Development of Supercritical Water Cracking Process to Upgrade Unconventional Extra Heavy Oil at Wellhead

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The Supercritical Water Cracking (SCWC) process is a partial upgrading process to produce low density and low viscosity crude from extra heavy crude. The SCWC process can convert Canadian oil sand bitumen with API° 8 to distillate products with API° 19-24, which satisfies the Canadian pipeline specifications. The advantages offered by the SCWC process are lower operating expenditure by eliminating diluent costs compared with the conventional dilution method, and the simple configuration without hydrogen and catalyst requirements leading to lower capital expenditure compared with the full upgrading method. The SCWC process was demonstrated with a bench unit (capacity is 0.15 barrel/day) and a pilot unit (5 barrel/day). In this paper, the characteristics and performance of the SCWC process are described, and the anticipated performance of the thermal cracking reaction in a larger scale unit also investigated by comparing conversions and product yields of the bench unit and the pilot unit. Analysis of product stability and long term operation with the pilot unit evaluated the conversion limit in terms of stable operation of the SCWC process in a large scale unit.

Keywords
Extra heavy oil, Partial upgrading, Thermal cracking, Supercritical water

1. Introduction

Extra heavy oil is an important natural resource to deal with the growth in worldwide oil demand. However, transportation from the wellhead to the refinery or shipping facility presents an important problem for the development of extra heavy crude oil reserves. Currently, three methods are used to enable its transportation, dilution technology, full upgrading technology, and partial upgrading technology (Fig. 1). Conventionally, dilution is applied to reduce the density and viscosity. Full upgrading technology has been commercialized to produce high quality synthetic crude oil (SCO). However, the capital expenditure (CAPEX) and operating expenditure (OPEX) are high because the facility configuration is complex and hydrogen and catalyst are required for processing. Partial upgrading technology is a new approach to produce SCO from heavy oil. In contrast to full upgrading, the partially upgraded product is sour SCO which contains some impurities, e.g. sulfur and nitrogen, but satisfies pipeline specifications in terms of density and kinematic viscosity. A Canadian provincial organization, Alberta Innovates, is focusing on the development of partial upgrading technologies and is targeting to treat up to 20 percent of its in-situ production by partial upgrading in 20301). Partial upgrading technology is expected to reduce the diluent requirement for heavy oil transportation with lower CAPEX and lower environmental risk compared to full upgrading.

Japan Oil, Gas and Metals National Corporation (JOGMEC) and JGC have been developing the Supercritical Water Cracking (SCWC) process since this paper was presented at the Kyoto Convention of JPI (46th Petroleum-Petrochemical Symposium of Jpn. Petrol. Inst.), Kyoto, Japan, Nov. 17-18, 2016.

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Fig. 1 Methods to Transport Heavy Oil from Wellhead to Refinery
2006 as a partial upgrading technology intended to promote the development of unconventional oil fields. Recently, the Japan Petroleum Energy Center (JPEC) has investigated the application of supercritical water to heavy oil upgrading\textsuperscript{21}. A consortium of eight Japanese universities conducted fundamental studies on the reaction path, reaction kinetics, detailed structure of product, application of cracking catalysts, and other topics. The National Institute of Advanced Industrial Science and Technology (AIST) has also investigated the advantages of supercritical water as a reaction medium\textsuperscript{39}. Such fundamental research will be important to establish the thermal cracking process with supercritical water.

The present study describes the characteristics and performance of the SCWC process, and evaluates the performance of the thermal cracking reaction in larger scale units by comparing conversions and product yields of a bench unit and a pilot unit. Product stability and long term operation with the pilot unit were analyzed to examine conversion limits in terms of stable operation of the SCWC process at the commercial scale unit.

2. Outline of the SCWC Process

2.1. Technical Features

Figure 2 shows a schematic diagram of the SCWC reaction. Thermal cracking occurs due to heat input from the supercritical water in the reactor and SCO is extracted immediately from the reactor by the up-flowing supercritical water. Therefore, excess cracking reaction of the SCO is prevented and this results in lower cracked gas yield. The supercritical water also has the characteristic of preventing polymerization of heavy oil molecules\textsuperscript{39}. Based on these technical features, a high yield of SCO and low yields of pitch and gas can be achieved.

2.2. Process Description

Figure 3 shows a simplified flow diagram of the SCWC process. A wide range of heavy oil sources such as bitumen, atmospheric residue, vacuum residue, and pitch from solvent deasphalting (SDA) can be used as the feedstock for the SCWC process. Preheated feedstock is introduced from the top of the reactor, and supercritical water is introduced from the bottom. The typical ratio of feedstock and water is 1.0 (by weight). Typical reaction temperatures and pressures in the reactor are 395-430 °C and 22-25 MPa G, respectively. Thermal cracking of the feedstock and extraction of...
SCO by supercritical water simultaneously occur in the reactor. A mixture of SCO and supercritical water is recovered from the top of the reactor and pitch is recovered from the bottom.

A high pressure separator and a low pressure separator are installed for the separation of SCO, cracked gas and sour water from the reactor effluent. Cracked gas is used for fuel after removal of acid gas. Sour water is fed to the sour water stripper and then passed to the waste water treatment unit. Treated water is recycled as feed water.

2.3. Experimental

The SCWC test was conducted with two scales of test units, the bench unit and the pilot unit.

(1) Bench Unit

A 0.15 barrel/day bench scale unit was built at JGC Technology Research Center in Ibaraki, Japan. This unit was designed to obtain data on the product yield, product quality, and reaction kinetics for extra heavy oil feedstock. Operation of this unit required only a small amount of feedstock and requires only a short time run, so was suitable for screening feedstock.

(2) Pilot Unit

A 5 barrel/day pilot scale unit was built at Canmet-ENERGY Devon Research Centre in Alberta, Canada. This unit was designed to obtain data for process scale-up from the bench scale unit to the commercial scale unit, such as the effects of reactor diameter, linear velocity, and so on. Process control was the continuous type control. Pressure and liquid levels in the reactor were controlled by control valves. The system did not include batch operation or solid handling.

(3) Comparison of bench unit and pilot unit

Table 1 compares the bench unit and the pilot unit. The pilot unit had larger throughput, reactor diameter, and higher linear velocity of the supercritical water under the operating conditions. Theoretically, the pilot unit can achieve the same conversion by selecting the same residence time and the same reaction temperature as the bench unit. Therefore, the test results of the bench unit and the pilot unit could be compared to identify the effect of the reactor size.

The severity of thermal cracking depends on the temperature and residence time in the reactor4). Thermal cracking occurs mainly at the pitch phase in the reactor of the SCWC process. Therefore, residence time is defined by dividing the volume of pitch in the reactor by the discharge rate resulting in a dimensionless number.

Many experimental runs were conducted at various temperatures and residence times with the bench unit and the pilot unit. The thermal severity index, SI, is used to evaluate data at different temperatures for determining equivalent reaction times at the same base temperature, 700 K. SI is defined by Eq. (1).

\[
SI = t \times \exp \left( - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{700} \right) \right)
\]  

(1)

Where;

SI: dimensionless severity index [-]

\( t \): dimensionless residence time [-]

\( E_a \): activation energy, taken as 209.8 kJ/mol

\( R \): gas constant, 8.314 J/(K mol)

\( T \): reaction temperature [K]

2.4. Conversion

Conversion in this study is defined by Eq. (2). VR fraction (\( > 540 \degree C \)) is the most dominant reactant in thermal cracking rather than distillate (\( < 360 \degree C \)) or VGO fraction (360-540 \( \degree C \)) in the SCWC process.

\[
\text{Conversion} [%] = \left( 1 - \frac{VR_{\text{product}}}{VR_{\text{feed}}} \right) \times 100
\]

(2)

Where;

\( VR_{\text{product}} \) [wt%]: distillation yield of VR fraction (\( > 540 \degree C \)) in Product (SCO and Pitch)

\( VR_{\text{feed}} \) [wt%]: distillation yield of VR fraction (\( > 540 \degree C \)) in Feedstock

3. Results and Discussion

3.1. Feedstock

In this study, Canadian oil sand bitumen was used for the feedstock. Table 2 shows the properties of the feedstock. The API gravity is around 8.0° and kinematic viscosity is higher than 600,000 cSt (1 cSt = mm² s\(^{-1}\)) at 10 \( \degree C \). Processing is required to transport bitumen with these properties from the wellhead to the refinery. About 50 wt% of bitumen is vacuum residue, so upgrading of bitumen is also essential to improve the distillate yield (\( < 360 \degree C \) and 360-540 \( \degree C \)) in downstream facilities.

3.2. Product Yield and Properties of Bench Unit Operation

Table 3 shows the conversion and product yield under three typical operating conditions with the bench unit. Conversion increased with higher temperature. Cracked gas yield and SCO yield both increased at higher conversion, whereas pitch yield decreased at higher conversion.

Table 4 shows the SCO and pitch properties under each operating condition. The target of SCO qualities is to satisfy pipeline specifications. For example, the

|                | Bench unit | Pilot unit |
|----------------|------------|------------|
| Throughput of feed [BPD] | 0.15 | 5.0 |
| Diameter of reactor (D) [m] | 0.025 | 0.10 |
| Height of reactor (L) [m] | 1.3 | 4.00 |
| \( L/D \) [-] | 52 | 40 |
| Linear velocity of SCW \( \text{a}) \) [mm/s] | 4.7 | 9.8 |

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\( a) \) SCW: supercritical water.
Canadian pipeline specifications require a density lower than 940 kg/m³ (API° 19) and kinetic viscosity lower than 350 cSt at 10 °C. The API gravity and kinetic viscosity of SCO obtained under all operating conditions satisfied these specifications. Condition 3 formed the most preferable product with the highest API and lowest kinetic viscosity. The sulfur content was not drastically changed after the reaction. Micro carbon residue (MCR) content in the SCO was reduced to less than 1 % under all conditions. Pitch product was heavier with lower API and higher kinetic viscosity at higher conversion.

### 3.3 Comparison of Reactor Performances

Table 5 compares the operating conditions, conversions, product yields, and product properties between the bench unit and the pilot unit. Condition 3 of the

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bench unit is shown as a reference. Similar operating temperature and residence time used at the pilot unit resulted in similar conversion, product yield, and product properties were achieved.

*Figure 4* shows the relationship between dimensionless SI and conversion. The plotted points and solid lines show the experimental data and the fitted curve of the experimental data for the bench unit and the pilot unit, respectively. The results of the bench unit and the pilot unit are indicated by the same curve, showing that reactor performance was not significantly influenced by reactor size in the range of the bench unit and the pilot unit.

### 3.4. Conversion Limit

As described above, heavier pitch was produced at higher conversion by polymerization of heavy hydrocarbon molecules, such as asphaltene. Polymerized asphaltene has lower solubility in oil, so that asphaltene precipitates and causes fouling in the reactor vessel. *P*-value is an analytical property to assess the stability of asphaltene in pitch\(^6\), which has been used to control visbreaker operation. A *P*-value higher than 1.1 is considered to indicate stable asphaltene in the pitch\(^7\).

*Figure 5* shows the relationship between conversion and *P*-value in the pitch produced from the pilot unit. However, *P*-value decreases with higher conversion. The *P*-value was only 1.42 at conversion of 38.4%. Therefore, the conversion was still in the acceptable operating range in terms of pitch stability.

### 3.5. Reliability of Operation

Long term operation with the pilot unit was conducted to confirm the reliability of the process. *Figure 6* shows the change in product properties during long term operation for 250 h.

### Table 5 Comparison of Reactor Performances

| Operation condition | Bench (Cond. 3) | Pilot | Method |
|---------------------|----------------|-------|--------|
| Temperature [°C]    | 430            | 425   |        |
| Feedstock flow rate [BPD] | 0.15 | 4.7   |        |
| Water flow rate [BPD] | 0.14 | 5.0   |        |
| Conversion (SCWC unit) [%] | 39.9 | 39.8 |        |
| VR (>540 °C) conversion [wt%] | 1.6 | 1.9 |        |
| Synthetic crude oil [vol%] | 61.9 | 61.1 |        |
| Pitch [vol%] | 38.4 | 39.3 |        |
| Total liquid [vol%] | 100.3 | 100.4 |        |
| SCO properties | | | |
| API [°] | 24.0 | 24.3 | ASTM D4052 |
| Kinetic viscosity at 10 °C [cSt] | 18.4 | 23.0 | ASTM D7042 |
| Pitch properties | | | |
| API [°] | −4.0 | −3.0 | ASTM D70 |
| Pentane insoluble [wt%] | no data | 45.6 | ASTM D4055M |

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Fig. 4 Comparison of Conversions between Bench and Pilot Units

Fig. 5 Pitch Stability and Conversion Limit for Pilot Unit
The API gravity of SCO was API°19, which satisfies the pipeline specification. Toluene insoluble in pitch as a component of polymerized asphaltene was unchanged, which indicates that polymerization in the reactor was adequately controlled. Therefore, the operation of the SCWC reactor was reliable during this testing period.

4. Summary

The SCWC process is a partial upgrading process which produces SCO transportable by pipeline from heavy oil. The SCWC process has advantages in operating cost reduction by eliminating the diluent costs for pipeline transportation and CAPEX reduction due to its simple process configuration, and minimal waste product.

The SCWC process produces SCO which satisfies pipeline specifications in terms of density and viscosity. The present pilot unit of the SCWC process demonstrated reliable operation with stable product properties.

The pilot unit adopted a control system capable of continuous operations. Comparison of conversions, product yields, and product properties between the bench unit and the pilot unit showed no effect of reactor size in the range of the bench unit and the pilot unit.

JGC continues to improve the SCWC process for application to various types of heavy oil, as partial upgrading technology or field upgrading technology can provide a more effective solution for heavy oil transportation.

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要 旨
超臨界水を用いた坑井元における非在来型重質原油改質技術の開発

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超臨界水を用いた重質油改質技術（SCWC, Supercritical Water Cracking）は超重質油を改質して低比重、低密度の改質油を得る技術である。API 比重 8°のカナダオイルサンドビーチメルンからは 19 〜 24°の改質油が得られ、比重・密度の観点からカナダのパイプラインの基準値を満たすことが確認できている。SCWC は、パイプライン輸送可能な改質油が希釈油を必要とせずに得られることや、シンプルな装置構成で得られることから、既存の希釈法やフルアップグレーディング法と比較して、コスト削減のメリットがあると考えている。SCWC プロセスによるベンチ装置（0.15 barrel/day）とパイロット装置（5 barrel/day）の 2 種類の装置を用いて実証を行った。これらの装置から得られた分解率、製品収率、製品性状を比較することで装置規模が与える影響を評価した。また、製品の安定性の分析やパイロット装置の 250 時間の長期運転により、SCWC プロセスが実現可能な分解率、およびシステムの信頼性を有していることを確認した。

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