Heavy oil with API gravity between 10° and 20° occurs as a type of unconventional oil deposit worldwide. Unconventional reservoirs are vastly undeveloped for the simple reason that the reserves are much more difficult, and therefore more costly, to produce, transport and refine than conventional types of oil and gas. The known estimated resources of heavy oil and bitumen globally total 6.2 trillion barrels. Exploitation of this huge amount of unconventional oil is now becoming necessary to meet the growing demand for light types of oil.

Direct upgrading of heavy crude oils is difficult. Distillation typically yields low levels of distillates, and the remaining residues cannot be added in significant amounts to fluid catalytic crackers because of their extraordinarily high levels of metals and Conradson carbon residue (CCR). These metals and the asphaltenic carbon fraction deactivate the catalyst by obstructing the pores, destroying the activity of the active centers, and generating pressure drops. The conventional solution has been coking, one of several thermal cracking processes, which has traditionally been the process of choice for upgrading heavy oils. Currently, the major heavy oil process used in U.S. refineries is delayed coking; which results in about 20-40 % of very low-value precipitate (coke), presenting potential disposal difficulties. The preferred alternative to delayed coking is a severe hydrotreatment process, which is significantly more expensive and produces only 50-60 % of useful residual oil, the remainder being a high-sulfur fuel oil, which is becoming difficult to market without sulfur removal. Two other processes, visbreaking and solvent deasphalting, practiced mainly outside the U.S., are equally inefficient and costly. The key common problem with these processes is the inability to convert asphaltene (AS) to oil, which results in the formation of coke, a product of low value.

Consequently, the need for better technology for refining heavy oil into clean fuels is becoming acute. In addition, environmental restrictions on both refining processes and refined products are becoming more stringent.

1.2. Pretreatment of Heavy Oils to Remove Metals

Heavy oils contain significant quantities of metals, mainly nickel, vanadium and iron, as well as contami-
nants containing sulfur and nitrogen heteroatoms\(^8\sim\)\(^{11,12a,12c}\), which pose problems for the economical upgrading of heavy oils. Although these metals are only present in trace quantities, they create a particular problem for refineries due to accumulation of metal contaminants on the catalysts resulting in permanent deactivation of both desulphurization and cracking catalysts\(^8\),\(^{13}\). Heavy oils and bitumen contain higher concentrations of vanadium than nickel with a few exceptions\(^7\),\(^8\),\(^{11},\(^{13})\). Vanadium compounds present in the saleable oil form vanadium pentoxide during combustion raising concerns of toxicity if emitted directly to the environment from a stack, as well as corrosion concerns for turbines if used in power generation\(^8\). These problems will be magnified as shortages of lighter oils are compensated by ever greater use of heavy oils. Therefore, removal of these metal contaminants from heavy oils and bitumen is highly desirable.

Conventional metal removal processes used in industry fall into three categories: deasphalting, coking, and catalytic hydrometallation\(^9\). Deasphalting is based on physical processes which precipitate some or all of the asphaltene (AS) fraction from the feed, resulting in significant removal of metal\(^17\) since the metal partitions preferentially within this highly polar, highly aromatic fraction. However, this precipitation process removes a large amount of convertible material along with the metal-containing species\(^19\), making the process non-selective. Coking, the most widely used technology, removes the metal almost completely in the coke byproduct\(^19\). However, the presence of any metal in the final product causes the above mentioned problems during combustion. Coke itself also represents significant loss of product as well as loss of a potential revenue stream. Finally, although catalytic hydrotreating is selectively capable of removing the metal as a metal sulfide deposit on the catalyst surface\(^6\), this process is not economical or practical for heavy, high-metal content residues because the metals cause poisoning of the catalysts\(^18\),\(^20\), increasing the catalyst cost as well as the energy cost in the form of elevated temperatures, pressures, and hydrogen consumption.

1.3. Literature Survey

Research into catalytic hydro-demetallation (HDM) as a selective process for demetallation of crude oil has been described in the open literature. The pioneering and remarkable HDM kinetics studies using model compounds were conducted by Wei and co-workers\(^5\).\(^{5a,5b,6,11,14}\). Further studies were effectively carried out by Weitkamp et al.\(^{21}\), Chen and Massoth\(^{22}\), Bonné et al.\(^{23a,23b}\) and Lopez et al.\(^{23}\) in the temperature ranges of 125-400 °C. These studies could remove 90 % of metals, but the process requires high investment and operation costs and long reaction time (8-9 h)\(^{4a,5a,6,7,11,14})\sim(16,18)\sim(22,23a,23b)\). Bonné et al.\(^{23b}\) and Rankel\(^{24}\) studied HDM reactions in the absence of a catalyst and found low conversion. Current research is driven by the search for greener or environmentally benign chemical processes\(^{25}\). Mandal et al.\(^{12a,12c}\) operated a pioneering non-catalytic study on demetallation of heavy oil using supercritical water (SCW), the state of water at a temperature and pressure above its critical points (374 °C and 22.1 MPa). Their model-compound study revealed that SCW is capable of removing metal from metalloporphyrins (MPs) without the addition of catalyst, hydrogen or hydrogen sulfide so as to reduce operation cost and reaction time and to create a green process.

This review examines the literature on the properties of SCW to remove metals from heavy oil and bitumen.

2. Porphyrins

The porphyrins are a group of naturally occurring intensely coloured compounds, with the name derived from the Greek porphura meaning purple. These molecules are involved in a number of biologically important roles, including oxygen transport and photosynthesis, and have applications in a number of fields, ranging from fluorescence imaging to medicine\(^26\). Porphyrins are classified as tetrapyrrolic molecules, with a heterocyclic macrocycle as the center of the molecule, known as porphine\(^21\). The fundamental porphine framework consists of four pyrrolic sub-units linked on opposing sides at the \(\alpha\)-positions, numbered 1, 4, 6, 9, 11, 14, 16 and 19 (Fig. 1(a)) through four methine (CH) bridges at the 5, 10, 15 and 20 positions known as the meso-carbon atoms/positions (Fig. 1(a)). The resulting conjugated planar macrocycle may be substituted at the meso- and/or \(\beta\)-positions at 2, 3, 7, 8, 12, 13, 17 and 18. If a single hydrogen atom is attached to each of the meso- and \(\beta\)-carbons and two of the inner nitrogen atoms (pyrrolenines) are protonated, the compound becomes a free-base porphine. The resulting compounds are known as porphyrins if the meso- and/or \(\beta\)-hydrogens are substituted with non-hydrogen atoms or groups.

3. Trace Elements in Heavy Oil

Trace elements contents in crude oils and bitumens range from less than a part per billion (ppb) to more than several thousand parts per million (ppm)\(^{27}\). The most abundant trace elements in petroleum are V, Ni, and Fe. Nickel and vanadium have been identified at levels ranging up to 200 ppm and 2000 ppm, respectively\(^{27}\). The concentrations of other trace elements are generally less than 100 ppm. These stable metals occur primarily as complexes and can be distilled at temperatures above 500 °C\(^{28}\). The exact molecular form of these metal complexes is still controversial among the researchers within this field. Treibs\(^{29a,29c}\)
was the first to demonstrate the presence of MPs of V and Fe in a wide range of petroleums and bitumens\(^30\); those of Ni were identified later. This discovery spurred searches for these complex compounds in a variety of samples of different geological origins. The molecular species of trace elements in petroleum other than V and Ni are still obscure\(^31\). Nickel and vanadium occur in oils and source-rock bitumens as MPs and non-porphyrin species. The porphyrins encountered in the crude oils, etioporphyrins (EPs) and deoxophylloerythroetioporphyrins (DPEPs), and their homologues are more frequently observed. Smaller amounts of benzo and other complex porphyrins are also found. Most vanadium atoms in petroleum have a valence of \( \text{IV} \), almost exclusively as vanadium ions, VO\(^{2+} \)\(^{5a,5b} \), and nickel occurs exclusively in the \( \text{II} \) valence state\(^11\). The chemical nature of nonporphyrins is not well established. These are polar compounds and largely occur as cations of organic acids. Nitrogen, oxygen and sulfur can all act as donors in various combinations in nonporphyrins\(^32\). These are predominantly associated with the ASs, the hydrocarbons that dissolve in toluene but are insoluble in \( n \)-heptane.

Major research on metals in petroleum include the pioneering contributions of Yen and coworkers\(^33\), analytical studies by Jones\(^34\), reviews by Valkovic\(^35\), Barwise & Whitehead\(^36\), and extensive studies by Filby and coworkers\(^27,37,38\). Curiale\(^39a,39b\) pointed to the importance of the biota as a possible source of the metals. Modern techniques of ICP-MS and others have provided an abundance of data, still incompletely interpreted. Treibs\(^29a\)\(^29c\) showed that these porphyrins derive from bacterial and plant chlorophylls, and to a lesser extent from hemins. The porphyrins chelate V and other metals during sedimentation by displacement of the original chelated metals, Mg (magnesium) and Fe (iron), respectively. Approximately 2 to 54 % of vanadium and 1 to 47 % of nickel in crude oils occur as extractable MPs\(^38\), with the rest present as other, non-extractable, largely unknown organic structures, which may include MPs strongly associated or incorporated into the ASs so that they cannot be separated.

The source of V, Ni, and Fe in the oils may also be the fossil organic matter\(^29a~29c,33\), because average transition metal concentrations in crude oil and marine organisms are generally close, within an order of magnitude\(^34,39a\), whereas transition metal concentrations in seawater are several (three or more) orders of magnitude lower, less than 1 ppb for V and 0.48 ppb for Ni\(^40\). However, Lewan and Maynard\(^41\) and Lewan\(^42\) attributed the prevalence of Ni and V in the oils to selective chelation of the organic matter by sea water, in which most other tetravalent and trivalent ions that could form stable porphyrins (e.g., Si, Al, Ti) are either almost absent or occur in oxygen-bearing hydrolyzed forms unavailable for chelation. Under reducing conditions, many divalent metals precipitate as sulfides, becoming equally unavailable, whereas Ni(II) and VO(II) continue to be available, even if at low concentrations\(^27\). Their availability in the depositional environment depends on the pH and redox conditions and sulfide activity\(^41,42\). In strongly reducing, anoxic environments, where the amount of bacterially generated sulfide exceeds the amount of available iron, vanadyl ions are available in the pH 4-8 range whereas nickel is precipitated as aqueous nickel sulfide complexes, so
that vanadyl porphyrins (VO-P) would predominate in the sediments, so expelled oils formed by catagenesis of organic matter in these sediments would have high V/ Ni ratios and high sulfur contents. Conversely, in less anoxic, H2S poor environments, vanadium occurs in the pentavalent form, not available for metallation, whereas Ni2+ cations are available. This would favor the formation of nickel porphyrins ( Ni-P), so that the expelled oils would have low V/ Ni ratio and low sulfur content. To compensate for the low concentrations of Ni and V in seawater, Lewan suggested that when sedimentation is slow, these ions migrate by diffusion from the entire overlying water column into the sediments, resulting in progressive enrichment due to selective retention by the porphyrins. Louda and Baker and Baker and Louda indicated that demetallation of chlorophyll and chelation of porphyrins by V and Ni occur during early diagenesis, at temperatures over 40 °C and significantly below the sediment-water interface, when the compacting buried sediments are no longer in open contact with the overlying water column. Therefore, metallation of organic species during diagenesis may occur at ion exchange sites of active clay mineral surfaces that retain high concentrations of metal ions acquired from the depositional environment. The origin of the non-porphyrin nickel and vanadium complexes and the complexes of other trace elements in crude oils may be primary or secondary. Primary processes include release of metal complexes from kerogen and formation of metal-organic complexes by mineral-kerogen reactions during catagenesis. Secondary processes such as interaction of oils with mineral matter or formation waters during migration, maturation or biodegradation may also affect the concentrations of some elements in crude oils, e.g. Hg.

4. Experimental Section

Mandal et al. used an 8.8 mL batch reactor fabricated from Hastelloy C-276 designed and tested by AKICO (Tokyo, Japan) for a maximum temperature of 500 °C and maximum pressure of 50 MPa. An electric furnace made by AKICO (Tokyo, Japan) was used to heat up the reactor isothermally during experiments. No corrosion product from this type of reactor was detected during control experiments at temperatures of 450 °C and 490 °C. Mandal et al. used vanadyl etioporphyrin (VO-EP), nickel tetrphenylporphine (Ni-TPP) and nickel etioporphyrin (Ni-EP) as model compounds because these materials are available in pure form and are the most common forms of MPs. Toluene was added to the reactor as a co-solvent with SCW. The detailed experimental procedures are summarized elsewhere.

4.1. Analysis

One of the primary characteristics of porphyrin macrocycles is intense absorption of UV/visible radiation. Therefore, electronic absorption (UV/visible) spectroscopy has been widely used in the identification and quantification of MPs in petroleum samples. Mandal et al. performed analysis using a UV/visible spectrophotometer (Shimadzu Model UV-1200) using a 12.5 mm × 12.5 mm × 45 mm cuvette and xylene as a solvent. The samples were scanned from 400 to 800 nm. The concentrations of porphyrin and its hydrogenated intermediate compounds were calculated by applying the Lambert-Beer law. According to this law, A = εlc, where A = absorbance, ε = molar absorption coefficient, l = length of solution the light passes through in cm, c = concentration of solution in mol dm–3.

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. A solution is burnt in a flame suitable to ionize the metal atoms. AAS can measure the total metal concentration irrespective of the chemical form of the metal in the solution phase. Mandal et al. measured the total concentrations of vanadium and nickel in liquid samples using an AAS (Shimadzu AA-6800) equipped with vanadium and nickel lamps. Ali et al. used X-ray fluorescence, XRF, to analyze the vanadium and nickel contents of liquid samples.

Mandal et al. used the following definitions in their study:

Conversion of MP is defined as:

\[
\text{Conversion} (\%) = \frac{W_{0,MP} - W_{1,MP}}{W_{0,MP}} \times 100
\]

where \(W_{0,MP}\) = weight of MP loaded and \(W_{1,MP}\) = weight of MP un-reacted at reaction time \(t\)

Percentage of metal removal is defined as:

\[
\text{Metal removal} (\%) = \frac{W_{P,0,M} - W_{P,M}}{W_{P,0,M}} \times 100
\]

where \(W_{P,0,M}\) = initial percentage of metal present in loaded MP and \(W_{P,M}\) = percentage of metal present in the samples at time \(t\)

The yield of product is defined as:

\[
\text{Yield} (\%) = \frac{W_{IC}}{W_{0,MP}} \times 100
\]

where \(W_{IC}\) = weight of intermediate compounds and \(W_{0,MP}\) = weight of MP loaded.

4.2. Upgrading Heavy Oil Using SCW

SCW acts as a solvent and a reactant in hydrolysis-based reactions, and water molecules often participate as collision partners. Very few studies have been carried out on the pyrolysis of hydrocarbons in SCW. Mandal et al. made a detailed study on heptylbenzene (HPB) decomposition in SCW. Water partial pressure and water density had negligible effects
on the overall heptylbenzene conversion. SCW accelerated phenylolefin and toluene formation by suppressing other reaction paths and formation of precipitate or char compared to pyrolysis without water. Ding et al.53) carried out the pyrolysis of hexadecane under super-critical conditions and Ederer et al.50) studied the reaction mechanism of 1-butylbenzene decomposition in SCW showing that water had no significant effect on the pyrolysis of alkylbenzenes. Very recently, SCWO54),55) was introduced as an important application of reactions in hydrothermal systems (water at high-temperature and pressure). However, most previous studies on SCWO have focused only on heteroatom-containing organic compounds56). Vogelaar et al.57) and Katritzky et al.58)−61) revealed that the effect of SCW on desulfurization of oil is marginal. Some indirect benefit of using SCW was reported for the in-situ generation of H252), as well as using SCW as the medium for hydrotreating Athabasca bitumen53). Mandal et al.12a)−12c) showed that SCW can remove metal from metal porphyrins non-catalytically and in an environmentally friendly way. Literature survey discovered that the effect of temperature on reaction of MPs in SCW is high, whereas WPP has a moderate effect.

4.3. Characterization of Metal Porphyrins

The porphyrin macrocycle is highly conjugated, and a number of resonance forms can be identified. The most significant characteristics of electrons in the UV-Vis absorption spectrum are one Soret band (S band) and several Q bands64). All types of free-metal porphyrins have one strong absorption band (S band) around 400 nm in the near UV region (>105), and four absorption bands (I, II, III and IV) ranging between 500-700 nm65),66) in the UV (Fig. 2). When the metal replaces two hydrogen atoms in the center of the porphyrin ring and forms a metal complex (MPs), the four Q bands in the visible region collapse into essentially two bands (α and β bands) due to the higher D4h symmetry in addition to the strong S band. These two bands are associated with the porphyrin divalent metal coordination link12a)−12c). The wavelength of this S band is always higher than that of free metal porphyrin. An electronic transition to the higher energy mixed state, the S2 state, is strongly allowed, whereas an electronic transition to the lower energy mixed state, the S1 state, is only weakly allowed. The band in the UV-Vis absorption spectrum due to a transition to the S2 state is the Soret band, and the band due to a transition to the vibrationless S1 state is the α band. Therefore, greater mixing will result in a less intense α band relative to the S band. The UV-visible spectrum of porphyrin also contains a vibronic band, the β band, that appears at slightly lower wavelengths than the α band. The β band is due to transitions to higher vibrational levels in the S1 state and serves as a “normalization band” in porphyrin absorption spectra. Table 1 shows the absorption wavelengths of some MPs.

4.4. Effect of WPP for Removing Metal

Water partial pressure (WPP) has a moderate effect on the demetallization process. The purpose of using SCW as the reaction medium is to break the nitrogen-metal (N-M) bonds of MP chelates. Mandal et al.12a)−12c) carried out experiments at 450 °C, with WPPs of 25-45 MPa and a reaction time of 60 min in a toluene environment using model compounds, which revealed that MP compounds react with SCW. The conversion of MPs increased with higher WPP (Fig. 3). The experiments for Ni-EP revealed that conversion of Ni-EP slightly increased linearly at WPPs of 25-35 MPa. Similar results were discovered during experiments using Ni-TPP at 450 °C with a reaction time of 60 min. Beyond this, the effect increased exponentially up to

| Table 1 | Location of Absorption Maxima for Metal Porphyrins5a),5b),8),65) |
|-----------------|-----------------|-----------------|
| Metal porphyrin | Solvent         | Wavelength at maximum [nm] |
|                 |                 | Soret band | β band | α band |
| Vanadyl etioporphyrin (VO-EP) | Dichloromethane | 406.6 | 523.80 | 559.5 |
| Vanadyl benzoetioporphyrin (VO-BEP) | Xylene | 414.0 | 544.7 | 578.7 |
| Vanadyl octaethylporphyrin (VO-OEP) | Dichloromethane | 407.3 | 533.2 | 570.9 |
| Vanadyl deoxophylloerythroetioporphyrin (DPEP) | Dichloromethane | 410.5 | 533.3 | 573.0 |
| Nickel etioporphyrin (Ni-EP) | Dichloromethane | 391.0 | 517.0 | 553.0 |
| Vanadyl meso-tetraphenylporphyrin (VO-TPP) | Xylene | 422.0 | - | 548.0 |
| Nickel meso-tetraphenylporphyrin (Ni-TPP) | Dichloromethane | 414.0 | - | 527.5 |

Fig. 2 Typical Porphyrin Absorption Spectrum (etio-type)
the WPP of 45 MPa and the value of Ni-EP conversion increased from 60.04 to 76.41%. The amount of nickel removed increased almost linearly and varied from 46.89 to 54.77% under the aforementioned experimental conditions. The most remarkable findings were that more hydrogenated species were generated above WPP of 40 MPa, indicating the capability of SCW to induce the hydrogenation reaction.

Additional experiments using VO-EP were performed at 450 °C, with a reaction time of 60 min and WPPs of 10-45 MPa in a toluene environment to evaluate the WPP effect on reaction of VO-EP with SCW. Experiments at WPPs of 10-20 MPa found that some un-dissolved VO-EP remained after reaction, but above the water partial pressure of 20 MPa, un-dissolved VO-EP was not detected. Similar effects occurred at shorter reaction times (below 60 min). Therefore, data for shorter reaction times are not accepted for reaction kinetic study. Similar experimental results were observed in experiments using Ni-EP and Ni-TPP, because water molecules enter into the un-dissolved MP molecules and reduced its solubility in toluene or xylene. Sato et al. discovered that water molecules act as a collision partner with increasing temperature and pressure. There are two steps of operation at high pressure and longer reaction time to overcome this problem: (1) dissolving MPs in SCW and toluene or breaking their solid structure to increase solid surface area by collision with SCW, and (2) reaction of MPs with SCW. MP conversions as a function of WPP are depicted in Fig. 3. Conversion of VO-EP was almost constant at WPP of 25-30 MPa, and VO-EP conversion increased linearly with WPP up to the maximum observed WPP. Percentage of vanadium removal also followed the same trend suggesting that vanadium removal increased with VO-EP conversion. Therefore, WPP had a remarkable effect on the reaction of VO-EP with SCW above 35 MPa. Nevertheless, donation of hydrogen to form hydrogenated species, the collision partner, the cage effect (how properties of a molecule are affected by its surroundings), water attack on species or thermolysis, and change of phase behavior would affect the basic characteristics of SCW during reaction with MPs.

4.5. Effect of Temperature

Demettallization takes place at high temperatures and pressures in the presence of SCW. Temperature has a considerable effect on the reaction. Mandal et al. carried out a lot of experiments at temperatures between 400 °C and 500 °C and WPP of 25 MPa to explore the temperature effect using MPs as model compounds. Figure 4 illustrates the high capability of metal porphyrin conversion which increased with reaction time and high temperature. The reaction data were explored up to a reaction time of 180 min and approximately 90.51% VO-EP and 95.02% Ni-EP were converted to intermediate and final products at 490 °C. The reaction did not complete at the high temperature of 490 °C, and the conversion did not change significantly over periods exceeding 90 min. This behavior indicates the occurrence of a reversible reaction and establishment of the equilibrium after a reaction time of 90 min at 490 °C.

Metal removal as a function of MP conversion is displayed in Fig. 5. Metal removal increased almost exponentially with conversion at all temperatures and approximately 80.26% vanadium and 76.41% nickel were removed at the highest conversion level. Bonné et al. reported that the fate of the central metal groups after demettallation under non-catalytic conditions remained obscure. However, metals are deposited on the catalyst surface as metal sulfides during the catalytic demettallation reaction. The fate of the central metal group in the reaction of MP under SCW conditions was also obscure, although the formation of metal hydroxides, metal oxides and metal ions is likely. Mandal et al. revealed that the yield of most hydrogenated species initially increased and then decreased slowly after reaching a maximum value at all
temperatures indicating that these are intermediates in the overall reaction. This observation agrees well with the chemistry of MPs. MPs can be hydrogenated several times successively under chemical reduction until the porphyrin macromolecule is broken, with loss of the porphyrinic character\(^{7}\). The intermediate products of chemical reactions are hydrogenated species of metal porphyrins (MPs). If metal is removed from the porphyrin structure, the porphyrin structure becomes very unstable under the experimental conditions and decomposes into light hydrocarbons. However, no gaseous product was detected under the experimental conditions.

### 4.6 reacted kinetic Study and Mechanism

According to the studies of Bonné \textit{et al.}\(^{23b}\) and Mandal \textit{et al.}\(^{12a} - 12c\), a comparative plot of conversions of free-base tetraphenyl porphine (H\(_2\)-TPP), Ni-TPP, vanadyl tetraphenyl porphine (VO-TPP), Ni-EP and VO-EP under different reaction conditions is given in Fig. 6. The operating temperature, pressure and catalyst for each experiment with and without catalyst were 287 °C, 5 MPa with hydrogen and sulfided Mo/Al\(_2\)O\(_3\) catalyst, respectively. In addition, the operating temperature and WPP for each experiment using SCW were 490 °C and 25 MPa, respectively. Metal-free porphyrin is obviously more reactive than MPs, which indicates that the central metal group stabilizes the molecule with respect to hydrogenation and ring fragmentation. The conversion of Ni-TPP in SCW is high compared to Ni-EP and VO-EP under identical reaction operating conditions. Zuang \textit{et al.}\(^{70}\) revealed that the MP complexes have higher thermal stability (no decomposition until 200 °C). Mandal \textit{et al.}\(^{71a} - 71c\) also showed that the solid MP complexes are stable below 400 °C, and WPP of 25 MPa in a non-toluene environment. Therefore, Mandal \textit{et al.}\(^{12a} - 12c\) explored reactions at temperatures between 400-500 °C and WPP of 25 MPa or above in the presence of toluene, which is stable under these experimental conditions. Chemistry of MPs revealed that MPs are hydrogenated several times successively under conditions of chemical reduction until the porphyrin macromolecule is disrupted, with loss of the porphyrinic character\(^{23b}\). Therefore, most researchers used hydrogen and catalyst for the hydrogenation reaction. Mandal \textit{et al.}\(^{12a} - 12c\), 71a\(^{ -} 71c\) used SCW, which is a hydrogen donor, without adding catalyst and H\(_2\)/H\(_2\)S, and found that hydrogenation reactions are involved during the course of reaction. Apparently, the thermal effect, the number of intermediate hydrogenated species and their concentration levels in the course of the reaction, and the central metal group are important during the reaction. As the covalent metal-nitrogen bonds are weakened, the porphyrin macrocycle may become more vulnerable to...
successive hydrogenation reactions and ring fragmentation caused by, for example, thermal cleavages. Four hydrogenated intermediates were found in the reactions of Ni-EP and VO-EP, but the concentration levels of vanadium analogues appeared to be much higher than nickel analogues. The reason may be that the VO$^{2+}$ group has a stronger electron attraction than Ni$^{2+}$, resulting in a less basic and, consequently, more readily reduced porphyrin macrocycle. Mandal et al.\textsuperscript{12b,12c} discovered that the reaction of MPs, VO-EP and Ni-EP, respectively, in SCW demonstrably followed first order kinetics and the temperature dependent rate constant can be expressed by the following Arrhenius equations:

\[
k_1(T) = 5.66 \times 10^{-8} \exp \left( \frac{-5689}{RT} \right), \text{ at constant pressure of 25 MPa (4)}
\]

\[
k_2(T) = 2.17 \times 10^3 \exp \left( \frac{-108}{RT} \right), \text{ at constant pressure of 25 MPa (5)}
\]

The activation energies of the reaction of VO-EP and Ni-EP under SCW are 8.93 kcal per mol and 10.03 kcal per mol, respectively. The activation energy of Ni-EP is 12.32% higher than VO-EP indicating that 12.32% higher energy is required to react Ni-EP with SCW than VO-EP. The rate equations of VO-EP and Ni-EP revealed that the rate constant of Ni-EP is higher than VO-EP for a constant temperature indicating higher reactivity. Smith and Wei\textsuperscript{6} disclosed that if both species of vanadyl and nickel compounds are present, vanadyl compounds are more reactive than nickel compounds under hydrodemetallization conditions. In 1991, Smith and Wei\textsuperscript{6} discovered that single species VO-EP reactivity is lower than that of single species Ni-EP, under conditions of 320°C, hydrogen pressure of 4.8 MPa, and sulfided CoMo/Al$_2$O$_3$ catalyst. Mandal et al.\textsuperscript{12b,12c} has also disclosed similar results using single species VO-EP and single species Ni-EP under SCW conditions.

Mandal et al.\textsuperscript{12b,12c} proposed a kinetic model which fits the experimental data well\textsuperscript{12c}. The kinetic analysis was carried out based on the assumption that each reaction follows the first-order reaction rate law. The first step of MP disappearance involved reversible hydrogenation of a peripheral double bond in one of the four pyrrole rings to form a hydrogenated species (Fig. 7). In parallel, metal was removed from the MP core by reacting with the OH of SCW and ring fragmentation phenomena due to the instability of metal-free porphyrins under the reaction conditions. Finally, the hydrogenated species reacted via a hydrogenolysis step which fragmented the ring and removed the vanadium. The reaction mechanism can be explained in terms of the free radical mechanism (Fig. 8). Literature review revealed that the hydrothermal reaction mechanism depends on water density: the reaction is controlled by the ionic reaction mechanism at high water density and low temperature; whereas the free radical reaction mechanism is prevalent at low water density and high temperature\textsuperscript{67,68}. Ionic product falls by orders of magnitude under SCW conditions\textsuperscript{69}, so radicals can be formed under the experimental conditions. In the case of MP, donation of d-orbital electrons from the central metal, vanadium, to the π-system of the porphyrin macrocycle contributes to the preservation of the aromatic character.
to form radicals. Thus, the reaction was initiated by producing H, OH and MP radicals; and propagated to form radicals of hydrogenated species as well as to form M(OH) and P radicals by reacting with MP and OH radicals. Finally, termination occurs by crosscombination of the free radicals to form stable products.

5. Conclusions

Various methods for demetallization of heavy oils have been developed to reduce the difficulties of the upgrading process. Catalytic demetallization is only viable for demetallization of heavy oil. The SCW upgrading process is the current most interesting environmentally benign process. SCW without the addition of catalyst can remove metal from MP complexes above 400 °C and WPP of 25 MPa. Demetallization is not observed to occur below these conditions. Formation of intermediate hydrogenated compounds during the reaction reveals that SCW is a hydrogen donor. Substantial amounts of MP are converted into intermediate compounds and intermediate products, in addition to MP decomposed by removing metals. The effect of WPP on the reaction is moderate, but the effect of temperature is considerably higher. Metal removal is sensitive to conversion of MPs and increases exponentially with higher conversion. The kinetics are consistent with first-order dependency on MP disappearance and can be explained with the free radical mechanism. The fate of metals after the reaction is not clear. Additional study on demetallation of heavy oil using SCW is required to observe the fate of metals after reaction before making the process industrially viable.

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要旨

超臨界水を用いた重質油からのニッケルおよびバナジウム除去技術

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重質油から経済的に使用可能な軽質油燃料（軽油や灯油など）を得るために高品質などの改善（低分子量化や軽質化）が必要となる。それに加え、現在稼働中のガスタービンシステムでは、重質油中のバナジウム、ニッケルの除酸ガスを引き起こすことが知られており、多くの実用機では軽質油燃料を使用することを必要としているが、その状況である。この課題を解決するために、重質油中のバナジウム、ニッケルを除去する技術（脱メタル技術）として物理的手法、化学的手法（電気化学や触媒反応）、効率的な脱メタル技術の確立のために脱メタル技術の開発が進められている。本報では、重質油からのバナジウム、ニッケル除去に対し、超臨界水を用いた場合の最近の研究事例について学術論文を中心に集約し、超臨界水中での脱メタルプロセスの適用を向けて実際可能性と課題について整理した。超臨界水反応場における水の分圧が金属ポルフィリンの水素化およびメタル脱離に一定の効果を示すことが明らかになった。しかしながら、反応物質が脱メタルに与える効果は圧力効果に比べ著しく高く、かつ脱メタル速度が金属ポルフィリン濃度に一次に依存するフリーラジカル機構により説明できることを明らかにした。この超臨界水中触媒下での脱メタル技術は、従来技術に比べ環境面、反応効率、製造コストなどあらゆる面で従来技術を代替する潜在的可能性を秘めている。利用可能な脱質プロセス開発のために、今後ますますの基盤・応用研究が推進されることを期待している。