

중질유 혹은 감압잔사유의 개질 반응 : Aquathermolysis와 Demetallization

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Upgrading of Heavy Oil or Vacuum Residual Oil : Aquathermolysis and Demetallization

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초 록

지구상에는 1조 6880억 배럴의 원유매장량으로 현재 추세로 채굴하면 향후 53.3년 채굴 가능할 것으로 예측되고 있다. OPEC은 원유값이 10년 내에는 \$100이 넘지 않을 것으로 예상하지만, 감산 정책의 정치적 이슈가 등장하면 원유값은 급격히 상승할 수도 있다. 따라서 일반 원유의 고갈에 대비해 비재래형 원유자원인 오일샌드나 비튜멘과 같은 중질유에 대한 관심이 높아지고 있다. 중질유는 일반적으로 레진이나 아스팔텐이라 부르는 탄소수가 60이 넘는 분자량이 높은 화합물 함량이 높아 점도가 높고 끓는점이 높다. 일반 원유를 감압 증류할 때 부생되는 감압잔사유(vacuum residue)는 물리화학적 물질들이 중질유와 비슷하다. 중질유의 채굴을 위해서는 점도를 낮추는 기술이 중요한데 본 리뷰 논문은 상업적으로 사용되고 있는 aquathermolysis 기술을 검토하여 보았고 감압잔사유에 적용하여 보았다. 감압잔사유에는 니켈(Ni)과 바나듐(V)과 같은 전이금속이 함유되어 있는데, 이를 고도화하기 위해서는 전이금속 제거가 선행되어야 한다. 본 리뷰 논문에서는 감압잔사유로부터의 전이금속 제거 기술에 대한 최근 연구결과를 정리하여 보았다.

Abstract

It has been estimated that the Earth has nearly 1.688 trillion barrels of crude oil, which will last 53.3 years at current extraction rates. The organization of petroleum exporting countries (OPEC) group forecasted that the oil prices will not jump to triple-digit territory within a decade, but it can quickly increase as the political issue for reducing oil production appears. With the potential of serious shortage of conventional hydrocarbon resources, the heavy oil, one of unconventional hydrocarbon resources including oil sand and natural bitumen has attracted worldwide interest. The heavy oil contains heavy hydrocarbon compounds, commonly called as resins and asphaltenes, with long carbon chains more than sixty carbon atoms. The high content of heavier fraction corresponds with the high molecular weight, viscosity, and boiling point. Physicochemical properties of residues from vacuum distillation of conventional oil, referred to as vacuum residues (VR) were similar to those of heavy oil. For the development of heavy oil reserves, reducing the heavy oil viscosity is the most important. In this article, commercially employed aquathermolysis processes and their application to VR upgrading are discussed. VR contains transition metals such as Ni and V, but these metals should be eliminated in advance for further refining. Recent studies on demetallization technologies for VR are also reviewed.

Keywords: aquathermolysis, viscosity, demetallization, Ni, V, porphyrins

1. Introduction

Recently, organization of the petroleum exporting countries (OPEC) published '2015 World Oil Outlook (WOO)' and warned a much more pessimistic energy crisis on the state of oil markets[1]. With regard to the price assumptions adopted in this Outlook, the OPEC reference

basket (ORB) value is assumed to average \$55/barrel during 2015 and to resume an upward trend in both the medium- and long-term. Generally, the long-term oil price assumption is based on the estimated cost of supplying the marginal barrel in production. The OPEC group estimates that the oil price rises by an average of about \$5 per year during this decade, and reaches \$80 per barrel in 2020. From there, it sees oil prices rising slowly, hitting \$95 per barrel in 2040. The oil industry decreases upstream investment by \$250 billion in 2015, and another \$70 billion could be decreased in 2016. Globally, the oil industry is set to reduce investment by \$1 trillion between 2015 and 2020 due to the collapse of oil prices in the market. The oil prices

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Table 1. Global Oil Product Demand, Shares and Growth between 2014 and 2040[1]

	Global demand (mb/d)							Shares (%)	
	2014	2015	2020	2025	2030	2035	2040	2014	2040
Light products	39.8	40.5	42.9	44.6	46.1	47.4	48.6	43.5	44.3
- Ethane/LPG	10.3	10.5	11.1	11.7	12.2	12.6	12.9	11.3	11.7
- Naphtha	6.2	6.2	6.6	7.1	7.7	8.1	8.7	6.7	7.9
- Gasoline	23.3	23.9	25.1	25.8	26.3	26.7	27.1	25.6	24.7
Middle distillates	33.8	34.5	37.3	39.4	41.1	42.8	44.3	37.0	40.3
- Jet/Kerosene	6.7	6.8	7.3	7.8	8.2	8.7	9.2	7.4	8.4
- Diesel/Gas oil	27.1	27.6	30.0	31.6	32.9	34.1	35.1	29.7	32.0
Heavy products	17.7	17.8	17.2	17.0	17.0	17.0	16.9	19.4	15.4
- Residual fuel*	7.9	7.8	7.1	6.8	6.6	6.4	6.2	8.7	5.6
- Other**	9.8	10.0	10.1	10.2	10.4	10.5	10.7	10.8	9.7
Total	91.4	92.8	97.4	100.9	104.2	107.2	109.8	100.0	100.0

*Includes refinery fuel oil

**Includes bitumen, lubricants, waxes, still gas, petroleum coke, Sulphur, direct use of crude oil, etc.

seem not jump to triple-digit territory within a decade, but it will quickly increase as the political issues for reduction of manufacturing appear. It seems very difficult to forecast the long term oil prices spike again, but oil shortage within a few years can be also possibly occur since the reduction of investment triggered already[1-5]. Until now, one of the most curious debate seems how much oil reserves are available and how long they would last. Oil reserves indicates the total amount of technically and economically producible oil. According to current estimates by OPEC, more than 80% of the world's proven oil reserves are located in OPEC Member Countries, with the highest proven oil reserves including non-conventional oil deposits are in Venezuela (20% of total global reserves), Saudi Arabia (18%), Canada (13%), and Iran (9%), and so on. OPEC Member Countries have made significant additions to their oil reserves in recent years, for example, by adopting best practices in the industry, realizing intensive explorations and enhanced recoveries. As a result, OPEC's proven oil reserves currently stand at 1206.00 billion barrels[1-8]. A little bit different estimation by British Petroleum Company has been reported in 2013. Earth has nearly 1.688 trillion barrels of crude, that will last 53.3 years at current extraction rates[5]. M. King Hubbert, the American geologist, predicted that the world oil production would be peak on near the year 2000. In 2001, Kenneth S. Deffeyes, professor of Princeton University, used Hubbert's theory to predict that the world oil production would become peak in 2005. Many pessimistic predictions regarding on the peak oil told us that the peak has already passed during the last decade[5-10]. On a long-term perspective, the control of OPEC will emerge again since the most of oil reserves are located within its control. However, the demand for crude oil worldwide has substantially increased over the past decade, straining the supply of conventional oil. This has led to consideration of alternative or undeveloped energy sources, among them heavy crude oil and natural bitumen are perhaps the most readily available for demand[5,6]. Moreover, the declining nature of the conventional oil reserves and increasing of global energy demand, heavy oil production will increase in the near upcoming oil crisis period. Therefore, it is our duty to prepare the alternative energy sources to prevent from upcoming of oil crises. Table 1 shows the

global oil product demand, shares and growth between 2014 and 2040. Global demand for oil product will increase by 20% during the quarter decade. Process development for converting bitumen to clean transportation fuels based on the long-established enhanced Fischer-Tropsch GTLs process have been announced[1]. These are based on the partial oxidation of bitumen to generate syngas for feed to the Fischer-Tropsch reactor. While technical feasibility aspects are not in doubt, questions remain as to the economic feasibility. This is in respect to the process capital and operating costs relative to the potential value-added in converting bitumen to high quality fuels products. An enhanced Fischer-Tropsch process is suitable for the synthesis of green fuels that has clean burning property because they are sulfur free.

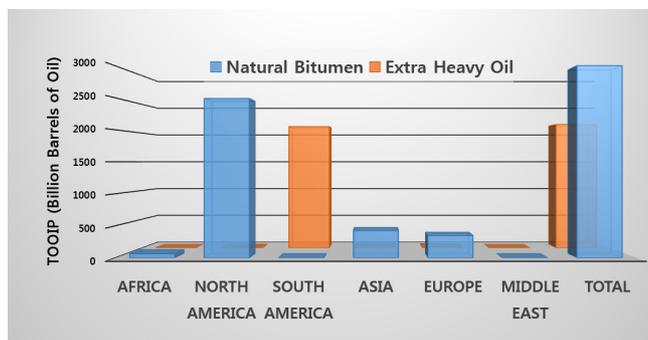
2. Heavy Oil and Natural Bitumen Resources

Until recent years, conventional light crude oil has been abundantly producible and has satisfied the world demand for energy source. With the potential of serious shortage of conventional hydrocarbon resources, heavy oil, a type of unconventional hydrocarbon resources such as oil sand and natural bitumen, have attracted worldwide interest. Until now, Among the consideration of alternative or insufficiently utilized energy sources, heavy crude oil and natural bitumen are readily available to supplement short- and long-term needs[2,3]. When natural bitumen is mobile in the reservoir and producible, it is called to extra-heavy oil. As natural asphalt, bitumen has been exploited since antiquity as a source of road paving, cement, and mortar between bricks and stones and is still used for these purposes in some parts of the world. The asphalt using for road paving has now replaced by manufactured asphalt that are satisfying to specific requirements. Heavy oil and natural bitumen are considered one of the most crucial sources to meet future energy demand. The total resources of heavy oil and bitumen in known accumulations are 3,396 and 5,505 billion barrels of original oil in place (OOIP) and among these, 30 and 993 billion barrels of oil are prospective additional oil, respectively[3,11]. Figure 1 shows the resources distribution of heavy oil and bitumen. In addition to large reserves in Canada and Venezuela, heavy oil is potentially

Table 2. Some Chemical and Physical Properties of Crude Oils[3,12-16]

Attribute	Unit	Conventional Oil	Heavy Crude Oil	Natural Bitumen
API Gravity	degrees	22-45	10-22	< 10
Viscosity (25 °C)	cp	13.7	~100,000	~1,300,000
Viscosity (54 °C)	cp	15.7	278.3	2371.6
Coke	wt%	2.9	13	23.7
Asphalt	wt%	8.9	38.8	67
Carbon	wt%	85.3	85.1	82.1
Hydrogen	wt%	12.1	11.4	10.3
Nitrogen	wt%	0.1	0.4	0.6
Oxygen	wt%	1.2	1.6	2.5
Sulfur	wt%	0.4	2.9	4.4
Gasoline + Naphtha	wt%	31.5	6.8	4.4
Asphaltene	wt%	2.5	12.7	26.1
Residue Vanadium	ppm	16.2	177.4	190
Residue Nickel	ppm	25.7	104.3	78
Residue Sulfur	wt%	1.5	3.9	4.6

produced from Russia, Saudi Arabia-Kuwait partition zone, Oman, Mexico, USA, Indonesia, China and a few countries in Europe[12]. Heavy oil contains heavy hydrocarbon compounds, which are commonly called resins and asphaltenes, with long carbon chains more than sixty carbon atoms[12]. High content of heavier fraction corresponds with high molecular weight, viscosity, and boiling point. However, its high viscosity and solidification often cause difficulties in exploiting it. The hydrocarbons in the oil sand and natural bitumen are extremely viscous and dense as wax at room temperature, makes extraction difficult. Based on the SARA analysis, heavy oil is known to be rich in heavier organic compounds, such as resin and asphaltenes and lighter linear alkanes are significantly low. Because of their high viscosity, they cannot be produced by conventional methods. They cannot be transported without heating or diluted with lighter hydrocarbons, or refined by older oil refineries without modification. Such heavy crude oils often contain high concentrations of sulfur and heavy transition metals, particularly nickel and vanadium that interfere with refining processes. Similarly to extra heavy oil, vacuum residual oil produced from vacuum distillation process of the conventional oil also have high viscosity and high sulfur and heavy metals. Table 2 shows some of the average chemical and physical properties of conventional, heavy crude oils and natural bitumen. The data are derived from multiple sources, some old and others adhering to standards employed in different countries. Some of the properties in Table 2 are important with respect to heavy oil and natural recovery from the ground and other properties serve as the basis for decisions for upgrading and refinery technologies. Moving across Table 2 from conventional oil to natural bitumen, increases may be seen in density (shown as reductions in API gravity), coke, asphalt, residuum yield (percent volume), pour point, dynamic viscosity, and the content of copper, iron, nickel, vanadium among the metals and in nitrogen and sulfur among the non-metals. Thus many techniques such as solvent vapor extraction

**Figure 1. The resources distribution of heavy oil and bitumen[3,12].**

(VAPEX), steam-assisted gravity drainage (SAGD), in situ combustion (ISC), thermal based heavy oil recovery methods, cyclic steam stimulation (CSS), gas bubbles nucleation and growth methods, carbonated water injection (CWI), catalytic or non-catalytic aquathermolysis, and electromagnetic heating method have been developed and adopted for heavy oil exploitation[1-3,11,12].

3. A Review for the Study on Viscosity Reduction and Upgrading of Heavy Oil

Due to the growing world oil demand and declining of the conventional oil reserves, spotlight is turning towards huge unconventional resources such as heavy-oil and oil sands deposits due to their enormous volume and worldwide distribution[11-13]. Thus, many researchers are devoting to reduce the viscosity of heavy oil for the production and transportation. They have proved that superheated water (240-300 °C) can heat up the asphaltene and resin molecules to break down to small molecules, and then the viscosity is reduced.

Table 3. Chemical Composition and Physical Properties of Heavy Oil[12]

Composition	Khafji VR	Safaniya, Arabian	Bitumen, Athabasca	Heavy Oil, Mexico	Heavy Oil, Venezuela
Carbon (wt%)	84.0	n.r	83.3	18.1	n.r.
Hydrogen (wt%)	10.3	n.r.	10.4	n.r.	n.r.
Nitrogen (wt%)	0.33	n.r.	0.44	1.2	n.r.
Sulfur (wt%)	4.9	4.3	4.6	0.05	3.0
Vanadium (ppm)	128	V+Ni	190	444	V+Ni
Nickel (ppm)	43	= 125	78	85	= 509
Gravity (° API)	6.5	13.0	9.6	12.1	9.4
Viscosity (cP) at 100 °C	1550	n.r	125	11.4	10.3
Asphaltenes (wt%) ^a	11.1	n.r	7.7	19	n.r
Carbon residue (wt%) ^b	20.1	12.8	13.6	18.1	14.1

n.r = not reported, ^a : insoluble in n-heptane, ^b: Conradson carbon capsule

3.1. Pyrolysis, aquathermolysis of heavy oil

Heavy crude oil is oil that has viscosity typically greater than about 100 cP and density greater than 930 kg/m³[14]. Bitumen, also referred to as extra heavy crude oil, is defined as being more viscous and denser than heavy oil with viscosity and density being higher than 10,000 cP and 1000 kg/m³ respectively[2,14]. In many oil sand reservoirs, the viscosity of bitumen exceeds 100,000 cP with average values typically just over 1 million cP[14]. There exists more than 6 trillion barrels of heavy oil and extra heavy oil on Earth (Figure 1). Due to declining rates of production of conventional oil, these oils are becoming more sought after by oil production companies. Roughly 1.7 trillion barrels of heavy oil and bitumen are hosted in sedimentary basin area of Alberta State in Canada, that is the single largest resource of heavy oil and bitumen on Earth with the largest being the Athabasca oil sand deposit. The physical situation is generally as follows[14].

1. The bitumen occupies roughly between 85 and 95% of the pore space, the remainder is filled with water. The sand grains are typically between 50 and 120 μ m in size with pore sizes between sand grains typically equal to about 10 to 30 μ m. The sand is typically composed largely of quartz.

2. The porosity of the reservoir ranges from 20 to 35%. The absolute permeability of the reservoir rock ranges from 1 to 8 darcy depending on the porosity, shape of sand grains, and depth of the reservoir.

3. The initial temperature of the reservoir is typically between 8 and 20 °C, and the viscosity of the bitumen is in the millions of cP. The initial reservoir pressure typically ranges from 8 bar up to about 35 bar depending on the depth of the reservoir for in situ recovery processes.

4. The solution-gas content is relatively low compared to conventional oil reservoirs with gas-to-oil ratios generally lower than 3 to 4 m³ gas per m³ of bitumen at reservoir conditions.

Several production methods such as vapor-assisted petroleum extraction (VAPEX), cold heavy oil production with sand (CHOPS), steam-assisted gravity drainage (SAGD), In situ combustion (ISC), cyclic steam stimulation (CSS), steam flooding, in-situ combustion (ISC), gas bubbles nucleation and growth, catalytic aquathermolysis (CAT),

electromagnetic heating, non-aqueous method in heavy oil recovery are used to recover the heavy oil[17-22]. Three in situ extraction processes are in the developmental stages that promise significantly to reduce the viscosity of resources[10]. In the VAPEX process, a solvent blend of propane, butane, naphtha, and methane is injected into the formation as a vapor by an upper horizontal well. The solvent mixes with bitumen to reduce its viscosity. Production occurs through a lower horizontal well. The process uses no water and produces no CO₂, but it is not yet commercial, because it is slow, and a practical system for recovery of the costly solvent has not been demonstrated. VAPEX is also more environmentally friendly, whereas a large amount of water is consumed and tremendous amounts of greenhouse gases are generated in the thermal-based heavy oil recovery processes[17]. In the Electro-Thermal Dynamic Stripping process the bitumen's viscosity is reduced by heat generated from electrical energy delivered by electrodes inserted into the formation. No water or gas is used in the process. Scaled-up tests must develop ways to enhance well production rates and allow increased spacing of electrode and production wells. The Toe-to-Heel-Air-Injection (THAI) process involves igniting bitumen at the toe of a horizontal production well and feeding the combustion front with compressed air injected by a vertical well. The heat reduces viscosity of the bitumen, allowing recovery through the production well. As the combustion front moves from the toe to the heel, a natural coking reaction uses precipitated asphaltenes as fuel, thus consequently raising the API gravity of the produced oil. This process, owned by Petrobank Energy and Resources in Canada, has been field tested in a pilot configuration for several years at the Whitesands project[10].

3.1.1. Steam-assisted gravity drainage (SAGD)

Steam Assisted Gravity Drainage (SAGD) is an enhanced oil recovery technology for producing heavy crude oil and bitumen [11,14,17-22]. The method encompasses the used of steam to increase the temperature of heavy oil and therefore lower its viscosity. The thermal-based heavy oil recovery methods, such as SAGD by injecting steam into the reservoir to assist the heavy oil gravity drainage, have been commercially and successfully applied for many years. It is an

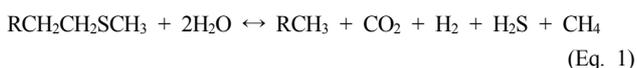
advanced form of steam stimulation in which a pair of horizontal wells is drilled into the oil reservoir, one a few meters above the other. High pressure steam is injected into the upper wellbore continuously to heat the oil and reduce its viscosity, causing the heated oil to drain into the lower wellbore, where it is pumped out. Steam Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS) Steam injection in the oil industry are two commercially applied primal thermal recovery processes used in the oil sands[14].

3.1.2. Aquathermolysis

Steam stimulation (huff and puff) is the most popular and effective technology to recover heavy oil in the world. In the steam injection process, the viscosity reduced according to its viscosity-temperature characteristic properties, reduce the flowing resistance through the pore media of reservoir, and increase the yield and production rate[6,11,22-26]. Aquathermolysis (also referred to as hydrous pyrolysis) refers to a high temperature conversion of oil components in oil sands by the action of steam, hot water, which is in vapor or liquid form or vapor-liquid two-phase coexistence form, resulting in pyrolysis of some components of heavy oil and extra heavy oil. Hyne et al.[27] introduced the term aquathermolysis (aqua = water; thermos = hot; lysis = loosening, dissolution) to represent the breakdown of components of oil sands and/or heavy oils through chemical reactions in the presence of steam/hot water[14,28]. Steam-injection, as a conventional method of exploitation, relying on the function of high-temperature steam, can only reduce the viscosity of heavy oil physically, with fewer changes of heavy components and lower viscosity reduction. Aquathermolysis reactions are relatively non-destructive, as compared to the higher temperature thermal cracking process[29-32]. There are very few detailed experimental studies on chemical interaction of Athabasca oil sands with water.

3.2. An overview of main mechanism

The major components of the heavy oil are resins, asphaltenes and associated derivatives. The main viscosity reduction mechanism is therefore how direct decomposition of these species irreversibly is performed. It has been established that hydrocarbon compounds in the heavy oil could be cracked even without the influence of water when the temperature exceeds 300 °C[6]. However, complexities are associated with the S-bearing compounds, whose decomposition by C-S bond breaking is very critical for the overall process[6]. A common chemical reaction (Eq. 1) believed to occur with these species involved their reaction with steam to produce methane, hydrogen sulfide, carbon dioxide, hydrogen and possibly low molecular weight hydrocarbons that are heavier than methane[29-36].



Some of the produced gases such as hydrogen and carbon dioxide are also very important in reducing the viscosity. Since the hydrogen comes from water, it can initiate viscosity reduction by attacking the

oil in a manner similar to the hydrogen donor compounds. The work of Wang and co-workers[34], indicated the addition of an acidic catalyst, like aromatic sulfonic iron, to catalyze a series of chemical reactions including the pyrolysis of side reaction chains of both saturated and unsaturated compounds, hydrogenation of unsaturated compounds (with or without heteroatoms) and isomerization. When the catalyst is present on this reaction system, the viscosity reduces very rapidly. In general, the catalysts employed for aquathermolysis are mineral, water-soluble, oil soluble, and dispersed catalyst. The other identified catalytic role includes polymerization on active metal sites, oxygenation of S-compounds, ring opening reactions of saturated and unsaturated cycles. However, appropriate selection of catalyst materials with good acidity, thermal stability and irreversible bond fission properties is necessary[35-39]. Otherwise, reconstruction of ruptured species and polymerization reactions could be reversibly catalyzed. The viscosity reduction with the catalysts is in the order of mineral < water-soluble catalyst < oil-soluble catalyst < dispersed catalyst. It has also been found that during aquathermolysis, the saturates and aromatics increase while the amount of asphaltene and resin decreases. The use of different hydrogen donors on aquathermolysis also improves the quality of the heavy crude oil. The most commonly used hydrogen donor is tetralin[40]. Moreover, when tetralin is used with a catalyst, the viscosity is also reduced more effectively. Salazar suggested that the combination of tetralin, tert-amyl-methyl ether (TAME) and methyl-tert-butyl ether (MTBE) shows the better hydrogen transfer from donor to the extra heavy crude oil[40].

3.3. Solid catalysts in aquathermolysis

Catalysts play an important role during the aquathermolysis reaction. One major role is the catalytic hydrolysis of the aliphatic sulfur bonds of the heavy oil compounds. Hydrogen sulfide is produced (Eq. 1) and the concentration of lighter hydrocarbons increased[28]. These compounds are characterized by lower molecular weights and viscosities compared to resins and asphaltenes. The use of catalysts in the real oil field indicates that the catalysts can substantially reduce viscosity and hence the catalytic aquathermolysis process can be used successfully for exploration of heavy crude oils[41-55]. However, the oil soluble and dispersed catalysts are slightly more active than the water-soluble catalyst. The cost of the former two types of catalysts may be higher than the preparation cost of simple water-soluble catalysts[33]. The Solid catalysts represent a large group of heterogeneous materials that could be acidic or basic in nature, are employed very often as commercial catalyzing a range of petroleum industrial processes. In the industry, the catalytic activity is dependent on the surface area, acidity-basicity (Brønsted/Lewis), shape selectivity, pore properties, stability, and availability and preparation routes. These factors are equally important to the aquathermolysis process[40-48]. The catalysts are materials such as zeolites and some oxides[50-55]. They are either anchored onto supporting materials such as zeolites and some oxides on zirconia, silica and alumina support or unsupported oxides such as metal oxide itself, carbides, etc[51,52]. Their documented properties would be considered and reasonable details would be provided on their potential applications in the catalytic aquathermolysis reaction[51-54]. It has

Table 4. Physicochemical Properties of VR

Gravity (° API)	CHNS contents (%)				Impurities (ppm)				HHV* (kcal/kg)
	C	H	N	S	Ni	V	Fe	Cl	
5.3	84.6	10	0.4	5.4	43	147	10	5	10,120

*Higher heating value (kcal/kg)

been previously shown that micron-sized metal particles improve the efficiency of some ex-situ processes such as pyrolysis, oil shale recovery, heavy oil upgrading, and heavy oil viscosity reduction. It is believed that catalyzing the hydrogenation reactions and thermal conductivity enhancement are the important functions of transition metal species. Some of these effects result in in-situ oil upgrading. Catalysts based on metal species like Ni and Fe attack bonds containing oxygen, sulfur and/or nitrogen and generate gases such as hydrogen, ammonia, hydrogen sulfide, carbon monoxide and carbon dioxide. Lighter hydrocarbons are similarly produced. The ability of the catalysts to break the complex structures of resins and asphaltenes formed the major driving force for viscosity reduction. The catalysts also promote heat transfer and favor the effect of steam. Catalytic systems such as acidic zeolites, heteropoly acids and their salts and hydrogen donor catalysts produced H^+ species that attack the resins and asphaltenes[6,33-37,50-52]. Consequently, lighter aromatics and alkanes of low molecular weights are produced. Production of gaseous species is low compared to metal ion catalysts. Mechanistically, the action of the catalyst breaks C-S bond of many S-bearing compounds and yield saturates in addition to the H_2S gas. Nitrogen containing compounds of such as pyridine, amides and derivatives of pyrrole are produced via C-N cleavages and rearrangements after the aeration process[34-37]. The mechanism also involved pyrolysis of the C-O or C-C in cyclic alkanes and bridging groups[6,34-37]. The main reaction routes involved pyrolytic fission, desulphurization, cyclization and ring openings, denitrogenation and/or deoxygenation[34-37]. Availability of hydrogen or hydrogen donors in the reaction systems also promote hydrogenation process. Catalysts stability entails its ability to be utilized for long period of time without activity decay, disproportionation, structural collapse, sintering due to high temperatures, active sites deactivation and/or compositional changes due to interaction with the reaction feed. In aquathermolysis, the reaction is normally carried out at low to mild temperatures (200 - 400 °C). Therefore, catalyst instability due to sintering or rapid structural collapse is basically very challenging problem. However, the presence of hot water in the reaction feed may create stability difficulties depending on the catalyst system, and consequently retards its viscosity reduction efficiency. Catalysts that have good water tolerance should therefore be more preferable for this application. Catalysts based on minerals, transition metal ions, their salts and derived complexes were very active, yielding viscosity reduction as high as 80%, with significant production of saturates and lighter aromatics[6,35,38-46]. However, their hot water solubility implies that catalyst recovery and subsequent reuse is fundamentally difficult. This can significantly limit industrial value due to cost and disposal implications. Similarly, transition metal ions with water affinity like Cu^{2+} , Fe^{3+} , Mo^{6+} and others

are prone to form stable aqua-complexes with water in the reaction medium, thereby limiting their accessibility to resins and asphaltenes in the heavy oil. This factor will definitely reduce their viscosity reduction efficiency[6,45-52].

Solid acids and bases are known for their water tolerance and stability. For examples, materials such as natural zeolites (heulandite and clinoptilolite) employed by Merissa et al.[50] and Ca-chabazite by Junaid et al.[51], transition metal oxides and their composites such as WO_3/ZrO_2 by Wang et al.[34,37] and modified SO_4^{2-}/ZrO_2 by Jing et al.[38] have shown excellent viscosity reduction. Among the prospective catalysts such as nitrides and carbides of transition metals like W and Mo, hydrated molybdenum oxides and zeolites, the hydrophobic zeolites have already been evaluated for their water tolerance in other aqueous reactions like isomerization and acylation[6]. Their superior properties could be extended for the aquathermolysis reactions. However, the zeolite materials must be synthesized in the fluoride routes or modified with organic silane compounds to avoid destruction to acidity, which is the main requirement for catalyzing cracking reactions and pyrolysis during the aquathermolysis process. Catalysts based on W and Mo are also known for their good thermal stability. They have been employed for different reactions at temperatures similar or higher than those considered for the aquathermolysis process without encountering stability problems.

4. A Review for the Study on Demetallization of Residual Oil

An petroleum oil refinery is an industrial process where crude oil is processed into more useful products such as petroleum naphtha, gasoline, diesel fuel, asphalt base, etc[56-58]. The first manufacture step of petroleum products is the separation of crude oil into the main fractions by atmospheric distillation. When crude oil is heated, the lightest and most volatile hydrocarbons boil off as vapors first and the heaviest and least volatile last. The vapors are then cooled and condensed back into liquids. The residue from atmospheric distillation is sometimes referred to as long residue and to recover more distillate product, further distillation is carried out at a reduced pressure and high temperature. This vacuum distillation process is important in maximizing the upgrading of crude oil. The residue from vacuum distillation, referred to vacuum residues (VR), is used as a feedstock for further upgrading or as a fuel component. Table 4 shows the physicochemical properties of VR obtained from SK Energy, Korea.

The concentration of metals in crude oil usually varies from a few ppm to more than 1000 ppm[29]. Usually they are in an oil-soluble form and become concentrated in the heavy vacuum residual oil frac-

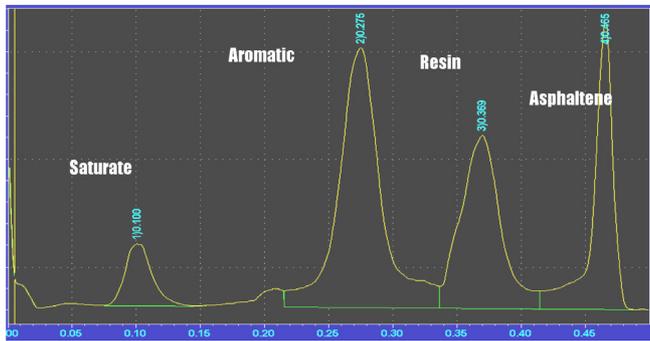


Figure 2. SARA analysis of VR, SK Energy (Elution condition: 1st Hexane 10 cm, 2nd Toluene 6 cm, DCM/Methanol (95/5) 2.5 cm).

tions in conventional refining processes. The metals found are sodium, potassium, lithium, calcium, strontium, copper, silver, vanadium, manganese, tin, lead, cobalt, titanium, gold, chromium and nickel. Among these metals the most abundant and undesirable are nickel (Ni) and vanadium (V). The metals are usually in combination with naphthenic acid as soaps and in the form of organometallic compounds complex such as metal porphyrins, M-porphyrin[16,29,43]. The heavy metals (M) in crude oil residue are agglomerated in asphaltenes in the form of M-porphyrin compounds. Treibs investigated the chromophores of porphyrin systems in the middle of 20th centuries to understand the physicochemical properties of them in the petroleum and bitumen contain metal porphyrins[29,59]. The subject of metal porphyrins in petroleum were extensively reviewed and published[16,20-22,29,43]. When the mixture of the heavy residual oil and bunker C oil is applied to fuel, the metals in the mixed oil could increase of gas and coke formation and decrease the yields of gasoline combustion. Metals in fuel oils produce ash, when the oil burn. Ash deposits in engines result in abrasion of the moving parts of the engines, and the ash is injurious to the walls of the boilers and furnaces. The presence of metal contaminants in fluidic catalytic cracking (FCC) feeds presents another and potentially more serious problem because although sulfur can be converted to gaseous forms which can be readily handled in an FCC unit. The nonvolatile metal contaminants tend to accumulate in the unit and during the cracking process. They deposit on the catalyst together with the coke[60-63]. Because both nickel and vanadium exhibit dehydrogenation activity, their presence on the catalyst particles tends to promote dehydrogenation reactions during the cracking sequence and this result in increased amounts of coke and light gases at the expense of gasoline production. Vanadium and nickel seriously affect cracking, when they accumulate on the particles of the catalyst over time, causing alteration in the catalyst structure[23]. Also, small amounts of nickel and vanadium in the charge stocks poison clay and synthetic catalysts.

These metals in the heavy residue cannot be eliminated by simple chelation process since they exist as very stable[29,56,64,65]. The nickel and vanadium metals in the vacuum residue (VR) have eliminated by the combination of solvent separation process and chelation process[64,65]. VR obtained from SK Energy, Korea contains Ni (about 50 ppm), V (about 150 ppm) and Fe (about 10 ppm), respectively. The solvent separation process is capable of removing all or a substantial

amount of metals from the vacuum residues that are destined for further processing such as in the middle of refining step. Distillation concentrates the metallic compounds in the residue. The majority of the metal compounds may precipitated along with the asphaltenes by hydrocarbon solvents. Thus, the removal of asphaltenes with n-alkane reduces the metal content of the oil by up to 95%. The metal-porphyrins in the asphaltene part of the vacuum residual oil can further eliminated by the adsorption process onto mesoporous adsorbents[16].

4.1. Solvent distillation

Distillation separates crude oils into fractions according to boiling point, so that each of the fractions will have their appropriate specifications for particular use[63-70]. The metallic components in the oil concentrate into the residues after distillation process. Based on the SARA analysis (Figure 1), it was found that VR is composed of saturates (7.3%), aromatics (43.7%), resins (25.5%), and asphaltenes (23.5%).

Yamada et al. reported a method of extraction by heating the oils to 177-238 °C, refluxing the oils with an organic solvent, and then centrifuging the mixture[29,71]. Thus, a residual oil containing 159 ppm V was heated to 182-216 °C for 1h at rate of 3 °C/min, refluxed with hexane, and then centrifuged to give a hexane soluble portion containing 0 ppm V[29]. Ni- and V-containing metalloporphyrins in heavy petroleum feedstocks were removed by solvent extraction with a solvent chosen from g-butyrolactone, acetonitrile, phenol, furfural, 2-pyrrolidone, dimethylformamide, pyridine-water mixtures, ethylene carbonate, propylene carbonate, ethylene trithiocarbonate, and dimethylsulfoxide: the solvent was regenerated by contacting it with a highly aromatic oil stream. Solvent extraction was carried out at 27-93 °C; regeneration was carried out at below 52 °C lower than the extraction step, suitably with vacuum gas oils, vacuum residues, and (preferably) catalytic cracking residues. The choice of solvent depends on a solubility parameter characterized by certain values of dispersion forces, dipole-coupled forces, and H-bonding forces. Preferred solvents are ethylene carbonate, propylene carbonate, ethylene trithiocarbonate, and dimethylsulfoxide[29].

4.2. Catalytic hydroprocessing

Catalytic hydroprocessing is a hydrogenation process used to remove compounds containing nitrogen, sulfur, oxygen and/or metals from liquid petroleum fractions. These compounds adversely influence equipment and catalysts in the refinery. A reduction in the amount of metals in the oil is accomplished by the process of hydro-demetallization (HDM), where the molecules that contain metals lose these atoms by reactions of hydrogenation. The products of HDM reactions can accumulate in the catalyst pores, causing the formation of deposits which end up obstructing those pores irreversibly, blocking access to the catalyst sites and leading to a progressive loss of catalytic activity[66-69]. Therefore, hydroprocessing units are installed prior to units for processes such as catalytic reforming and catalytic cracking so that the expensive catalyst is not contaminated by untreated feedstock. One of the most practical and effective methods of feedstock demetallization (especially for vanadium and nickel) is the use of HDM catalysts. It

has been shown that the most active HDM catalysts are those prepared from synthetic aluminium oxide or natural aluminium silicate enriched with the oxides of molybdenum, cobalt and nickel. The natural aluminosilicate activated with sulfuric acid was found to be best at removing vanadium and nickel[29]. Further, HDM catalysts with very small amounts of oxides of active metals belonging to sixth and seventh subgroups of the periodic table of the elements were found to be several times more effective than the usual hydro-desulfurization catalysts. The use of model compounds in reaction kinetic studies has provided valuable insight into the fundamental processes occurring in resid HDM. The reaction of Ni and V porphyrins under commercial HDM conditions involves a sequential mechanism on two distinct types of catalytic sites. The porphyrins are initially hydrogenated, forming precursor species that subsequently undergo ring cleavage reactions, depositing the metal on the catalyst surface. The resulting metal deposition ultimately deactivates the catalyst through fouling and pore blockage. Investigation of nonporphyrin metallic compounds has not been very extensive, and their behavior during HDM are not known. It is expected that these compounds will behave roughly the same as porphyrin compounds. There are indications that the nonporphyrin metallic compounds may cause more severe problems than the porphyrins.

4.3. Analysis of metalloporphyrin

The American Society of Testing Materials (ASTM) recommends metal determination in crude oil and residual fuels by using dry ashing or dilution in organic solvents according to ASTM D 5863 and ASTM D 5708 methods. They provide the methods for Ni, V, Fe and Na determinations by flame atomic absorption spectrometry (FAAS) and Ni, V and Fe determinations by ICP OES, respectively[38]. Flores suggested that a method for light and heavy crude oil digestion using microwave-induced combustion (MIC) in closed vessels to determine the Ag, As, Ba, Bi, Ca, Cd, Cr, Fe, K, Mg, Li, Mn, Mo, Ni, Pb, Rb, Se, Sr, Tl, V, and Zn by inductively coupled plasma mass (ICP-MS) spectrometry[38]. Many researchers have attempted to quantify metalloporphyrins in crude oil by using the extinction coefficients of isolated V(II) compounds or model compounds. Freeman and O'Haver applied derivative UV/Visible spectroscopy to quantify the concentration of metalloporphyrins in de-asphalted bitumen samples[69]. They found significant absorbance by non-porphyrinic compounds in the region of the Soret Band at around 400 nm and therefore had to resort to using the α band. In order to counteract the reduced sensitivity of this peak, data smoothing and second derivative algorithms were applied to the spectrum. These data analysis algorithms serve to improve the signal-to-noise ratio, which is a major difficulty when dealing with complex mixtures where significant background absorbance is present. In the end, they concluded that the optimal algorithm was a second derivative, 3 point sliding average algorithm. Freeman et al. extended this analysis further by applying third derivative UV/Visible spectroscopy for the qualitative identification of metalloporphyrins[69]. The use of the third derivative of the absorbance allows for a much more precise identification of the exact wavelength (to within ± 0.1 nm) of an absorbance maximum since the third derivative is characterized by a

steep zero crossing at an absorbance peak. This method allowed the investigators to differentiate a number of different metalloporphyrins based on the UV/Visible spectra alone. This method requires that the petroporphyrins separated and/or purified prior to analysis. In this research, the nickel and vanadium metals in the vacuum residue have been eliminated by the combination of solvent separation process and chelating process[6,69]. The solvent separation process is capable of removing all or a substantial amount of metals from the vacuum residues that are destined for further processing such as in the middle of refining step. Park applied UV/Visible spectroscopy and SIMS-TOF to prove the elimination of Ni and V in the asphalted phase of the heavy vacuum residual oil by MCM-48 adsorbent[16]. Distillation separates crude oils into fractions according to boiling point, so that each of the processing units following will have the feedstock that meet their particular specifications. The metallic constituents concentrate in the residues. The short-path distillation of atmospheric residues from California crude oil at 358 °C removed 98% of metalloporphyrins [29]. The vapor phase contained metal complexes 92% of which were metalloporphyrins. The hydrotreatment of this distillate diluted with gas oil in a fixed bed of a low-activity catalyst removed all the metalloporphyrins. The spectroscopic analysis of metalloporphyrins remaining in the distillate-gas oil after very mild treatment suggested that they were degraded to chlorins which were intermediates in either thermal or catalytic residuum demetallization[30,29,54].

5. Concluding Remarks

An energy crisis will occur when the supply of energy resources do not meet the consumption level. It will come suddenly that the maximum rate of global petroleum extraction reach to peak. Therefore, any kinds of researches regarding on refining of heavy oils will be good at upcoming conventional oil shortage period. The residue from vacuum distillation of conventional oil, referred to vacuum residues (VR), has similar physicochemical properties with heavy oil. In this article, we have studied about aquathermolysis reaction and applied it to VR upgrading technology. Since viscosity reduction of heavy oils is important, aquathermolysis technology has been studied intensively, and then applied onto upgrading of VR.

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