by precipitation method	50-60	-	-

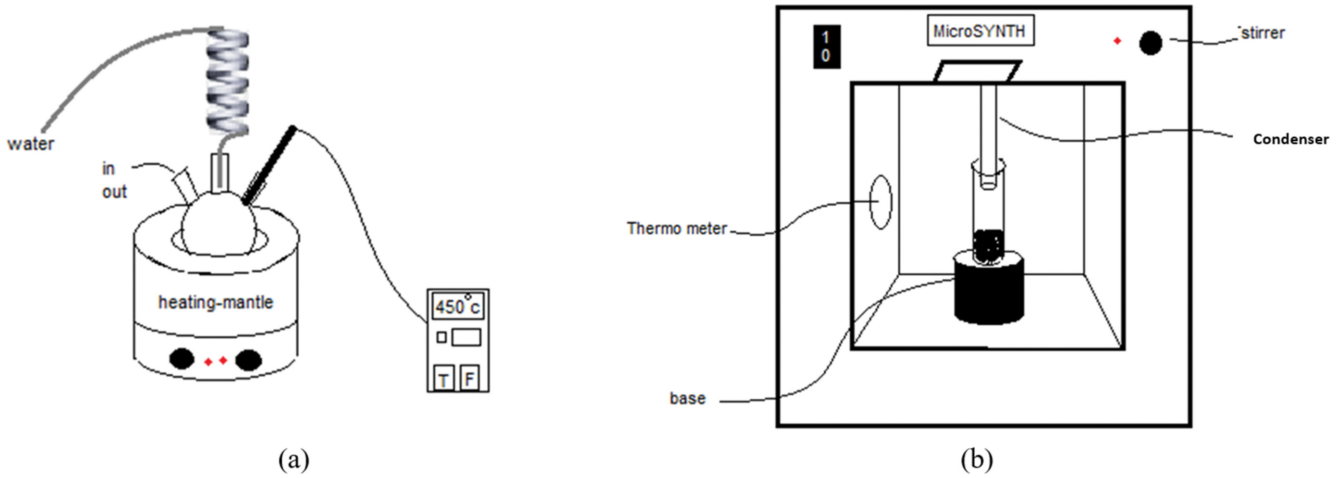


Fig. 1. (a) Schematic of the experimental setup for upgrading extra-heavy crude oil, (b) Schematic representation of the electromagnetic heating system.

pyrexbatch reactor and a volume of 500 milliliters equipped with three gates designed for entering catalysts and thermometer (Fig. 1(a)). To avoid vaporization, a vertical condenser containing cold water (0 °C) was attached to the reactor outlet. In the experiments, the batch reactor was charged with a 20 milliliter sample of extra-heavy crude oil. Due to the high viscosity of the sample oil, the reactor was first heated to 70-80 °C, then by adopting a stirrer and producing turbulence, nanocatalyst powder was poured into the reactor to gain a homogeneous mixture. Thereafter, to avoid explosive reactions, the reaction mixture was heated at a moderate rate (2 °C per minute) to reach 450 °C. The processes last about 3.5 hours. After that, the heating process was stopped and the mixture was cooled to room temperature to measure the mixture viscosity using a Brookfield viscometer. All samples were measured with the same volume and containers and under the same conditions at room temperature. The experiments were repeated at least three times for the basic runs.

3-2. Indirect Heating

Milestone microwave system equipped with a temperature sensor system and a stirrer was used as the indirect heating system (Fig. 1(b)). The microwave system was connected to a computer for setting the desired values and printing the results. Materials show different absorption behavior when they encounter a source of microwave radiation. The absorbent coefficient is considered as a criterion, considering the tendency of materials to absorb microwave radiation [26]. Extra-heavy crude oil is not capable of absorbing microwave radiations due to its low absorbent coefficient. Hence, some materials should be added to the oil sample as a microwave susceptor. In this study, after different concentrations were examined, sodium hydroxide 10%wt was used as the microwave susceptor. Based on the observations, catalysts were started to spark after 90 seconds. Therefore, viscosity reduction of 4 grams of extra-heavy crude oil with and without absorbent after 90 sec was measured in order to appraise the impact of sodium hydroxide 10%wt. The results indicated a 9% viscosity reduction and 47% in final temperature (140 °C) for extra-heavy crude oil by adding sodium hydroxide 10%wt.

RESULTS AND DISCUSSION

1. Synthesized NiO Nanocatalyst

Based on Wu et al.'s (2007) investigation, nickel oxide nanocata-

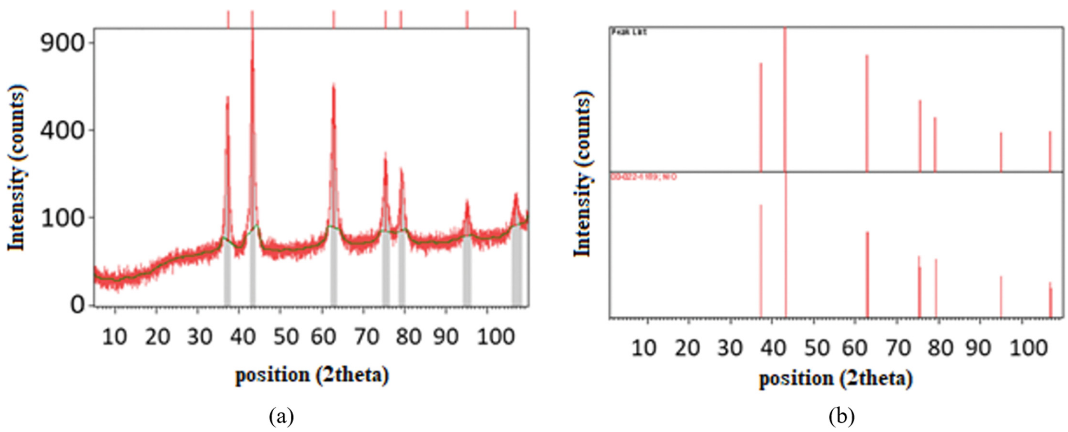


Fig. 2. (a) XRD image of synthesized nickel oxide, (b) comparison of synthesized and reference nickel oxide XRD image.

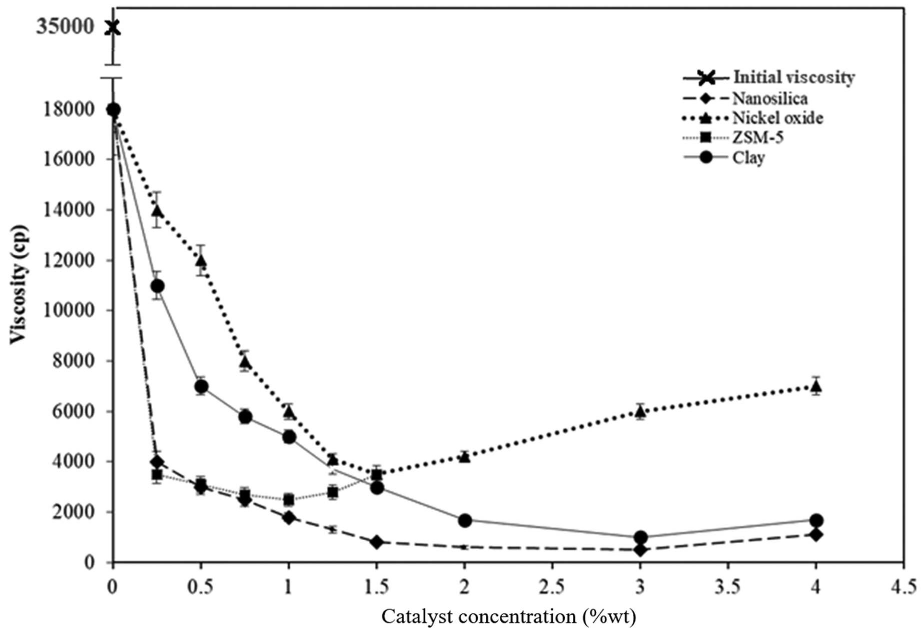


Fig. 3. Viscosity reduction of extra-heavy crude oil using different catalysts through direct heating at 450 °C.

lyst was synthesized using a precipitation method. Fig. 2 represents the XRD analysis of the synthesized nickel oxide nanocatalyst. Nanocatalyst crystalline mean size calculated using the Scherrer equation was 19.5 nanometers. Findings reveal that there is a good agreement between synthesized nickel oxide and natural nickel oxide. In addition, to investigate the morphology and mean size of the nanocatalyst, scanning electron microscopy (SEM) analysis was performed. Regarding the SEM image of the synthesized nickel oxide nanocatalyst, polygonal flat particles with a tablet-like surface were generated after the precipitation process. Particle size was about 50-60 nanometers [27].

2. Effect of Direct Heating

To consider the impact of direct heating on the viscosity of extra-heavy crude oil, the sample oil was heated to 450 °C with no nanocatalysts. The result showed an almost 48% decrease in the sample oil viscosity. Eventually, the sample oil viscosity decreased to 18,000 cP.

3. Oil Viscosity Reduction Using Nanocatalysts

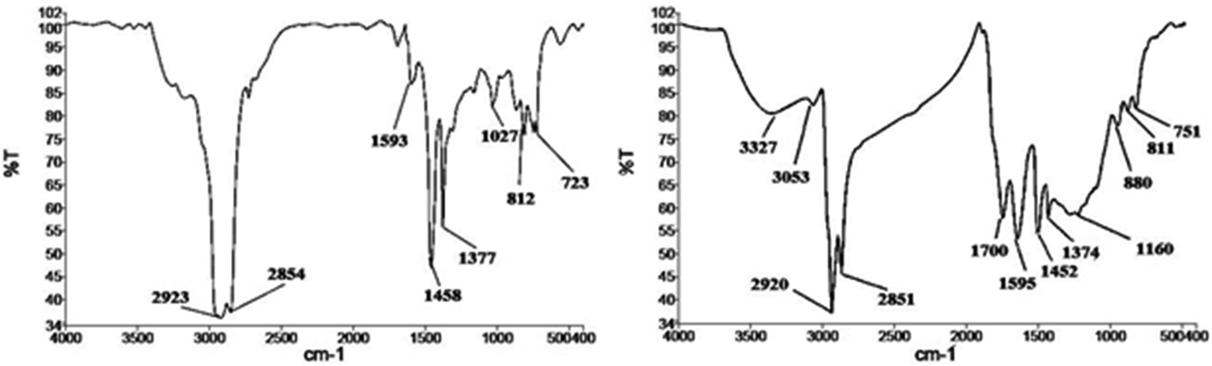
Before the main investigations using purchased nanocatalysts, the catalysts were kept at 200 °C for 30 minutes to be entirely dried [28]. Fig. 3 represents the effect of catalysts on the viscosity reduction of extra-heavy crude oil at 450 °C. Based on the findings, all catalysts represent similar behavior; augmenting catalyst concentration makes a remarkable alteration in the oil sample viscosity, leading to a point that represents the maximum performance. At this optimum concentration point, the catalyst has the highest efficiency, and adding more catalyst represents an undesirable effect, viscosity increment. In another investigation using nanosilica, Maghzi et al. [29] observed that there was an optimum concentration for nanosilica, and the best efficiency was gained at 3%wt catalyst concentration.

Regarding Fig. 3, at lower concentration, increasing ZSM-5 concentration leads to the reduction of crude oil viscosity, whereas ZSM-5 concentration 1%wt, oil viscosity is reduced to 2,500 cP, a 91.6% decrease. Besides, according to the figure, increasing ZSM-5 concentration more than 1%wt increases the final crude oil viscosity, indicating ZSM-5 concentration 1%wt is the optimal concentration for viscosity reduction of extra-heavy crude oil. Moreover, nanosilica has better influence than ZSM-5 on the viscosity reduction of extra-heavy crude oil. For nanosilica, the optimum catalyst concentration is 3%wt. At this concentration, the viscosity of crude oil reaches 500 cP, which represents a 98.3% reduction in contrast to initial oil viscosity. It is observed that at catalyst concentration 4%wt, oil viscosity increases.

Table 2. Nanoclay components

Component	Percent
Silica	51
Al_2O_3	19.7
LOI	15.5
Fe_2O_3	5.7
MgO	3.5
CaO	2
Na_2O	1
K_2O	0.8
Ti_2O	0.6

Nanoclay behaves as nanosilica extremely due to the clay structure. Table 2 shows the component fraction of nanoclay. Regarding the table, more than 70% of nanoclay content is constructed of silica and alumina. Therefore, it is expected that nanoclay could have an effective impact on the viscosity reduction of extra-heavy crude oil because zeolite (as a combination of silica and alumina) has demonstrated to have a significant role in viscosity reduction processes, and also silica was reported to be effective in viscosity reduction studies. Corresponding to Fig. 3, adding nanoclay to the crude



(a) (b)

Fig. 4. FTIR images obtained from upgraded oil samples, (a) in the presence and (b) absence of nickel oxide nanocatalyst.

Table 3. The components of upgraded oil according to the peaks and wavelengths produced by analysis of FTIR

Wavelength	Bond	Functional groups
3,327	-C≡C-H, C-H	Alkyne
3,053	=C-H, C-H	Aromatic, Alkene
2,921	C-H	Alkane
2,851	C-H	Alkane
1,700	C=O	Carbonyl
1,595	C-C	Aromatic, Alkene
1,452	C-C, C-H	Aromatic, Alkane
1,375	C-H	Alkane
1,163	($-CH_2X$) C-H, C-O	Alcohol, Carboxylic acid, Alkyl halide
881	=C-H, C-H	Aromatic, Alkane
812	=C-H, C-H	Aromatic, Alkane
751	=C-H, C-H	Aromatic, Alkane

oil reduces the final crude oil viscosity about 96.6% to 1,000 cP. Nanoclay truly participates in cracking reactions and reduces oil viscosity due to its high silica content.

According to Fig. 3, the optimum catalyst concentration for the viscosity reduction of extra-heavy crude oil using nickel oxide nanocatalyst is 1.5%wt. At this point, a 90% reduction in sample crude oil viscosity is observed and oil viscosity reaches 3,000 cP. Nickel oxide nanocatalyst has a slighter effect on crude oil viscosity as it has a different structure compared to the other nanocatalysts.

FTIR is used to determine the formation of the organized bonds between particle surface and mixture. Fig. 4 depicts the FTIR analysis of upgraded extra heavy oil using direct heating at 450 °C in the presence and absence of nickel oxide nanocatalyst. In this figure, peaks represent different components.

Table 3 illustrates the components of upgraded oil according to the peaks and wavelengths from analysis of FTIR. According to the analysis, determining sulfuric components is not available. However, the presence of different hydrocarbon components confirms that sulfuric components in extra-heavy crude oil are cracked, as there is no special peak for sulfuric components in the FTIR image.

The EDAX mapping and composition analysis of oil residues after the viscosity reduction experiments using nickel oxide and silica nanoparticles at 450 °C are shown in Fig. 5. Based on the EDAX analysis, as the percentage of silica or nickel decreased, the length of the peak became shorter. The presence of sulfur, which was significantly present in all samples, indicated that the bonds of this element were broken. This resulted in molecular weight loss and reduced viscosity. The significant amount of carbon indicated the deposition of some broken hydrocarbons and also the formation of coke above 400 °C.

4. Comparison of Nanosilica and Nickel Oxide Nanocatalyst

To have better investigations, nanocatalysts were verified and purified for SEM analysis obtained from upgraded oil. Nanosilica was adopted as a nanocatalyst with the most effect on the crude oil viscosity reduction and separated using the precipitation method. Also, for a clear comparison, synthesized nickel oxide was separated using the centrifuge method. Fig. 6(a) shows SEM images for nickel oxide nanocatalyst from upgraded oil with 0.3, 1.5, and 3% catalyst concentration (catalyst accumulation is specified by red circles). From the figure, in all three concentrations, surfaces are flat with gross hollows. It was mentioned that increasing nanocatalyst concentration sometimes intensifies particle agglomeration, leading to the reduction of nanocatalyst activity. In Fig. 6(a)(I) and (II), a uniform dispersion is approximately observed, while in Fig. 6(a)(III) with 3%wt catalyst concentration, some irregular agglomeration was formed. Thus, these particle assemblages reduce nano-

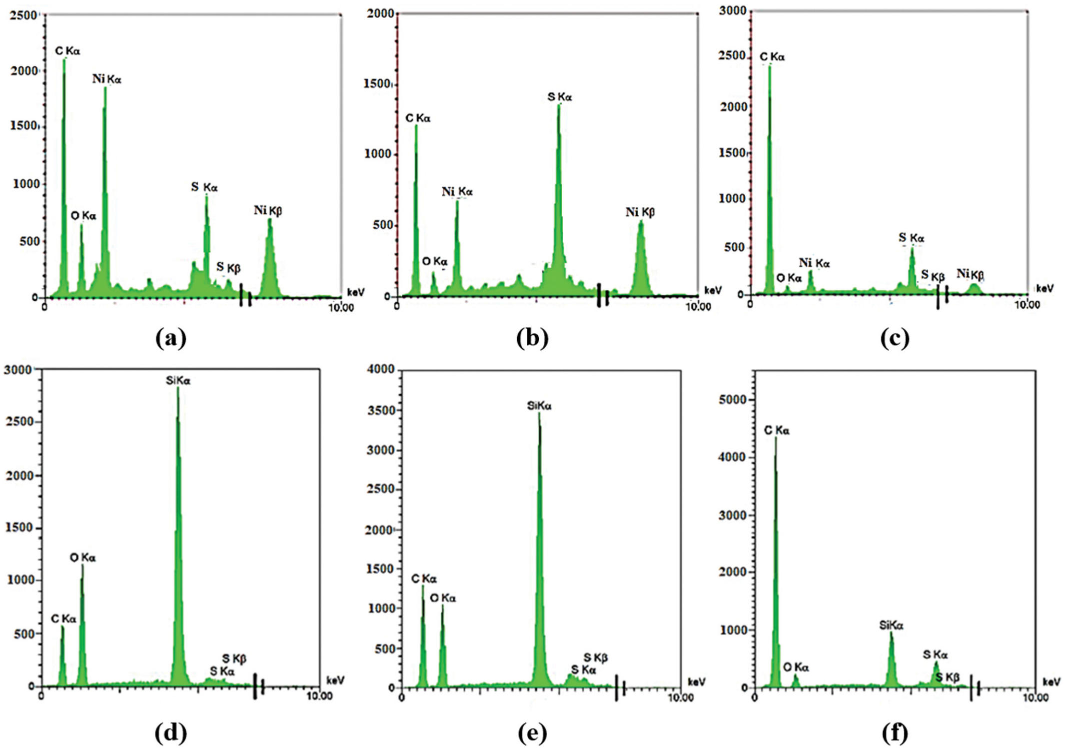


Fig. 5. EDAX and composition analysis of oil residues after the viscosity reduction experiments using nickel oxide nanoparticles at concentration of (a) 3%wt, (b) 1.5%wt, and (c) 0.3%wt, and silica nanoparticles at concentration of (d) 5%wt, (e) 3%wt, and (f) 1%wt.

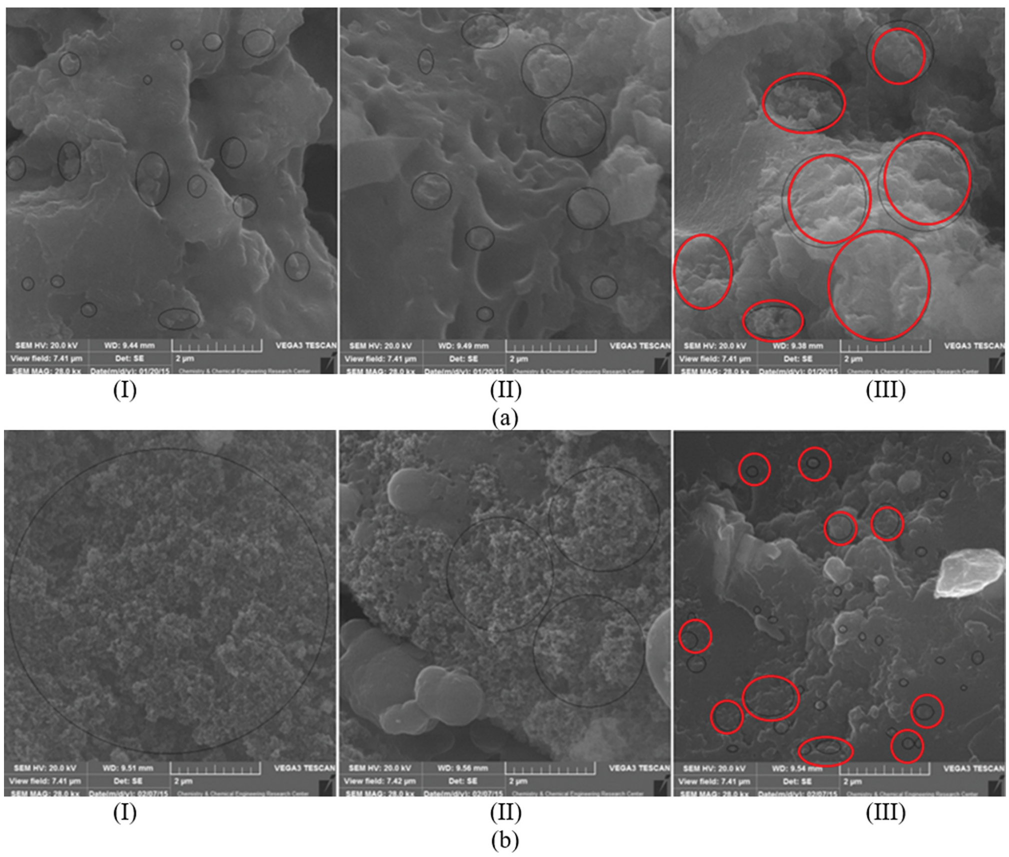


Fig. 6. (a) SEM image of precipitated nickel oxide at (I) 0.3%wt, (II) 1.5%wt and (III) 3%wt, (b) SEM image of precipitated nanosilica at (I) 0.3%wt, (II) 1.5%wt and (III) 3%wt.

Table 4. Results of viscosity reduction for different crude oil samples using microwave radiation

Sample	Crude oil amount (g)	Catalyst concentration (%wt)	Final temperature (°C)	Viscosity reduction (%)
Crude oil	4	-	95	None
Crude oil with NaOH (10%wt)	4	-	140	10
Crude oil with ZSM-5	4	1	145	45
Crude oil with NiO nanocatalyst	4	1.5	151	55
Crude oil with nanoclay	4	3	146	60
Crude oil with nanosilica	4	3	147	50

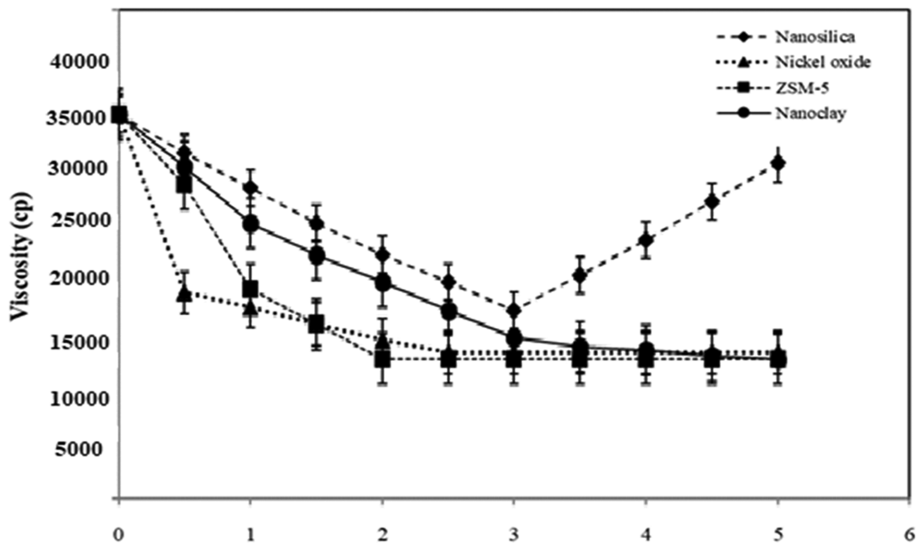


Fig. 7. Viscosity reduction of different extra-heavy crude oil samples using microwave radiation.

catalyst activity. Consequently, adding nickel oxide nanocatalyst with a concentration of more than 1.5%wt diminishes the particle impact on viscosity reduction of crude oil due to particle agglomeration and reaction activity reduction.

Fig. 6(b) shows a scanning electron microscope image for nanosilica of upgraded oil with 0.3, 1.5, and 3%wt catalyst concentration (catalyst accumulation is specified by red circles). As in the previous case, in Fig. 6(b)(III) the agglomeration of particles decreases the activity of nanocatalysts compared to the other concentrations.

All in all, at catalyst concentrations less than 0.5%wt, ZSM-5 and nanosilica have the best efficiency. While increasing nanocatalyst concentration, the efficiency of ZSM-5 drops. At catalyst concentration around 1%wt, ZSM-5, nickel oxide, and nanoclay have the best efficiencies and nanosilica still has the best efficiency. At concentration around 1.5%wt, the effect of agglomeration is overcome, and the activity of nanocatalysts declines due to the diminution of catalyst surface area, especially for ZSM-5 and nickel oxide nanocatalyst. Regarding the concerns for severe precipitation of zeolite catalysts and nickel oxide nanocatalysts during the process, despite the fact that this sediment was hardly observed in other cases, it adhered to the vessel wall with some special oil compounds. After shaving, we identified that most of the compounds were oily components, and only a very small portion of deposited particles could be catalysts. Notably, to prevent and reduce it, a stirrer was used for this process.

5. Viscosity Reduction Using Microwave Radiation

Table 4 represents the results of viscosity reduction for different crude oil samples. It is mentioned that catalyst concentrations were set at their optimum conditions.

Fig. 7 depicts viscosity changes of extra-heavy crude oil by applying different catalysts using microwave radiation. Applying microwave radiation, A maximum reduction of 63, 63, 59, and 50% was achieved for extra-heavy crude oil samples with ZSM-5, nanoclay, nickel oxide, and silica nanocatalysts, respectively. The initial viscosity of extra-heavy crude oil was 35,000 cP. Worth mentioning: adding absorbent did not make a significant change in extra-heavy crude oil viscosity. According to the figure, nickel oxide nanocatalyst and ZSM-5 have the most impact on the viscosity reduction. In microwave radiation nanoparticles act as hot spots leading to a higher viscosity reduction. For the crude oil sample with nanosilica catalyst, increasing nanoparticle concentration to 5%wt increases the crude oil sample viscosity. This is to the lower density of nanosilica, about 0.1 g/cm^3 compared to the other nanocatalysts. In microwave radiation, the power to particle volume ratio is an important parameter affecting the process efficiency. Compared to ZSM-5 and nickel oxide nanoparticles with 2-3 and 6.6 g/cm^3, respectively, the high volume to mass ratio of nanosilica alleviates the process efficiency.

CONCLUSION

Viscosity reduction of extra-heavy crude oil was investigated using silica nanocatalyst, clay nanocatalyst, and synthesized nickel oxide nanocatalyst. Results showed that ZSM-5 and nanosilica represented the best efficiency at lower concentration. However, at higher catalyst concentration, nanoclay and nanosilica had the most influence on the viscosity reduction and the efficiency of ZSM-5 declined. The results of viscosity reduction using nanoclay were predictable due to its similar structure to nanosilica. Findings revealed that applying microwave radiation in the viscosity reduction process could increase the efficiency and decrease process duration, reaching more than 60% viscosity reduction in 90 seconds. Analysis of particles separated from upgraded oil using the precipitation method suggested that at higher concentration the efficiency of nanocatalyst fell due to the agglomeration of particles by which active surface area decreased for cracking reactions. At low particle concentration, fewer particle collisions prevent agglomeration, which is suitable for industrial uses and in turn improves the upgraded efficiency. However, some nanocatalysts may have more stability and eventually less tendency to be agglomerated. The presented results obtained through experiments provide beneficial information for the development of high-performance upgrading processes.

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