The study of dispersed catalyst on upgrading of unconventional oil

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Abstract. Hydrotreating with dispersed catalyst at ppm level can provide an efficient, economical alternative to upgrading heavy oil. In this study, slurry phase hydro-conversion process is used for viscosity reduction. Several reaction conditions have been investigated using highly dispersed catalyst. Residue conversion of extra-heavy oil up to 30% can meet the viscosity requirement for shipping, and the conversion of bitumen from oil sands up to 50% can meet the viscosity requirement for pipeline systems. These hydrogenation reactions with temperature ranging from 390°C to 420°C had higher liquid yield (from 98.5 wt% to 93.2 wt%). In addition, hydro-upgrading product contains lower concentrations of impurities compared to raw feed. Based on our research, an efficient and environmental friendly alternative upgrading process with low process temperature was proposed. The process uses dispersed catalyst for extra-heavy oil and oil sands bitumen treatment. Product properties meet the requirements for transfer and further application.

1. Introduction

Sources of unconventional oil become more and more important as conventional oil is depleting. There are two major deposits. These two deposits are oil sands in Canada and the extra-heavy crude oil in Venezuela [1-3], and the estimated reserves are shown in figure 1. These unconventional oils are extremely heavy and viscous, with high concentrations of heteroatoms (e.g., nitrogen, sulfur and metals, particularly nickel and vanadium), making extraction extremely difficult. Due to high viscosity, these two deposits can’t be mined using traditional methods, transported without heating or dilution with light hydrocarbons such as synthetic crude oil or natural gasoline, or refined by conventional refineries without large modifications. The processing of these heavy oil fractions is not easy due to the high content of impurities, as well as the high content of maltenes and asphaltenes [4].

Heavy oil upgrading technologies developed for unconventional fossil oils are based on two general routes: carbon rejection with poorer quality of products, and hydrogen addition with high liquid yield and good quality of distillates. Several carbon rejection technologies such as coking, has high feedstock flexibility, but large loss of liquid yield [5], while visbreaking or thermal cracking may produce less stable products and some coke [6,7]. Hydrogen addition technologies using fixed or ebullated bed have higher liquid product yields, but the value of these processes is reduced by the high investment, severe catalyst deactivation, and the byproducts of gas and coke [8]. Slurry phase hydro-
conversion has obvious advantages, which can deal with heavy crude and residue oils with high contents of impurities, and has a strong adaptability to different sources of heavy petroleum. Additionally, there is no bed plugging problem. The major effect of catalysts in slurry phase hydroconversion is to inhibit or prevent coke formation in thermal cracking conditions (i.e., >400°C) [9]. During slurry phase hydroconversion process, reactions start with carbon-carbon bond cleavage to produce light hydrocarbons as in thermal cracking process, and the hydrogen free radicals then inhibit polymerization reactions and coke formation during the process [10]. Dispersed catalysts promote faster reactions by exposing all catalytic active sites to reactants [11]. Both mass transfer coefficient and heat transfer coefficient are higher. The oleo-soluble based catalyst precursors are highly dispersed in the heavy oil and have higher activity. Therefore, oleo-soluble precursor as catalyst is extremely popular for slurry technologies. Slurry phase process can be a suitable option for upgrading of heavy crude and residue oils.

![Figure 1. Total world oil reserves.](image)

Viscosity is one of the most important physical properties for heavy crude oil. Unconventional oils need to be upgraded to meet the shipping or pipeline transportation requirements. The complicated processes make oil sands bitumen and extra-heavy oil upgrading highly skill-intensive and capital-intensive [12]. There is no suitable upgrading technology for the viscosity reduction of unconventional oil that is effective and economical. The aims of this study are to investigate the effect of highly dispersed catalyst on the viscosity reduction of the extra-heavy oil and the oil sands bitumen.

2. Material and methods

2.1. Materials

The extra-heavy oil was the atmospheric residue of Merry16 from Venezuela, and the bitumen from Athabasca oil sands was obtained from the PetroChina Canada Facility at MacKay River, Alberta, Canada. Composition of the feeds used in this study had poor qualities, as shown in Table 1. The measured impurities, maltenes, and asphaltenes were in accordance with the values reported in the literature [13].

|                       | Extra-heavy oil | Bitumen |
|-----------------------|-----------------|---------|
| API Gravity           | 8.4             | 8.9     |
| °API @ 15°C           |                 |         |
| Sulfur                | 4.22            | 5.44    |
| Nitrogen              | 0.94            | 0.44    |
| CCR                   | 16.73           | 15.06   |
| Nickle                | 76              | 63      |
| Vanadium              | 529             | 168     |
Maltenes wt% 16.83 15.41  
C7-asphaltenes wt% 11.55 9.36  
Viscosity @ 70.0°C cSt 6108 7034  

2.2. **Characterization of catalyst**

The morphology of highly dispersed MoS₂ catalyst derived from molybdenum-organic precursor was analyzed by high-resolution transmission electron microscopy (HRTEM) on a FEI F20 Tecnai G2 electron microscope operating at 200 kV. Samples were prepared by adding drops containing MoS₂ catalyst dispersed in Ethanol to a carbon-coated copper grid.

2.3. **Test reactions**

Hydro-conversion reactions were conducted in a Parr autoclave (500 ml capacity). The stainless steel autoclave reactor was filled with 150 g of ARs and certain amount of dispersed catalyst (≤100 ppm of feed loading). Highly dispersed catalyst was derived from oleo-soluble metal precursor. The reactions were conducted at certain temperatures for no more than 3 hours.

2.4. **Simulated distillation and residue conversion calculation**

Boiling range distributions were obtained by a high temperature simulated distillation method, which has a wide boiling range covering of C₅–C₁₂₀ n-alkane up to 720°C. This is a current version modified from the ASTM D2887 method. Oil samples diluted with carbon disulfide were tested by an Agilent 7890B GC equipped with a flame ionization detector (FID). Residue conversion rates are calculated based on the boiling range distribution of feed and products:

\[
\text{Residue conversion, \%} = \left( \frac{\text{MRF} - \text{MRP}}{\text{MRF}} \right) \times 100\% \tag{1}
\]

where **MRF** and **MRP** are mass contents of residue in unreacted feed and product.

2.5. **Viscosity measurements**

Viscosities of feeds and products were tested using glass capillary viscometers. Liquid is sucked into the upper bulb, and then it flows down the capillary into a lower bulb. The time taken for the liquid to pass through marks of viscometers is measured. The kinematic viscosity was determined by multiplying the time taken by the given factor of the glass capillary viscometer.

3. **Results and discussion**

3.1. **Morphology of catalyst**

![Figure 2. High-resolution transmission electron micrograph (HRTEM) of dispersed catalyst.](image-url)
Many metal precursors are used for slurry phase process [14-16], molybdenum has the best hydrogenation activity among monometal oleo-soluble dispersed catalysts. Bimetallic catalysts are also attractive [17,18]. For hydro-conversion reactions, it is obvious that highly dispersed catalyst with fewer layers could be beneficial for reaction activity. However, due to the nano-sized stacked structure, investigations on catalyst dispersion are difficult. The techniques based on high powered microscopes, such as transmission electron microscopy (TEM), could be used to measure the particle size [19]. In this study, the catalyst is activated by in-situ sulfidation under suitable conditions in hydrogenated diesel, and it decomposed to nano-sized particles. Figure 2 shows the morphology of MoS$_2$ catalyst dispersed in Ethanol. The MoS$_2$ catalyst is highly dispersed, which mainly consists of single-layer MoS$_2$. The slab length is about 10 nanometers. Highly dispersed nano-sized catalyst is good for residue hydro-conversion since there is little diffusion limitations between liquid and solid phases, which is confirmed by the industrial plant of EST process [20].

### 3.2. Upgrading of extra-heavy oil

Nowadays, Venezuela is producing much more extra-heavy crude than those downstream refineries can process. Additionally, Venezuela produces insufficient light hydrocarbons to use as diluent to transport extra-heavy crude to market. The partial upgrading of extra-heavy crude is an effective, economical solution for crude transport.

Increasing the load of catalyst can improve the liquid yield of products [21]. But for industrial processes, high catalyst loading (e.g., 2 wt% of feed loading) would not be economical and feasible. Based on our experiments, it is suggested that dispersed catalyst at ppm level exhibits considerable activity for upgrading of Venezuela’s extra-heavy oil, and the viscosity of the product at 50°C would be less than 380 cSt, which is suitable for shipping. To propose a proper solution for Venezuela’s extra-heavy oil hydro-upgrading, the upgrading experiments of extra-heavy oil were conducted at low temperature with low hydrogen pressure and consequently, the conversions of residue were low (<50 wt%).

![Figure 3. Suitable reaction conditions.](image1)

![Figure 4. Effects of conversion on viscosity.](image2)

The reaction conditions, such as temperature, pressure, reaction time, significantly affect the yield of liquid, the quality of products and the coke formation [22,23]. Based on the experiments conducted with certain amounts of Mo-based dispersed catalyst, as shown in figure 3, hydrogen pressure within 2 MPa is insufficient for viscosity reduction of Venezuela’s extra-heavy oil. If the reaction temperature reduces below 390°C, it needs higher pressure or longer reaction time to obtain proper products with a maximum viscosity at 50°C of 380 cSt. When the temperature is above 390°C, it also needs higher pressure to prohibit polymerization reactions and to prevent coke formation. The reaction conditions above the curve in figure 3 are suitable for Venezuela’s extra-heavy oil hydro-upgrading to meet the
shipping requirements. Figure 4 shows that the viscosity of the product is correlated with the conversion of residue, and the conversion should be above 30 percent to meet the viscosity requirement for shipping. As shown in figure 4, hydrotreating with higher pressure leads to the removal of impurities, and is beneficial for the viscosity reduction. The reactions conducted under mild conditions with temperature between 390°C and 410°C produced a liquid yield ranging from 98.5 wt% to 95.1 wt%.

3.3. Upgrading of oil sands bitumen
Bitumen produced from oil sands is generally upgraded into synthetic crude oil, but the complicated steps involved in upgrading processes make oil sands bitumen processing highly skill-intensive and capital-intensive. Partial upgrading of bitumen is considered as a more economical technology option for oil sands development [24]. In this paper, dispersed catalyst with higher activity and stability was used for bitumen partial upgrading. The viscosity of product at 30°C would be less than 80 cSt, which is suitable for pipeline transport. Experiments were conducted at moderate temperature and pressure, with residue conversions below 80 wt%.

![Figure 5. Suitable reaction conditions.](image1)

![Figure 6. Effects of conversion on viscosity.](image2)

Experiments were conducted with certain amounts of Mo-based dispersed catalyst, as shown in figure 5. Hydrogen pressure less than 6 MPa is insufficient for hydro-upgrading of oil sands bitumen. When the reaction temperature is below 410°C, higher pressure or longer reaction time is needed to get proper products with a maximum viscosity of 80 cSt. When the temperature is above 410°C, hydrogen pressure over 6 MPa is needed to prevent the formation of coke. Junaid et al [25] have demonstrated that the residue conversion was raised with increased reaction severity. The reaction conditions above the curve in figure 5 are suitable for the hydro-upgrading reactions of bitumen for pipeline transport. Figure 6 shows the relationship between the conversion and viscosity. The conversion of residue should be above 50% to meet the viscosity requirement. These reactions with temperature below 420°C produced higher liquid yield (> 93.2 wt%). The hydro-conversion at higher pressure, and the removal of impurities are also beneficial for the viscosity reduction. Additionally, an increase in loading of catalyst corresponding to more active sites is also promising.

The Slurry phase process with oleo-soluble catalyst is suitable for upgrading of these two heavy oils. The process would be feasible for other unconventional oils, such as Liaohe super heavy crude oil and super heavy oil in Fengcheng Area in Karamay Field, since the qualities of other unconventional oils are even better.

4. Conclusion
Based on the reaction results, several conclusions could be drawn:
Mo-based dispersed catalyst with ppm level loading is very effective for unconventional oil
upgrading at low severity reaction conditions. It would provide an alternative method for partial upgrading with low capital cost. Highly dispersed catalyst offers significant advantages and flexibilities over the conventional thermal upgrading techniques, as the residue conversion of thermal upgrading is limited within 30 percent.

For Venezuela's extra-heavy oil upgrading with dispersed catalyst, the reaction temperature should be over 380°C. The hydrogen pressure should be higher than 2 MPa, and the residue conversion should be above 30 percent to meet the viscosity specification for shipping.

For oil sands bitumen upgrading with dispersed catalyst, the reaction temperature should be over 400°C. The hydrogen pressure should be higher than 6 MPa, and the residue conversion should be above 50 percent to meet the viscosity specification for pipeline transport.

The hydro-conversion with dispersed catalyst at higher pressure, longer reaction time, and an increased catalyst loading are beneficial for the viscosity reduction.

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References
[1] Pruden B, Muir G and Skipel M 1993 Oil sands our petroleum future (Alberta Research Council, Edmonton, Alberta, Canada)
[2] Atkins L, Higgins T and Barnes C 2010 Heavy crude oil global analysis and outlook to 2030 Hart Energy Consulting Report (Houston, TX, USA)
[3] Alboudwarej H, Felix J and Taylor S 2006 Highlighting heavy oil Oilfield Review 18 34-53
[4] Speight J G 2007 The Chemistry and Technology of Petroleum 4th ed. (CRC Press, Boca Raton)
[5] Strausz O P 1984 Specific problems in the upgrading of Alberta oilsands bitumen J Jpn Petrol Inst 27 89-100
[6] Dutta R P, McCaffrey W C, Gray M and Muehlenbachs K 2001 Use of 13C tracers to determine mass-transfer limitations on thermal cracking of thin films of bitumen Energy Fuels 15 1087-93
[7] Casalini A, Mascherpa A and Vecchi C 1990 Modifications induced by visbreaking on composition and structure of atmospheric residues Fuel Sci Technol Inter 8 427-45
[8] Chronicles J and Germain R R 1989 Bitumen and heavy oil upgrading in Canada Pet Sci Technol 7 783-821
[9] Russell R C, Mohammad H S and Myriam Perez De la R 2006 Catalytic properties of single layers of transition metal sulfide catalytic materials Catalysis Reviews 48 1-41
[10] Manh T N, Ngoc T N and Joungmo C 2016 A review on the oil-soluble dispersed catalyst for slurry-phase hydrocracking of heavy oil Journal of Industrial and Engineering Chemistry 43 1-12
[11] Angeles M J, Leyva C, Anchevta J and Ramirez S 2014 A review of experimental procedures for heavy oil hydrocracking withdispersed catalyst Catalysis Today 22 74-94
[12] Mohan S R, Vicente S, Jorge A and Diaz J A I 2007 A review of recent advances on process technologies for upgrading of heavy oils and resudua Fuel 86 1216-31
[13] Yao G X 2012 Current status and development prospects for processing of venezuelan extra-heavy crude and Canadian oil sand bitumen Sino-global Energy 17 3-22
[14] Abdullah A-M, Abarasi H, Gary L, Malcolm G and Joseph W 2015 Effectiveness of different transition metal dispersed catalysts for in situ heavy oil upgrading Ind. Eng, Chem. Res 54 10645-55.
[15] Ruby Bearden Jr. 1979 US 4134825[P]
[16] Eletskii P M, Mironenko O O, Sosnin G A, Bulavchenko O A, Stonkus O A and Yakovlev V A 2016 Investigating the process of heavy crude oil steam cracking in the presence of dispersed catalysts. II: investigating the effect of Ni-containing catalyst concentration on the yield and properties of products Catalysis in Industry 8 328-35

[17] Giuseppe B, Giacomo R, Alberto L, Roberto M, Daniele M, Erica M, aniele M and Paolo P 2013 Hydroconversion of heavy residues in slurry reactors: Developments and perspectives Journal of Catalysis 308 189-200

[18] Sang G J, Jeong-Geol N, Chang H K, Ki B L, Nam S R and Seung B P 2011 A new approach for preparation of oil-soluble bimetallic dispersed catalyst from layered ammonium nickel molybdate Materials Science and Engineering B 176 606-10

[19] Rodriguez-DeVecchis V M, Ortega L C, Scott C E and Pereira-Almao P 2015 Use of nanoparticle tracking analysis for particle size determination of dispersed catalyst in bitumen and heavy oil fractions Ind. Eng. Chem. Res. 54 9877-86

[20] Giuseppe B, Giacomo R, Daniele M, Alberto L, Paolo P, Nicoletta P, Roberto M and Erica M 2013 The role of MoS2 nano-slabs in the protection of solid cracking catalysts for the total conversion of heavy oils to good quality distillates Catal. Sci. Technol. 3 176

[21] Hugo O-M, Jorge R, Rogelio C, Gustavo M and Jorge A 2012 Heavy oil upgrading at moderate pressure using dispersed catalysts: Effects of temperature, pressure and catalytic precursor Fuel 100 186-92

[22] Zhang SY, Deng WN, Luo H, Liu D, Que GH 2008 Energy Fuels 22 3583-3586

[23] Kim S-H, Kim K-D and Lee Y-K 2017 Effects of dispersed MoS2 catalysts and reaction conditions on slurry phase hydrocracking of vacuum residue Journal of Catalysis 347 127-37

[24] Zhang Yi, Ng Siauw, Alvarez-Majmutov A and Chen Jin Wen 2018 Catalytic cracking of thermally cracked HGO from oil sands bitumen 25th Canadian Symposium on Catalysis 161

[25] Junaid A S M, Street C, Wang W, Rahman M M, An W, McCaffrey W C and Kuzmicki S M 2012 Integrated extraction and low severity upgrading of oilsands bitumen by activated natural zeolite catalysts Fuel 94 457-64