[Review Paper]

Upgrading of Ultra-heavy Oil with Iron-based Oxide Catalysts Using the Chemical Reaction Engineering Approach

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Our recent studies of the application of iron-based oxide catalysts to upgrading of heavy oils under sub-/super-critical water conditions are reviewed. The effect of reaction parameters on the product yields were investigated for the reaction of bitumen over iron-based oxide catalyst. Reaction pressure greatly affected the product yield, indicating that formation of carbonaceous solid product, called coke, decreased with increase in pressure, and the yield of lighter component (Gas Oil and VGO) was the highest under sub-critical water conditions using both batch and flow type reactors. Kinetic analysis and reaction paths for the decomposition of bitumens were investigated. The decomposition reaction of VR (vacuum residual oil) in bitumen was assumed as second order kinetics, and the activation energy was calculated as 132 kJ/mol. Reaction kinetics were analyzed in details using the Lumping Model. The assigned reaction rate constant for each lump revealed that VR was consecutively converted into VGO, Gas Oil, and Gas, and coke formation was suppressed under sub-critical water conditions, as compared with the main reaction path. Therefore, the reaction process using iron-based oxide catalyst can be applied for the on-site upgrading of heavy oil including bitumen derived from the SAGD (Steam Assisted Gravity Drainage) method, in which bitumen is mined with water under high temperature and pressure.

Keywords
Heavy oil, Iron-based oxide catalyst, Super-critical water, Sub-critical water, Kinetic analysis

1. Introduction

1.1. Upgrading of Heavy Oils

Recent rapid economic growth of developing countries has led to increased demands for energy sources worldwide. Fossil fuels remain an important source of energy and still provide a major part of the world energy supply. However, the potential for expansion of the reserve-production ratio of crude oil in the world may be limited1). On the other hand, plenty of unused carbon resources such as oil-shale, Orinoco-tar, and oil-sand bitumen are available, in addition to the conventional refinery products of AR (atmospheric residual oil) and VR (vacuum residual oil). Future technological developments for upgrading these heavy oils are expected to be more than double the reserve-production ratio of crude oil.

Upgrading of heavy oils requires increasing the ratio of hydrogen to carbon (H/C ratio). The main technologies can be classified as decarbonization2), hydrogenation3−5), gasification6) and steam cracking7) as shown in Table 1. Pyrolysis, which is a type of decarbonization process, breaks up the residual oils by heating in the absence of a catalyst, such as the Visbreaker, Fluid Coker and EUREKA processes. RFCC (residue fluid catalytic cracking) is a typical decarbonization process with catalysts. Hydrogenation is intended to desulfurize and decompose heavy oil with resultant increased hydrogen/carbon (H/C) ratio by adding hydrogen gas under high pressure and temperature in the presence of a catalyst. However, the high consumption of hydrogen gas in the hydrocracking process presents an economic challenge. In addition, the hydrogen gas is generally produced from petroleum-derived feedstock such as naphtha, so the supply-demand balance of hydrogen is

| Table 1 Upgrading Processes for Heavy Oils |
|------------------------------------------|
| **Type**        | **Specifications** | **Process example** |
| Hydrogenation   | Hydrodesulfurization | RCD-Isomax, Gulf-HDS |
|                | Hydrocracking       | Isocracking, Unicracking |
| Decarbonization | Pyrolysis           | Visbreaking, EUREKA Coking |
|                | FCC                 | RFCC |
| Gasification    | Texaco              | |
| Steam cracking  | Aquaconversion      | |
difficult. Therefore, steam catalytic cracking is regarded as a promising process, in which hydrogen is generated from co-supplied water. The Aquaconversion process has been proposed, but various water-soluble alkali metal materials were used as catalysts, so that the process cost was high. Accordingly, steam catalytic cracking processes using inexpensive solid catalysts are needed.

1.2. Steam Assisted Gravity Drainage (SAGD) Method for Mining Bitumen

Approximately 80 % of oil sand bitumen is located at great depths, so the steam assisted gravity drainage (SAGD) method is very important, in which high temperature and high pressure steam is introduced into the deeper layers to recover bitumen. The original bitumen recovered by SAGD method has very high viscosity, so that conventional pipeline transportation is not possible. Therefore, post-mining treatment is essential to decrease the viscosity. Various methods of post-mining treatment have been studied with regard to various parameters, such as energy balance and thermal efficiency, to establish practical feasibility.

Hydrothermal treatment under high temperature and pressure is a reasonable and promising method for upgrading oil sand bitumen.

1.3. Development of Iron-based Oxide Catalysts

Catalysts for upgrading heavy oil require the following characteristics: i) activity for decomposing heavy oil, ii) structural stability to aqueous conditions under high temperature and pressure, and iii) resistance to formation of coke on the catalyst. We have developed iron-based oxide catalysts containing CeO2, ZrO2, Al2O3 (CeO2-ZrO2-Al2O3-FeO catalysts) and have investigated the reaction process using such catalysts.

Figure 1 shows the function of each component of the CeO2-ZrO2-Al2O3-FeO catalyst. Iron oxide provides the main sites of reaction, where the oxidative cracking of heavy oils occurs using the lattice oxygen. Active oxygen species from the co-supplied water are generated over ZrO2, and supplied to the oxygen vacancy sites of FeO to maintain the activity and stability of the catalyst. Simultaneously, active hydrogen species from water are consumed in the upgrading reaction.

Our previous study investigated the effect of supported ZrO2 on the production of active species of hydrogen and oxygen from water by TDS (thermal desorption spectroscopy) analysis. The amount of active hydrogen species produced over ZrO2-FeO was higher and the peak production occurred at lower temperature, as compared with FeO. The alkene/alkane ratio in lighter hydrocarbons decreased with increase in amount of co-supplied steam in the reaction of AR over ZrO2-Al2O3-FeO catalyst. Therefore, hydrogenation of alkene to alkane proceeded during the upgrading of heavy oil over iron-based oxide catalyst.

CeO2 has the so-called oxygen storage/release capacity, which is effective for balancing the amount of active oxygen species generated from water over the catalyst. Addition of Al2O3 was effective for increasing the surface area of the catalyst, and for enhancement of the physical stability of the catalyst.

Iron-based oxide catalysts have been used for the catalytic reaction of various types of biomass such as palm shell oil, glycerol, cacao pod husk, lignin, pyroligneous acid, and ethanol fermentation residue as compared with FeO, which succeeded in the production of useful chemicals. In addition, iron-oxide based catalyst effectively upgraded conventional heavy oils such as AR and VR in the presence of superheated steam under one atmosphere pressure.

The present review examines our recent studies of the application of iron-based oxide catalysts to upgrading of heavy oils, especially bitumen, under sub-/supercritical water conditions.

2. Experimental

2.1. Preparation and Characterization of Iron-based Oxide Catalyst

Iron-based oxide catalyst (CeO2-ZrO2-Al2O3-FeO) was prepared by a co-precipitation method, using aqueous Ce(NO3)3·6H2O, ZrO(NO3)2, Al(NO3)3·9H2O, and Fe(NO3)3·9H2O (FUJIFILM Wako Pure Chemical Corp.) as precursors. The compositions of CeO2, ZrO2, and Al2O3 were set as 2.5, 7.5, and 7.0 wt%, respectively. The crystal structure and porous properties of the catalyst were analyzed by XRD (X-ray diffraction, JDX–8020, JEOL Ltd.) and N2 adsorption isotherms (Belsorp-mini; MicrotracBEL Corp.), respectively.

2.2. Experimental Procedure

Upgrading of bitumen was carried out using batch and flow type reactors. Canadian oil sand bitumen diluted with benzene to 10 wt% to reduce its viscosity was mainly employed as the feedstock. The prepared catalyst was confirmed to be inactive for benzene. Main reaction conditions for each reactor were as follows: Wcat/Wbitumen = 4, Wcat/Wbitumen = 10-20, P = 19-22 MPa, T = 693 K and t (reaction time) = 60 min for the batch type reactor, and Wcat/Fbitumen = 4 h, F_H2O/
2.3. Analytical Procedure

The gas and liquid products were separately collected after the reaction. Gas products were analyzed by GC (GC-8A, Shimadzu Corp.) with FID (hydrogen-flame ionization detector) and TCD (thermal conductivity detector) equipped with activated charcoal and Porapak Q columns, respectively.

The liquid product was separated into water and oil phases with a centrifuge, and the oil phase was analyzed by HPLC (CTO-10A, Shimadzu Corp.) with a PL-gel Mixed-D column using a RI detector. The molecular weight distributions of the bitumen and oil product from HPLC were converted into carbon number distributions by assuming the unit structure of heavy oil as \(-\text{CH}_2\). The product yield was divided into three groups according to the carbon number: gas oil (Gas Oil, carbon numbers 14-20), vacuum gas oil (VGO, 21-40) and vacuum residual oil (VR, >41). Carbonaceous solid deposited on the reactor wall was designated as residue, and coke deposited on the surface of the catalyst was analyzed with an elemental analyzer.

The details of the above experimental procedure were described in our previous studies\(^3\),\(^4\).

3. Results and Discussion

3.1. Clarification of Reaction Cycle over Iron-based Oxide Catalyst Using Heavy Oxygenated Water\(^3\)

The iron-based oxide catalysts are assumed to consume lattice oxygen during the decomposition of heavy oil, which is replaced by active oxygen species from water, resulting in retained catalytic activity and stable structure, as discussed in section 1.3. To confirm this reaction cycle, bitumen was reacted over iron-based oxide catalyst using heavy oxygenated water (H\(_2\)\(^18\)O) and the carbon dioxide produced during the reaction was analyzed using a quadrupole mass spectrometer (Q-Mass).

Figure 2 shows the changes in the gaseous products evolved during the reaction over the iron-based oxide catalyst under one atmosphere pressure. The intensity of the \(m/z = 46\) (corresponding to CO\(^18\)O) increased after supplying the heavy oxygenated water, and the spectrum derived from CO\(^18\)O responded to the supply of heavy oxygenated water. Therefore, at least a part of the carbon dioxide was derived from the heavy oxygenated water, and the iron-based oxide catalyst activity involved the proposed reaction cycle.

3.2. Effect of Reaction Conditions Using Batch Type Reactor

The effect of reaction conditions on the product yields and catalytic stability was investigated for upgrading bitumen over iron-based oxide catalyst using the batch type reactor\(^3\). Figure 3 shows the effect of reaction pressure on the yields of lighter components (Gas Oil and VGO) and coke after upgrading of bitumen at 693 K for 1 h. High yield of lighter components was obtained under higher pressure (around 10-
20 MPa), reaching approx. 70 C-mol%, and the yield of coke decreased with higher pressure. Catalytic reactions under sub-/super-critical solvent conditions are effective for suppressing coke formation on catalysts in reactions such as decomposition of lignin-derived liquid over iron-based oxide catalysts \(^{25}\), and alkylation and transalkylation reactions over zeolite catalysts \(^{35,36}\). Therefore, the coke precursor from the reaction of bitumen was presumably dissolved or dispersed in water under sub- and super-critical water conditions. On the other hand, the recombination reactions of the lighter components seem to proceed under super-critical water conditions, leading to the decrease in the light component yield.

The effect of the concentration of bitumen was also investigated under sub-critical water conditions in the range of 10-100 wt% at 693 K. Yields of lighter components (Gas Oil and VGO) were almost the same (72-73 C-mol%) using different concentrations of bitumen at 19-22 MPa. The reaction was carried out at the weight ratio of water to bitumen \((\text{W}_{\text{H}_2\text{O}}/\text{W}_{\text{Bitumen}}) = 20\), so that the amount of water was adequate and the phase condition predominantly depended on the water state loaded into the reactor.

Assuming that part of the lighter components derived from the upgrading reaction, corresponding to so-called white oil, acted as a solvent of bitumen and was recycled in the process, the effect of diluent solvent was investigated on the product yield for the upgrading of bitumen. Figure 4 shows the reaction results. Almost the same product yields were obtained, and the catalyst maintained the hematite structure after the reaction using different types of lighter component. In addition, NMR (nuclear magnetic resonance) analyses of product liquids revealed negligible reactivity of solvent toward the catalyst. Therefore, white oil obtained during the upgrading of bitumen acted as a solvent of bitumen.

### 3.3. Continuous Upgrading of Bitumen Using High Pressure Flow Type Reactor

Based on the results using the batch type reactor in the previous section 3.2., continuous upgrading of bitumen over iron-based oxide catalyst was evaluated with the high pressure flow type reactor. Figure 5 shows the effect of reaction conditions on the upgrading of bitumen. The yield of lighter components (Gas Oil and VGO) increased to about 70 C-mol%, and the coke amount decreased to 6 C-mol% under the sub-critical water condition, which was consistent with the result obtained from the batch type reactor as shown in Fig. 3.

Durability of catalytic reaction was also examined. Upgrading of bitumen was carried out at 693 K under the sub-critical water condition (19 MPa) for 6 h, with similar product yield to the reaction for 2 h and preserved hematite structure after the reaction \(^{33}\).

To investigate the reaction path for upgrading heavy oil, bitumen was separated into maltene and asphaltene by solvent fractionation using pentane, then the catalytic reaction was conducted using these components as feedstock \(^{37}\). Figure 6 shows the results after the reaction using maltene and asphaltene as feedstock under different conditions. The yields of solid product under normal pressure conditions were about 30 C-mol% from maltene and 80 C-mol% from asphaltene, mainly consisting of residue. In contrast, the yields of solid product under high pressure conditions decreased to about 10 C-mol% and 20-25 C-mol% from maltene and asphaltene, respectively. Moreover, 50-60 C-mol% of...
lighter component was produced from asphaltene under the sub- and super-critical water conditions.

3.4. Kinetic Study for Upgrading Bitumen over Iron-based Oxide Catalyst

The reaction kinetics of the upgrading of bitumen using iron-based oxide catalyst was investigated. Kinetic analysis for the decomposition reaction of bitumen was carried out. Decomposition of heavy components such as VR and residual oil follow second order kinetics\(^{38),39}\). We assumed second order reaction for the decomposition of VR, calculating the reaction rate constant by the integral method. Volume change before and after the decomposition reaction is negligible because of the large volumes of water and benzene compared with that of bitumen. Therefore, we used the following Eq. (1) to calculate the rate constant.

\[
\frac{W}{F} = \frac{1}{k_{\text{VR}O^2}} \cdot \frac{X_{\text{VR}}}{1 - X_{\text{VR}}} \quad (1)
\]

The findings for the reactions of bitumen over iron-based oxide catalyst in the temperature range of 623 to 693 K were used for the analysis\(^{33}\), by calculating the rate constant at each reaction temperature. Figure 7 shows the Arrhenius plot of reaction rate constant for the decomposition of VR. The Arrhenius plot exhibited good linearity, and the apparent activation energy \(E_a\) for the decomposition of VR was calculated from the slope as \(E_a = 132 \text{ kJ/mol}\). For reference, kinetic analysis of the decomposition reaction of AR under normal pressure using iron oxide catalyst found the activation energy of the main heavy component decomposition reaction was 139 kJ/mol\(^{38}\).

Reaction conditions: (a) 8 wt% maltene solution in benzene, \(W_{\text{cat}}/F_{\text{maltene}} = 5 \text{ h}, P = 0.1-26.9 \text{ MPa}, T = 693 \text{ K (19.0 MPa, 26.9 MPa)}\) and 773 K (0.1 MPa), \(t\) (reaction time) = 2 h. (b) 2 wt% of asphaltene solution in benzene, \(W_{\text{cat}}/F_{\text{asphaltene}} = 20 \text{ h}, P = 0.1 \text{ MPa-26.9 MPa}, T = 693 \text{ K (19.0 MPa, 26.9 MPa)}\) and 773 K (0.1 MPa), \(t\) (reaction time) = 2 h.

Fig. 6 Product Yields after Reaction of (a) Maltene and (b) Asphaltene over CeO\(_2\)-ZrO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\) Using a Flow Reactor

Heavy oil contains many types of molecules, so we carried out the reaction rate analysis in detail using the Lumping Model, in which the products were classified into the following lumps: VR, VGO, Gas Oil and Coke. Figure 8 shows the outline of the Lumping Model, and the reaction rate constant of each route was designated as \(k_i\) (\(i = 1-7\)).

The decomposition of the VR lump was represented as second-order as discussed in the section 3.4. On the other hand, the decomposition reaction rates of the other lumps (VGO and Gas Oil) were assumed as first-order as based on previous investigations of VGO and Gas Oil components\(^{38),40),41}\). Based on the lumping
model in Fig. 8, the reaction rates of each lump are expressed as the following Eqs. (2)-(6), and each reaction rate \( r_i \) can be expressed as Eq. (7), where \( y_i, r_i \), and \( C_0 \) are the composition ratio of the \( i \) lump, reaction rate of each component and concentration of bitumen at the reactor inlet, respectively.

\[
\begin{align*}
  r_{\text{VR}} &= -(k_1 + k_2 + k_3 + k_4) C_0^2 y_{\text{VR}}^2 \\
  r_{\text{VGO}} &= -(k_5 + k_6) C_0 y_{\text{VGO}} + k_7 C_0^2 + y_{\text{VR}}^2 \\
  r_{\text{Gas Oil}} &= -k_3 C_0 y_{\text{Gas Oil}} + k_8 C_0 y_{\text{VGO}} + k_9 C_0^2 y_{\text{VR}}^2 \\
  r_{\text{Gas}} &= k_3 C_0 y_{\text{Gas Oil}} + k_8 C_0 y_{\text{VGO}} + k_9 C_0^2 y_{\text{VR}}^2 \\
  r_{\text{Coke}} &= k_1 C_0^2 y_{\text{VR}}^2 \\
  r_i &= \frac{d y_i}{d \left( \frac{W}{F} \right)}
\end{align*}
\]

The differential equations of (2) to (7) were solved using the Runge-Kutta method and the rate constants were calculated by the least squares method. This analysis was performed based on a pseudo-Newton method.

Figure 9 shows the change in product distribution with respect to \( W/F \), with experimental data and analytical values. The calculated rate constants of each route are summarized in Table 2. Figure 9 revealed that the analytical values were in good agreement with the experimental data.

The production/consumption route of each lump was examined based on the rate constants in Table 2. The rate constants of VR consumption were as follows: \( k_1 > k_2 > k_3 > k_4 \) (\( \sim 0 \)), suggesting that the pathway from VR to VGO predominates over the reaction of VR. The consumption route of VGO had rate constants of \( k_5 > k_6 \). Therefore, VGO was mainly converted to Gas Oil. Production of Gas from VR and VGO was determined by, \( k_3 \) and \( k_6 \), indicating that Gas was predominantly produced from VGO.

These results indicate that VR was consecutively converted into VGO, Gas Oil and Gas (\( \text{VR} \Rightarrow \text{VGO} \Rightarrow \text{Gas Oil} \Rightarrow \text{Gas} \)).

Moreover, VR was preferentially converted into VGO, by comparing the decomposition of VR into VGO (\( k_1 \)) with Coke (\( k_4 \)). Our kinetic analysis showed that the formation of coke was effectively suppressed in the reaction of bitumen under sub-critical water conditions using iron-based oxide catalyst.

4. Conclusion

Upgrading of bitumen using iron-based oxide catalyst was carried out under sub-/super-critical water conditions, and the reaction process was analyzed by the chemical reaction engineering approach. The upgrading reaction under sub-critical water conditions achieved both high yield of light component and reduced formation of coke. Reaction kinetics were investigated in detail using the Lumping Model, indicating that the reaction under sub-critical water conditions was effective using iron-based oxide catalyst. Therefore, the reaction process using iron-based oxide catalyst is expected to be applied for on-site upgrading of heavy oil including bitumen derived from the SAGD method, as shown in Fig. 10.

Moreover, we have developed another type of catalyst, TiO\(_2\)-ZrO\(_2\) catalyst, for upgrading heavy oil\(^{[22]}\). Details are omitted in this review due to limitations of space, but the TiO\(_2\)-ZrO\(_2\) catalyst has acidic properties, resulting in higher yield of lighter component and lower yield of coke compared with the iron-based oxide catalyst under atmospheric pressure.

Reserves of heavy oil have been confirmed worldwide, but characteristics such as viscosity, composition

| Table 2 | Reaction Rate Constant for Each Reaction Route |
|---------|-----------------------------------------------|
| 2nd order rate constant \( [10^{-2} \text{ m}^3 \text{ (kg-oil)}^{-1} \text{ (kg-cat)}^{-1} \text{ h}^{-1}] \) | 1st order rate constant \( [10^{-2} \text{ m}^3 \text{ (kg-oil)}^{-1} \text{ (kg-cat)}^{-1} \text{ h}^{-1}] \) |
| \( k_1 \) (\( \text{VR} \Rightarrow \text{VGO} \)) & 4.12 | \( k_3 \) (\( \text{VGO} \Rightarrow \text{Gas Oil} \)) & 2.03 |
| \( k_2 \) (\( \text{VR} \Rightarrow \text{Gas Oil} \)) & 0.74 | \( k_6 \) (\( \text{VGO} \Rightarrow \text{Gas} \)) & 0.22 |
| \( k_3 \) (\( \text{VR} \Rightarrow \text{Gas} \)) & 0.00 | \( k_7 \) (\( \text{Gas Oil} \Rightarrow \text{Gas} \)) & 0.71 |
| \( k_4 \) (\( \text{VR} \Rightarrow \text{Coke} \)) & 0.65 | |

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and metal content greatly depend on the location. Therefore, the development of catalysts and reaction processes for each type of heavy oil will be required for stable energy supply to society.

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Nomenclatures

- $C_0$: concentration of bitumen at the reactor inlet
- $C_{VR0}$: concentration of VR at the reactor inlet
- $k_1,2,3,4$: second-order rate constant of each reaction route $[\text{m}^6 (\text{kg-oil})^{-1} (\text{kg-cat})^{-1} \text{h}^{-1}]$
- $k_5,6,7$: first-order rate constant of each reaction route $[\text{m}^3 (\text{kg-cat})^{-1} \text{h}^{-1}]$
- $r_i$: reaction rate of each component $[(\text{kg-oil}) (\text{kg-cat})^{-1} \text{h}^{-1}]$
- $X_{VR}$: conversion of VR in bitumen $[-]$
- $y_i$: composition ratio of lump $i$ $[(\text{kg-product}) i/(\text{kg-oil})]$

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要  旨

酸化鉄系触媒を用いた超重質油の軽質化に関する反応工学的研究

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本論文では，我々が開発した酸化鉄系触媒を重質油の水接触分解放しプロセスに適用した最近の結果をまとめた。まず，反応パラメータが酸化鉄系触媒の重質油分解活性に及ぼす影響を検討した。回分と流速反応のいずれの条件下においても，反応圧力が生成物収率に及ぼす寄与は大きく，高圧条件ほど炭素析出分の生成が抑制され，また亜臨界水条件下において，軽質化収率が最も多く得られることが分かった。さらに，重質油分解反応に関する反応速度解析と分解反応速度を検討した。ビチューメン中のVR（vacuum residual oil）成分の分解速度は2次と表され，その活性化エネルギーは132 kJ/mol と求められた。Lumping Model を用いた詳細反応速度解析を行い，各ランプの速度定数の割り当てから，VR 成分はVGO（Vacuum gas oil），Gas Oil，Gasへと逐次的に分解され，亜臨界水雰囲気下ではコーキ生成が抑制されることを示した。これより本触媒プロセスは，SAGD（Steam Assisted Gravity Drainage）法のように，高温高圧水に伴して産出される重質油に対し，油井オンサイトでの分解反応を適用できると期待される。