Viscosity Reduction of Heavy Oil Using Nanocatalyst in Aquathermolysis Reaction†

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Abstract
Enhanced oil recovery (EOR) in the last several years has become an important factor in oil production due to the shortfall in high quality crude oil. Heavy oil as one of the unconventional hydrocarbons is still vastly abundant in nature and is hence frequently explored with EOR. The viscous characteristic of heavy oil necessitates further in-situ upgrading processes to be executed before extraction. An interesting upgrading method is through aquathermolysis under the addition of catalyst. This review focuses on presenting nanoparticle catalysts, such as nickel-, iron- and cobalt-based nanocatalyst. The explanation covers topics from synthesis methods and characterization up to the effect of reducing the viscosity of heavy oil. Lastly, concluding remarks and future perspectives are highlighted regarding the visibility and available approaches of developing nanofluids for EOR.

Keywords: aquathermolysis, catalyst, enhanced oil recovery, heavy oil, nanoparticles

1. Introduction
Global energy demands increase quite considerably every year due to the ever-increasing population of mankind. Therefore, oil and gas acting as main sources of energy up until now (IEA, 2014), need to be explored even further to meet those demands. Recently, in its annual “Statistical Review of World Energy 2014”, British Petroleum (BP) in 2014 reported that global oil consumption increased above the average, by 1.4 % or equivalent to 1.4 million barrels per day (b/d) (Petroleum B., 2014). However, since the predicted scarcity of high quality crude oil supply is starting to take effect, interest is shifting towards an abundant natural resource that has rarely been developed extensively before, which is unconventional hydrocarbon in the presence of heavy oil. As shown in Fig. 1, heavy oil and bitumen are predicted to account for about 70 % of the total remaining hydrocarbon resources (Alboudwarej H. et al., 2006). Several well-known fields of heavy oil are found scattered among many oil fields in different countries, such as Orinoco, Venezuela (Martinez A.R., 1987), Alberta, Canada (Semple K. and Westlake D., 1987), Liaohe and Shengli, China (Wen S. et al., 2007; Wu C. et al., 2010), Mariner, United Kingdom (Knudsen M.T. and Hill D., 2012), and Duri, Indonesia (Arfie M. et al., 2005).

The main characteristic of heavy oil is its density or specific gravity that is defined to be less than 20° API (Dusseault M., 2001) and its high viscosity due to the high average molecular weight of its structure, as stated by Hyne (Hyne J. et al., 1982). Therefore heavy oil has a poor

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flow rate and hence is very difficult to transport. Heavy oil is also known for its low quality because of high amounts of asphaltenes and resin, whereas the saturated and aromatic hydrocarbon contents are relatively low. Moreover, higher contents of asphaltenes and resin, both of which have a high average molecular weight, will consequently cause difficulties in exploitation and induce high production costs. Another constituent of unconventional hydrocarbon is extra heavy oil, defined to have a gravity below 10° API and a viscosity of more than 100 Pa·s by the World Energy Council in 2010, with a contribution of around 25% to total world oil reserves.

2. Aquathermolysis reaction

Several reaction methods have been developed and adopted in order to enhance heavy oil recovery and reduce its viscosity. A variety of methods exist, ranging from chemical flooding to water flooding and gas drive for non-thermal treatment, while steam injection, hot water flooding and in-situ combustion for thermal treatment are popular and frequently used (Owen J. and Floyd J., 1981). Hyne et al. have proposed another reaction, called aquathermolysis, which is a promising way to reduce the viscosity of heavy oil (Hyne J. et al., 1982). During the aquathermolysis reaction, heavy oil will be added with water or steam at 200–280°C with the reaction time varied from a few hours up to several days.

Laboratory-scale aquathermolysis can be executed in a high-pressure reactor, usually an autoclave, which is capable to withstand pressures up to 3 MPa. Meanwhile in-situ aquathermolysis frequently uses the “Huff and Puff” process, which takes place deep inside the well and consist of three main steps, i.e. injection of steam, well shutdown, and finally production of oil as depicted in Fig. 2 (Maity S.K. et al., 2010). Later, it was discovered that aquathermolysis reaction solely using water hydrolysis did not proceed as well as predicted since the heteroatoms S, N, and O in the heavy oil molecule can interact with each other by means of hydrogen bonding or Van der Waals forces, and polymerize to form larger molecules. Hence, this is not a very effective way to reduce heavy oil viscosity (Chen Y. et al., 2008).

Based on the problems described above, a better solution is needed to address the problems arising in the aquathermolysis reaction. Usage of catalyst, either a mineral, water-soluble, oil-soluble, or nanoparticle catalyst, is proposed to have the necessary effects to overcome the problems. This is due to the fact that a catalyst only acts as an intermediary substance between the reactant and the product in order to lower the activation energy of the reaction and therefore does not alter the general reaction during the process.

Clark et al. studied the addition of aqueous metal to further reduce the viscosity of heavy oil compared to the steam-only aquathermolysis method (Clark P. and Hyne J., 1984). The usage of catalyst in aquathermolysis proved to be a success, since it enables prevention of regression due to polymerization while also promoting pyrolysis to break larger molecules of the heavy oil into smaller ones and various other synergistic reactions like hydrogenation and ring opening as illustrated in Fig. 3. Below is the chemical reaction for aquathermolysis (Hyne J. et al., 1982):

\[
RCH_2CH_2SH_3 + 2H_2O \rightarrow RCH_3 + CO_2 + H_2 + H_2S + CH_4
\]

The cleavage of the C-S bonds results in a reduction of the average molecular weight, bringing along the reduction of viscosity, improvement of flow properties and simplifying the exploitation and transportation of heavy oil. Actually, not only the C-S bonds but also the C-N and C-O bonds are broken in a catalytic aquathermolysis reaction. However, due to the lower bond energy of C-S, the decrease of sulfur content in heavy oil after catalytic aquathermolysis is more significant. Overall, with the help of a catalyst in the aquathermolysis reaction, it is

![Fig. 2](image_url) A simplified flow diagram of “Huff and Puff” process used commercially for recovery of heavy crude oils. Reprinted with permission from Maity, S.K. et al. Copyright © 2010, American Chemical Society.
noticeable that the amount of asphaltenes and resins will decrease and, in contrast, the amount of aromatic hydrocarbon and saturated hydrocarbons will increase (Chao K. et al., 2012). The whole process of aquathermolysis with the introduction of a catalyst is called catalytic aquathermolysis.

The catalytic aquathermolysis process can also cause domino effects like increasing the H/C ratio of the oil due to hydrogenation during aquathermolysis reaction. In fact, Hamedi Shokrlu and Babadagli found that the presence of metal nanocatalyst improved the heat transfer capabilities during the process of steam injection (Hamedi Shokrlu Y. and Babadagli T., 2010). This thermal promotion effect occurs because metals known for high thermal conductivity can improve the thermal conductivity of hydrocarbon or the porous medium inside the reservoir.

The presence of hydrogen donor additives during the aquathermolysis process can have a favorable effect on the general reaction. As stated by Liu and Fan, a hydrogen donor, represented by tetralin in their work, can improve the stability of viscosity reduction of heavy oil (Liu Y. and Fan H., 2002). When the hydrogen donor was added, besides the additional viscosity reduction of the heavy oil, there was also the noticeable benefit of the diminution of viscosity regression after the reaction. The reason this regression occurs under the absence of a hydrogen donor is that active chains produced as a by-product of the aquathermolysis reaction can react with each other to create a high molecular weight chain. On the other hand, under a sufficient amount of active H₂, the active chain will instead react with the active H₂ to produce a low molecular weight chain.

Another source of hydrogen donor can be found in zeolite. Silicate and aluminate, both having the shape of a tetrahedral, are the main building units of zeolite. The main source of hydrogen donor inside zeolite is the presence of Brønsted acid site, usually located in the vicinity of Si-O-Al bonds. With the possibility of seed-assisted or organic structure-directing agent (OSDA)-free synthesis (Kamimura Y. et al., 2011; Purnomo C.W. et al., 2012), valuable synthetic zeolite is now easier to produce. Because of this, synthetic zeolite is often employed as catalyst in the field of oil processing (Degnan T.F. et al., 2000; Van Donk S. et al., 2003) with MFI, FAU, Beta and MOR-type zeolite being the most frequently used due to their larger pore size that is well fitted with the corresponding molecular size (Xu B. et al., 2006).

However, the percentage of viscosity reduction in static/laboratory experiments is usually higher compared with dynamic/in-situ experiments. This difference appears because in-situ conditions are more complicated and complex, such as the gradual drop of steam temperature with the increase of depth from the surface. This condition causes a decreasing amount of energy which is required for the reaction to take place and provides less momentum to make contact with the heavy oil. Another condition that contributes to reduced viscosity reduction in dynamic experiments is the adsorption of catalyst by rock or minerals inside the well. Accordingly, recent developments in the synthesis of catalyst are aimed at overcoming these problems by designing a low-temperature activated catalyst by using ultrasonic or elastic wave stimulation to assist the catalytic aquathermolysis reaction.

Wave stimulated aquathermolysis, started back in 1994, when Beresnev and Johnson noticed that elastic wave stimulation (by an earthquake for example) implies some changes, the most noticeable one being an increase of water level and oil production in the reservoir (Beresnev I.A. and Johnson P.A., 1994). This notion was later validated in a number of related works, such as Guo, et al. and Pride et al., based on high-frequency vibration and numerical simulation theory, respectively (Guo X. et al., 2004; Pride S.R. et al., 2008). Integration of either high-frequency or low-frequency vibration in catalytic aquathermolysis has recently been performed (Xu H. et al., 2012; Xu H.X. and Pu C.S., 2011). They reported that both types of vibration assisted catalytic aquathermolysis, producing synergistic effects on the performance of heavy oil viscosity reduction as well as the composition of saturated, aromatic, resin and asphaltenes (SARA) of the heavy oil. Compared to a catalytic aquathermolysis-only process, low-frequency vibration-assisted catalytic aquathermolysis produces better viscosity reduction, up to 6.6 %, with lower average molecular weight crude oil.
3. Nanocatalysts

Depending on the catalyst-reactant phase, catalysts can be grouped into two different kinds: homogeneous, if the catalyst and reactant are in the same phase (e.g. liquid-liquid), and heterogeneous, if the catalyst and reactant are in a different phase (e.g. solid-liquid). Meanwhile based on their solubility, catalysts can be grouped into mineral, water-soluble, oil-soluble, and dispersed catalyst. In this review, we will limit the discussion to catalyst based on dispersed nanoparticles in the form of powder.

One of the advantages of nanoparticle catalysts is their relatively high surface area, which makes them ideal for catalytic aquathermolysis, so as to increase the light fraction of crude oil and hence improve the overall quality of the heavy oil. In addition, nanocatalysts have the advantage of easier separation process in the catalytic aquathermolysis process and, after proper thermal treatment, they are available to be re-used in the process with adequate performance (Junaid A.S.M. et al., 2014).

3.1 Nickel-based nanocatalysts

Nickel (Ni) is a chemical element with atomic number 28, which belongs to the first row transition metals. Because of this, nickel has a partially filled 3d orbital electron band and is very reactive to chemical reactions, in particular when in the powder form, having a larger surface area. On the other hand, in an ambient air environment, nickel will slowly react with oxygen to form nickel oxide compound. Nickel is quite abundant on earth, but it is rarely found in pristine condition. It has been proposed that nickel-iron is one of the components that form the earth’s core.

Lenggoro et al. reported their effort to synthesize nickel oxide via spray pyrolysis using several precursors, such as nickel chloride, nitrate and formate (Lenggoro I.W. et al., 2003). The resulting particles have a broad range of sizes, with only the nickel nitrate precursor resulting in the nanoparticle range, whereas the chloride and formate precursor result in submicron particles. In another attempt, Ai et al. studied the synthesis of nickel oxide nanoparticles via a wet chemical method using ethylene glycol (EG) as solvent (Ai D. et al., 2004). Apart from being the solvent, the role of ethylene glycol can be extended to agglomeration-preventing agent, forming a protective layer around the nickel particle, thus creating a well-dispersed nanoparticle.

Meneses et al. further developed nickel oxide nanoparticles using gelatin instead of EG as the organic precursor (Meneses C.T. et al., 2007). Although very small particles sizes (3.2 nm) were successfully obtained, the polydispersed characteristic of the nanoparticles still persisted as a major problem until Li, et al. (2007) found a better way to synthesize nano-nickel using the micro emulsion method. In the attempted method, oil phase (e.g. cyclohexane, methyl cyclohexane) was used to prepare nano-nickel catalyst that could act as hydrogen donor to further improve the heavy oil characteristics via some mechanisms already explained in the section about the aquathermolysis reaction. The nano-nickel particles obtained had a spherical shape and an average diameter of 6.3 nm. Li et al, further applied nano-nickel as catalyst in an aquathermolysis reaction of Liaohe extra heavy oil at 280 °C (Li W. et al., 2007). As predicted, the best viscosity reduction of heavy oil as measured at 50 °C, was achieved under the presence of nano-nickel catalyst, with up to 98 % viscosity reduction. Aside from the viscosity reduction, an increase in H/C ratio and reduced amount of asphaltenes, resin, and sulfur content was also noticed in the catalytic aquathermolysis-reacted heavy oil. The nano-nickel via microemulsion experiment was again attempted by Wu et al., this time under much lower reaction temperature of 200 °C, yet high catalytic performance with more than 90 % viscosity reduction was obtained (Wu C. et al., 2013).

It has been reported that there is the possibility of a metal catalytic reaction of heavy oil without the addition of water or steam or non-aquathermolysis reaction. However, the reduction of viscosity would be more significant after water or steams is added into a system (Hamedi Shokrul Y. and Babadagli T., 2010). The development of nano-nickel-based catalyst for use in aquathermolysis was further reported by Wu et al., who utilized San56-13-19 extra heavy oil as the subject of an aquathermolysis reaction at 200 °C (Wu C. et al., 2013). The nano-nickel catalyst was successfully prepared by the microemulsion methods according to (Wu Z. et al., 2008). Transmission electron microscopy (TEM) characterization indicated that the size of the nano-nickel catalyst was around 4.2 nm. Viscosity reduction was around 90.36 % as measured by Bruker Avance-500 NMR spectrometer, and group composition after reaction also changed, with a decrease in asphaltene and resin of 5.28 % and 6.48 %, whereas saturated and aromatic hydrocarbons increased by 6.73 % and 5.03 %.

Based on these findings, Noorlaily et al. have tried to synthesize nickel oxide nanoparticles employing microwave-assisted co-precipitation methods (Noorlaily P. et al., 2013). Using NiCl2·6H2O as nickel source, with NH4HCO3 and ethylene glycol as reductant and solvent respectively, spherical morphology, uniform size distribution around 65 nm, and a large surface area particle of 158.4 m²/gram were obtainable. Fig. 4 shows the x-ray diffraction patterns of the nickel oxide nanoparticles produced. Applying Scherrer’s equation to the strongest peak, the crystal sizes of NiO were predicted to be 4.77 nm, 9.08 nm and 15.26 nm, respectively, at for
3.2 Iron-based nanocatalysts

Iron (Fe) is one of the metal elements that compose the earth’s crust, therefore it is the fourth most abundant element in terms of weight, at around 5 wt%. Iron has an atomic number of 26 with electron configuration [Ar] 3d6 4s2. In general, there are two forms of iron based-nanocatalyst, which are often encountered as specified by the oxidation states of the iron: hematite and magnetite (α-Fe2O3) and magnetite (Fe3O4). Iron in general is classified as magnetic materials, with the relationship of magnetic properties of materials to their catalytic activity has been long investigated in the field of magneto-chemistry. As early as 1946, Selwood P.W. described the close relationship of magnetic properties to adsorption phenomena, whereas adsorption of several strongly paramagnetic compound is found to be more prominent due to the strong tendency in forming electron pairing arising from the unpaired electrons spin (Selwood P., 1946). Therefore, magnetic materials in general, indicated by magnetic moment, are good adsorbent and suitable to be used as catalyst, just like the one applied by Khamarui, et al. (Khamarui S. et al., 2015). Another advantage of having magnetic nano metal-oxides particles is their synergetic to be implemented in the electromagnetic-solvent heating. In an extensive review paper written by Bera and Babadagli, magnetic nanoparticles in the radio frequency electromagnetic heating will increase and improve the overall reaction rates since they will fluctuate and create more contact with the reactant molecules (Bera A. and Babadagli T., 2015). Because usually the optimum amount of additional Fe as catalyst range only around 0.1–1 wt% (Greff J.H. and Babadagli T., 2012), the amount of Fe ions could well be insignificant compared with the amount of other minerals inside the reservoir. Consequently, there is only slight chance of corrosion caused by the addition of Fe-based catalyst, although it does not completely rule out the possibility that there would arise some minor contributing factor.

3.2.1 Hematite (α-Fe2O3) and maghemite (γ-Fe2O3)

Fe2O3 is a polymorph material with two naturally occurring and hence commonly found substances of iron. The two naturally occurring forms are the α phase and the γ phase, with the difference between those two arising from the most fundamental crystal structure. While α-Fe2O3 (hematite) has a rhombohedral crystal structure like corundum (α-Al2O3), γ-Fe2O3 (magentite) has a cubic crystal structure. The magnetic characteristics of hematite and maghemite also show some distinction. Hematite is found to be weakly ferromagnetic in between 260 K and 950 K, while maghemite shows ferromagnetic properties, making it often being used for recording tape component. The characteristics described above are restricted to bulk form; there is a discrepancy between nanoparticle and bulk form, especially regarding magnetic properties. Magnetic nanoparticles usually show superparamagnetic phenomena due to the finite-size limit that is distinctive for every material. However, there is similarity between hematite and maghemite, with both consisting of Fe2+ divalent iron compound, usually known as ferrous ion. In contrast, Fe3O4 (magnetite) consists of both ferrous and ferric ion.

As a matter of fact, all three iron oxides—hematite, maghemite, and magnetite—are connected and therefore can be produced by transformation into each other. Fe2O3 can be produced by α-Fe2O3 reduction, while when appropriately annealed and re-oxidized, Fe2O4 will result in the formation of γ-Fe2O3 (Aharoni A. et al., 1962). Finally, to complete the cycle of transformation, γ-Fe2O3 can be heated to the required temperature to create hematite. Shimomura et al. have suggested that γ-Fe2O3 could also be formed directly as an intermediate phase during the reduction of α-Fe2O3 (Shimomura Y. et al., 1954). This was proven afterwards by Randrianantoandro et al., as they succeeded to create γ-Fe2O3 directly from α-Fe2O3 employing high-energy ball milling with the aid of ethanol (Randrianantoandro N. et al., 2001). In another attempt to produce γ-Fe2O3 nanoparticles, some researchers are using a microemulsion method that utilizes a surfactant to stabilize the mixture as well as a precipitating agent (e.g. NH3, NaOH) (Sahoo S. et al., 2010; Tueros M.J.)
Hematite, meanwhile, reportedly can be synthesized using various methods, such as co-precipitation (Zhang H. et al., 2008), hydrothermal (Giri S. et al., 2005), sol-gel (Woo K. et al., 2003) and forced hydrolysis (Musić S. et al., 1997). In his work, Music used precursors such as FeCl₃·6H₂O and 10% solution of tetramethylammonium hydroxide (TMAH). Later on, in 2003, Musić et al. published a paper explaining the factors influencing forced hydrolysis of FeCl₃ solution (Musić S. et al., 2003). Another way to synthesize α-Fe₂O₃ is through hydrothermal methods. Giri et al. (2005) explained that hematite, with size and nature depending strongly on pH was successfully created under a complex microemulsion system. A narrow-distribution ultrafine dispersed Fe₂O₃ nanoparticle was reported by Zhang H., et al., where a co-precipitation method was employed with NaOH as the precipitating agent (Zhang H. et al., 2008). NaCl salts produced as a by-product of the reaction can help encapsulating the precursor, so that in the end the nanoparticle size varies only from 1.9 nm to 2.6 nm.

Wang et al., then tested the influence of Fe³⁺ ion catalyst under the synthesizing method of Chen et al. which utilizes Fe₂O₃ or Fe and aromatic sulfonic acid to prepare what is called amphiphilic metallic chelate catalyst (Chen Y. et al., 2008; Wang Y. et al., 2010). The catalytic aquathermolysis experiments were conducted using an oil/water ratio of 7:3 and 0.3 g of catalyst. The viscosity of the heavy oil after the reaction showed a decrease of around 95% under a recorded ambient temperature of 50 °C. Apart from the viscosity reduction, Wang et al. also characterized the composition and content level of SARA before and after the reaction. All parameters showed improved quality of the heavy oil, since the level of saturated and aromatic hydrocarbons and the H/C ratio increased, while resin and asphaltenes decreased under a recorded ambient temperature of 50 °C.

Nurhayati et al., have reported the synthesis of α-Fe₂O₃ nanoparticles using a microwave-assisted calcination method (Nurhayati T. et al., 2013). They reported that the method could reduce the preparation time needed, while keeping the heat distributed evenly throughout the process because of resonance and relaxation from the electromagnetic radiation, as explained by Lagashetty, et al. (Lagashetty A. et al., 2007). The precursors used were FeCl₃·6H₂O, with NaOH as a precipitating agent, which was later titrated into the FeCl₃ solution. The morphology and size of the nanoparticles characterized using SEM can be seen in Fig. 5. Firstly, the overall stoichiometric reactions that occurred during the course of this experiment can be represented by:

\[
\text{FeCl}_3 \cdot 6\text{H}_2\text{O}(aq) + 3 \text{NaOH}(aq) \rightarrow \text{Fe(OH)}_3(s) + 3 \text{NaCl}(aq) + 6 \text{H}_2\text{O}(l) \quad (2)
\]

Fe(OH)₃(s) → FeOOH(s) + H₂O(l) \quad (3)

2 FeOOH(s) [heated] → Fe₂O₃(s) + H₂O(l) \quad (4)

Furthermore, the microwave heating process would give the initial stage of crystal growth. The crystal growth mechanism may be a combination of O-R (Ostwald-ripening) and O-A (oriented-attachment) pathways, whereas the secondary crystal growth occurred during the calcination process.

The development of nanocomposites in order to combine the strength of two or more materials has gained popularity since a nanocomposite of hematite with silicon was studied thoroughly back in 1988, when Ishikawa and Matijevic attempted to synthesize it (Ishikawa T. and Matijević E., 1988). The goal of composing another material with hematite is to prevent agglomeration due to its magnetic surface interaction. As already studied by Vasquez-Mansilla et al. (Vasquez-Mansilla M. et al., 1999) and by Willis, et al. (Willis A.L. et al., 2005), magnetic interaction on the surface of antiferromagnetic hematite would give the initial stage of crystal growth. The crystal growth mechanism may be a combination of O-R (Ostwald-ripening) and O-A (oriented-attachment) pathways, whereas the secondary crystal growth occurred during the calcination process.
Swardhani et al. have reported a preparation of carbon-coated α-Fe₂O₃ nanoparticles using microwave-assisted calcination method (Swardhani A.P. et al., 2014). It resulted in creating nanoparticles with a mean size of 199 nm from calcination temperature increase, with optimum calcination temperature giving the optimum result. It is interesting to note that the presence of carbon will give a smaller internal crystal size of hematite and on the other hand an increase of the surface area, therefore increasing its effectiveness and making it more suitable to be used as catalyst. Fig. 6 presented the SEM image of the resulting nanocomposite, indicating that the carbon coated around the shape of Fe₂O₃ nanorod. Another work in α-Fe₂O₃ nanocomposite synthesis was done using zeolite (Iskandar F. et al., 2014). Using the same methods as for the α-Fe₂O₃/C nanocomposite, it was observed that the nanoparticles size grows larger as the microwave heating time and calcination temperature increase, with optimum calcination temperature thus giving better α-Fe₂O₃/zeolite crystallinity, at 450 °C. This pattern of improving crystallinity with increasing temperature is something that has to do with the sintering process that comes from excessive thermal energy, as explained more comprehensively by Wang, et al. (Wang Y. et al., 2009).

3.2.2 Magnetite (Fe₃O₄)

Fe₃O₄, usually called magnetite, is another type of iron oxide that is commonly encountered. It consists of both Fe²⁺ and Fe³⁺ ions that form both the octahedral and tetrahedral of the inverse spinel crystal structure. Fe₂O₃ shows ferrimagnetic phenomena at room temperature, having some magnetic domains that oppose each other. However, there is net magnetization in the direction of the dominant domain with magnitude relatively the same as in ferromagnetic materials. Interest in studying Fe₂O₃ nanoparticles appear from the broad domains it can be applied in, such as magnetic recording, biomedics, etc (Ito A. et al., 2004; Mornet S. et al., 2004).

As usual, the number of variations of the method to synthesize Fe₂O₃ is incredibly vast. Jiang, et al. tried to synthesize nano-Fe₂O₃ particles using co-precipitation, a simple and relatively high-yield method. FeSO₄·7H₂O and FeCl₃·6H₂O were used as Fe source, while NH₄OH, produced by mixing ammonia with aqueous solution, was titrated until the pH of the mixture reached 10-11 (Jiang W. et al., 2004). Control of pH is very critical during the synthesis process, since it was proven to affect the size distribution of the nanoparticles created. In his work, Jiang successfully synthesized Fe₂O₃ nanoparticles with relatively small average size and narrow particle distribution, i.e. 25.3 nm and 5.9 nm, respectively. In other works, some researchers carried out hydrothermal methods in order to synthesize Fe₂O₃ nanoparticles (Daou T. et al., 2006; Mizutani N. et al., 2008). Although both discuss the same methods, the interesting point is having two authors using a different approach. Daou’s report emphasized that magnetite nanoparticles with a mean size of 39 nm and good dispersity were correctly synthesized, as proven using XRD and other characterization techniques. Meanwhile, Mizutani emphasized the challenge of the effect of ferrous/ferric ions molar ratio, with a higher ions molar ratio resulting in more crystallinity and larger particle size. The full reaction regarding the transformation mechanism can be written as follow:

\[
Fe(OH)_2 + 2FeOOH \rightarrow Fe_3O_4 + 2H_2O \quad (5)
\]

with the FeOOH transformed from ferric hydroxide (Fe(OH)₃). Other methods performed to synthesize Fe₂O₃ are chemical vapor deposition (Chao L.T. et al., 2006), which resulted in Fe₂O₃ thin film deposited on Si substrate, and microemulsion (Koutzarova T. et al., 2006), by which nanopowder of polydispersed size was obtained.

Nugraha et al. have reported the synthesis of Fe₂O₃ nanoparticles (Nugraha M.I. et al., 2013). During the experiment, the co-precipitation approach to synthesize Ni₂Fe₃₋ₓO₄ was chosen due to its simplicity. The result showed that the average particle size was 43 nm and that the best composition for enhancing oil recovery is when there is no nickel impurity, with reduction of heavy oil viscosity approaching 30 % after the catalytic aquathermolysis reaction. Like Fe₂O₃, nanocomposite of Fe₃O₄
was also studied in the hope of modifying the surface characteristics of the nanoparticles and stabilizing the nanoparticles dispersion so that catalytic performance could be improved. Lan, et al. tried to coat Fe₃O₄ nanoparticles with oleic acid (Lan Q. et al., 2007). Employing a co-precipitation method followed by hydrothermal synthesis, the resulting colloidal system indicated no precipitate that showed its stability. Recently, Haryono et al. have tried a modification of this method using a three-neck flask (Haryono A. et al., 2013). They obtained a smaller particle size, in the order of around 2 nm. However, as we already knew, oleic acid suffers from detrimental structural change in high temperature conditions, which is typical in hydrothermal synthesis methods. Thus, an alternative was given by Stjerndahl, et al. (Stjerndahl M. et al., 2008), making use of SiO₂ or silica instead of oleic acid. Under a water-in-oil microemulsion system, the loading of iron oxide crystals, thickness of silica shells and particle size are tunable. More detailed picture of phase influence is given in Fig. 7, with darker component indicating the superparamagnetic iron oxides (SPIOs).

Iskandar et al. have reported a first attempt of magnetite nanocomposite Fe₃O₄/Zeolite synthesis by employing simple microwave heating methods (Iskandar F. et al., 2014). The reason behind the selection of zeolite as a matrix phase in the nanocomposite was that zeolite is well-known for its ability to act as a hydrogen donor that is essential in improving the quality of the heavy oil during catalytic aquathermolysis and is also easy to find since it is abundant in quantity, either as heulandite or as clinoptilolite (Merissa S. et al., 2013). However, in order to be ready for use, natural zeolite requires thermal treatment to activate and reduce the amount of metal content while at the same time increasing the surface area as well as the ratio of Si/Al. In terms of catalytic performance, i.e. the rate of heavy oil viscosity reduction, the Fe₃O₄/zeolite nanocomposite we produced, with heulandite type of natural zeolite, reached levels of up to 92 % for a Fe₃O₄: zeolite ratio of 20:80.

### 3.3 Cobalt-based nanocatalysts

Cobalt oxide is composed of both Co²⁺ and Co³⁺ ions, just like Fe₃O₄. Co₃O₄ is an inorganic compound that has antiferromagnetic properties at room temperature. Approaches that have been used to synthesize Co₃O₄ are thermal decomposition (He T. et al., 2004), mechanochemical (Yang H. et al., 2004) and hydrothermal methods (Dong Y. et al., 2007). Using thermal decomposition, it has been detected that an intermediate product is produced, with the final Co₃O₄ nanocrystals created were later separated by centrifugation and washed with cyclohexane three times. In another study, Yang stated that via mechanochemical milling of Co(NO₃)₂·6H₂O with NH₄HCO₃ and continued by thermal treatment, approximately 38 nm crystal size was obtained. The reaction stoichiometry of both the milling and calcination process is given by:

\[
2\text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + 5 \text{NH}_4\text{HCO}_3 \rightarrow \text{Co}_2(\text{OH})_2\text{CO}_3 + 4 \text{NH}_4\text{NO}_3 + \text{NH}_3 + 4 \text{CO}_2 + 14 \text{H}_2\text{O}
\]

(6)

![Fig. 7](https://example.com/fig7.png) TEM micrographs of shell-coated Fe₃O₄/SiO₂ nanocomposites under different synthesis conditions, (a–c) within microemulsion region, (d) in the two-phase region. Reprinted with permission from Stjerndahl, et al. Copyright © 2008, American Chemical Society.
\[ \text{Co}_2(\text{OH})_2\text{CO}_3 + \text{O}_2 \rightarrow 2 \text{Co}_3\text{O}_4 + 3 \text{H}_2\text{O} + 3 \text{CO}_2 \quad (7) \]

Nassar, et al. reported that using \( \text{Co}_3\text{O}_4 \) nanoparticles with a surface area of 41 m\(^2\) based on BET characterization, the reduction of asphaltenes content of heavy oil could reach 32% at 300 \( ^\circ \text{C} \) (Nassar N.N. et al., 2011). Further analysis on asphaltenes cracking activation energy, based on the Coats—Redfern method, indicated a significant decrease of the activation energy in the presence of nanoparticles catalyst, making the reaction possible to undergo at lower temperature.

4. Concluding remarks and future perspective

Based on the above reviews, all discussed materials are found to have synergistic effects when used as catalyst during catalytic aquathermolysis and hence are able to greatly improve the reduction of heavy oil viscosity and enhance the heavy crude oil recovery and quality. Table 1 summarizes several characteristic features of nanoparticles and their catalytic performance during enhanced oil recovery through aquathermolysis. Although no specific report regarding the optimum size of catalyst to be used in catalytic aquathermolysis, small nanoparticles and porous materials are certainly ideal and becoming the main subject of interest as they inherited high surface area which indicate excellent catalytic performance. As for porous materials, pores in the range of mesopores (2–50 nm) is more suitable in heavy oil conversion as reported by Van Donk, et al. due to better accessibility of large molecules (Van Donk S. et al., 2003). There are many other nanoparticles, including their variations and derivatives, that have not yet been synthesized due to the enormous amount of methods and complexities in this field, therefore further study in exploring new discoveries is still very much wide open.

In the future, we expect to see that the development of nanocatalysts in enhanced oil recovery will be heading towards colloidal mixtures of nanoparticles with base fluid, known as nanofluids, as first described comprehensively by Wang et al. for the purpose of increasing the heat transfer (Wang Y. et al., 2009). The superiority of using nano-sized particles in base fluids is due to the fact that they would increase the contact between the reactant molecule and the catalyst, such as the water-oil-catalyst surface in the aquathermolysis reaction, which leads to a more progressive reaction. Moreover, nanofluids offer

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Synthesis Method</th>
<th>Particle Size</th>
<th>Catalytic performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>microemulsion</td>
<td>6.3 nm</td>
<td>viscosity reduction: 98.2 % H/C: 1.46; ( M_W = 422 )</td>
<td>Li, et al. (2007)</td>
</tr>
<tr>
<td>NiO</td>
<td>co-precipitation</td>
<td>4.2 nm</td>
<td>viscosity reduction: 90.36 % H/C: 2.09; 28.06 % decreased of asphaltenes ( M_W )</td>
<td>Wu, et al. (2013)</td>
</tr>
<tr>
<td>NiO</td>
<td>unknown (purchased)</td>
<td>60–70 nm</td>
<td>viscosity reduction: 22 %</td>
<td>Noorlaily, et al. (2013)</td>
</tr>
<tr>
<td>NiO</td>
<td>unknown (purchased)</td>
<td>12 nm (crystal size)</td>
<td>% conversion of asphaltenes at 300 ( ^\circ \text{C} ): 37 %</td>
<td>Nassar, et al. (2011)</td>
</tr>
<tr>
<td>( \alpha\text{-Fe}_2\text{O}_3 )</td>
<td>mixing \text{Fe}_2\text{O}_3 with aromatic sulfonic acid</td>
<td>—</td>
<td>(1) maximum viscosity reduction up to 93.3 %.</td>
<td>Chen, et al. (2008)</td>
</tr>
<tr>
<td>( \alpha\text{-Fe}_2\text{O}_3 )/zeolite</td>
<td>microwave assisted co-precipitation + calcination</td>
<td>135 nm</td>
<td>viscosity reduction: 89 % (for ( \alpha\text{-Fe}_2\text{O}_3 )/zeolite composition of 1:3)</td>
<td>NURhayati, et al. (2013)</td>
</tr>
<tr>
<td>\text{Fe}_3\text{O}_4</td>
<td>microwave assisted co-precipitation</td>
<td>43 nm</td>
<td>viscosity reduction: 30 %</td>
<td>Nugraha, et al. (2013)</td>
</tr>
<tr>
<td>\text{Fe}_3\text{O}_4</td>
<td>obtained from nanostructured and amorphous materials</td>
<td>22 nm (crystal size)</td>
<td>% conversion of asphaltenes at 300 ( ^\circ \text{C} ): 33 %</td>
<td>Nassar, et al. (2011)</td>
</tr>
<tr>
<td>\text{Fe}_3\text{O}_4/zeolite</td>
<td>microwave assisted co-precipitation</td>
<td>96 nm</td>
<td>viscosity reduction: 92 % (for ( \text{Fe}_3\text{O}_4 )/zeolite composition of 1:4)</td>
<td>Iskandar, et al. (2014)</td>
</tr>
<tr>
<td>\text{Co}_3\text{O}_4</td>
<td>unknown (purchased)</td>
<td>22 nm (crystal size)</td>
<td>% conversion of asphaltenes at 300 ( ^\circ \text{C} ): 20 %</td>
<td>Nassar, et al. (2011)</td>
</tr>
</tbody>
</table>
more stability compared to the use of micron- or millimeter-dimension particles, which can cause severe abrasion and clogging problems. Another prospect of nanofluids, observed by Eastman, et al., is that nanofluids consisting of nano-copper particles dispersed in ethylene glycol have up to 40% better thermal conductivity properties compared to those of pure fluid (Eastman J.A., et al., 2001). Based on this fact, nanofluids show great potential for various industries, one of which is the oil and gas industry where in-situ steam flooding is customarily used to enhance oil recovery. To find out what causes the increase in thermal conductivity, Keblinski, et al. proposed four possible mechanisms of heat flow in nanofluids, i.e. Brownian motion of the particles, molecular layering of the liquid at the liquid-particles interface, the nature of heat transport in nanoparticles, and effects of nanoparticle clustering (Keblinski P. et al., 2001).

Related to the preparation method, simple liquid-solid interdiffusion will not work towards achieving good nanofluids. Special methods, for example using surface activators and dispersants, or ultrasonic vibration, are available to create stable nanofluids that produce no precipitate over longer times (Xuan Y. and Li Q., 2000). Zeta potential analysis is one of the most effective ways to predict nanofluids stability. Generally, nanofluids preparation methods can be divided into two groups: single-step methods and two-step methods, as discussed comprehensively in the review paper by Li et al. and Haddad et al. (Haddad Z. et al., 2014; Li W. et al., 2007). One important aspect to note is the necessity to compromise the optimum value of nanoparticles inside the base fluid so as to get the best thermal conductivity, yet still a very stable colloidal suspension.

Another way to achieve this objective is to use beads milling, with which a stable colloidal nanoparticle suspension can be prepared. An illustration of the beads mill apparatus can be seen in Inkyo et al., which used bead particles with a diameter of only 15 μm, the smallest at the time, and employed centrifugal force in the upper part of the apparatus to separate the beads from the nanoparticle suspension (Inkyo M. et al., 2006). As a result, nanoparticles with a size of only 15 nm dominated the composition after 180 minutes of milling and low contamination from zirconia (ZrO2), the beads’ constituent material, was achieved.

Our preliminary work of water-based Fe2O3 nanofluids preparation showed initial success in increasing the viscosity reduction of heavy oil compared to the use of nanoparticles (Iskandar F. et al., 2015). The result also reflected that the presence of surfactant under the addition of 20 wt% ethylene glycol had a negligible effect on catalytic performance degradation.

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