Comparison of upgrading of heavy oil and vacuum distillation residues by supercritical water

Richard Djimasbe*, Ameen A. Al-muntaser, Muneer A. Suwaid, Mikhail A. Varfolomeev

Department of Petroleum Engineering, Kazan Federal University, Kazan 420008, Russia

E-mail: oiltchad91@gmail.com

Abstract

The purpose of this work is to test the upgrading technology by supercritical water of two different raw materials heavy oil and vacuum distillation residue. The experiments were carried out under the same conditions (temperature 400 °C, pressure 236 bar). The products obtained after upgrading were analyzed. Density, viscosity, SARA-composition, elemental composition and composition of saturates fraction were determined. The results revealed that after upgrading at 400 °C during 60 minutes raw materials heavy oil and vacuum residues yielded light oil 85.6 % and 64.7 %, coke at level of 11.3 % and 13.7 % and gaseous products 3.1 % and 21.6 %.

1. INTRODUCTION

The problem of shortage of light oil is increasing day by day because of the excessive consumption of energy. This question interest many scientists and researchers for some decades and a lot of research has been done to find an alternative source for fossil energy. One of the options is the development of unconventional crude oil reserves such as heavy oil, shale oil, oil sand [1]. Heavy oil and natural bitumen are mainly composed of high molecular weight hydrocarbons, resins and asphaltenes. The exploitation of these resources is very difficult due to high viscosity and bad transport properties of heavy oil, where asphaltenes and resins are the main factors.

The process of upgrading of heavy oil under supercritical water (SCW) conditions is an approach that can be used nowadays in the field of heavy oil exploitation or shale oil extraction and residues refining. Apart from heavy oil and oil sands production methods like steam-assisted gravity drainage (SAGD) and cold heavy oil production with sand (CHOPS), the supercritical fluid technology can be alternative to improve recovery, transportation and refining [2]. Cheng et al. found [3] that asphaltenes can be partially dissolved and dispersed under the effect of supercritical water.
One of the common problems encountered during the production or refining of heavy oil is the presence of asphaltenes in the oil. Asphaltenes are defined as one of the highest molecular weight components of crude oil. They present solid substances of black or brown color with average molecular weight 1000-5000 and density 1.1 g/cm$^3$ [4]. They can be softened only in an inert atmosphere and at high temperatures 200-300 °C.

Regarding the supercritical conditions (T = 374 °C and P = 221 bar), the water decreases its dielectric constant by about 78 to 10, where it has a solvent-like property such as acetone, benzene, toluene, etc. [5-6]. The water in the supercritical state is capable to supply the hydrogen to saturate the radicals formed from the oil component molecules at the time of thermal cracking and the hydroxyl group can cut off the bridge of the naphthenic alcohol in the oil and this prevents the formation of coke [7-8]. The asphaltenes are the main target in upgrading of heavy oil under the supercritical water conditions.

The process of upgrading of heavy oil using supercritical water was studied by Timko et al. [9]. Authors observed high level of heavy oil upgrading and desulphurization. Kozhevnikov et al.[5] studied the conversion of asphaltenes in a supercritical water environment at 380 °C and 226 bar during 3 hours. They indicated the formation of maltenes, gaseous products and coke from the hydrothermal destruction of asphaltenes. Gao et al. [10] used the D$_2$O as a isotope tag to study the hydroconversion of the Tahe residue in the SCW treatment. The results showed the role of water in the transformation of hydrocarbons. They determined [10] that the proportion of water molecules involved in hydrogen exchange was about 40% when the water content in the reaction mixture was 10% by weight. Olukcu et al. [11] suggested in their study that the absence of $n$-alkenes and the presence of alcohol in the product could be due to the transfer of OH from water to organic free radicals generated from an oil shale when extracting by SCW. Fedyaeva et al. [12] also confirmed in their study that the involvement of water contributed to the upgrading of bitumen in an up flow reactor with the proof of the appearance of oxygen and the increase in the concentration of hydrogen in the products and the conversion residue.

The interest of this research work is to study in details the treatment of heavy oil and vacuum distillation residue from Tatarstan Republic by supercritical water for the upgrading purpose. Currently, Republic of Tatarstan has large reserves of heavy oil and bitumen’s. So, new technologies are required for their extraction and refining. To study the mechanism of upgrading process different physical-chemical methods has been used in this study. They helped to identify changes in composition and properties of heavy oil and vacuum residue.
2. EXPERIMENTAL SECTION

2.1 Materials

Experiments were carried out on two raw materials. One of them is heavy oil from Tatarstan oilfield. Second sample is the vacuum residue from Refinery Company of Tatarstan Republic. The studied crude oil is considered as heavy oil because of its density and viscosity (971 kg/m$^3$ at 20 °C, API gravity 14.1 and 2073 mPa*s at 25 °C) and elemental composition (C 83.68%, H 11.44%, S 4.52%, and others 0.36%). The vacuum residue sample has density 1.2 g/cm$^3$ with a viscosity of 26056 mPa*s. It contains 5.97 % of paraffin’s.

Table 1. Density and viscosity of studied heavy oil and vacuum residue.

| Sample            | Density, kg/m$^3$ | Viscosity, mPa*s at 25 °C |
|-------------------|-------------------|----------------------------|
| Tatarstan heavy oil | 971               | 2073                       |
| Vacuum residue    | 1200              | 26056*                     |

*The viscosity of initial vacuum residue determined at 40 °C because of its solid state

Table 2. SARA composition of heavy oil and vacuum residue.

| Sample       | Saturate  | Aromatic | Resins  | Asphaltenes |
|--------------|-----------|----------|---------|-------------|
| Heavy oil    | 28.79     | 44.32    | 20.98   | 5.91        |
| Vacuum residue | 28.67     | 40.14    | 26.78   | 4.39        |

2.2 Methods

The experiment was carried out at 400 °C and at initial pressure 236 bar. The heavy oil or vacuum residue sample was charged into the autoclave-reactor model 4848 (Parr Instruments, USA) together with water in a ratio of 1:1 (75 g of distilled water and 75 g of heavy oil or residue). The reactor was hermetically closed. To remove the low volatile impurities and provide the initial pressure in the reactor, nitrogen was injected at 10 bars before starting the experiment. During the experiment, the heavy oil and vacuum residue were stirred with a rotation speed 140 rpm (rotation per minute). The reactor has a load capacity of 500 ml. The reactor is equipped with an automatic control system. The average heating rate of the reactor at the first stage was (dT/dt = 8 °C/min) and when the temperature reaches 380 °C the heating rate was decreased to 4 °C/min. After reaching the desired temperature of 400 °C, the experiment was continued at this temperature for 60 minutes and then stopped. M. Hosseinpour et al. reported that it is important to use fast cooling system of the product to stop the reaction [13]. The same procedure was used in our work. After cooling the sample, the liquid products were separated on upgraded oil and water using the centrifuge. If the emulsion was stable and did not separate by centrifugation, vacuum evaporator was used to
remove water. Viscosity was measured by Brookfield DV-II Pro viscometer according to GOST 3900-85. Density was determined by the standard method of the relative density test (pycnometer method) according ASTM D 2320-98 method [8].

The SARA analysis of the two samples (heavy oil and vacuum residue) after upgrading was done according the ASTM D-2007. The asphaltenes for each upgraded liquid products were precipitated by $n$-heptane with a ratio (oil:$n$-heptane) of 1:40. After 24 hours, the precipitated asphaltenes were separated from the maltene fraction by paper filtration, and the asphaltenes remaining in the paper were prepared and washed in the soxhlete extractor. After extraction, the solvent was evaporated and the residue in the flask was weighed for the balance calculation. At the same time, the maltene fraction was dried and the residue was prepared for adsorption in the glass chromatographic column. The column was loaded with aluminum oxide and then the residues of the maltenes were added to the aluminum oxide in the column for the adsorption of the maltenes. Then the saturates, aromatics and resins fractions were separated by respective solvents (180 ml of $n$-heptane for saturates, 180 ml of toluene for aromatics and a mixture of toluene with isopropyl alcohol in a ratio of 1: 1 200 ml for the resins). The respective 3 fractions are then evaporated and stabilized for material balance calculation.

Fig 1. The autoclave reactor Parr 4848
3. RESULTS AND DISCUSSION

3.1. Products yields

Two experiments for thermal treatment of heavy oil and vacuum residue by supercritical water were carried out at 400 °C. After the experiment the liquid products and coke were collected and their mass was determined. Based on these data the material balance of upgrading process was calculated. The mass of gaseous products was determined by the subtraction of the coke and upgraded oil masses from the mass of initial heavy oil. The mass fraction of each product was calculated by the following formula:

\[ (x_1, \%) = \frac{M_2 \times 100}{M_1}, \]  

\[ (x_2, \%) = \frac{M_3 \times 100}{M_1}, \]  

\[ (x_3, \%) = \frac{(M_1 - M_2 - M_3)}{M_1}, \]  

where \( x_1 \) is the mass fraction of upgraded oil; \( M_1 \) is the initial mass of crude oil, (g); \( M_2 \) is the mass of upgraded oil after experiment, (g).

\( x_2 \) is the mass fraction of the coke; \( M_1 \) is the initial mass of crude oil, (g); \( M_3 \) is the mass of coke after experiment, (g).

\( x_3 \) is the gaseous mass fraction.

Table. 3 Material balance of products after supercritical water treatment

| Sample         | Products yields , % | Gases | Oil  | Coke |
|----------------|---------------------|-------|------|------|
| Heavy oil      | 3.1                 | 85.6  | 11.3 |      |
| Vacuum residue | 21.6                | 64.7  | 13.7 |      |

3.2. Physical properties of the upgraded oil

Viscosity and density of upgraded oil obtained after SCW treatment were measured. Results are presented in Table 4. Viscosity of upgraded heavy oil and upgraded oil from vacuum residue significantly decreased, 209.4 and 1350 times respectively. Density of liquid products also decreased from 971 to 918 \( \text{kg/m}^3 \) for heavy oil and from 1200 to 995 \( \text{kg/m}^3 \) for vacuum residue. These changes induced by supercritical water effect on the heavy oil, which results in conversion of heavy fractions to light components [14].
3.3. Analysis of SARA- fractions

In order to understand the chemical transformation of heavy oil and vacuum residue induced by SCW effect, the SARA composition of liquid products was determined. Comparison on Fig. 2 shows, that saturates fraction increased significantly after upgrading from 28.79 to 78.51 % for heavy oil sample and from 28.67 to 57.24 % for vacuum residue sample. At the same time the fraction of aromatics, resins and asphaltenes decreased respectively from (44.32 % to 16.45 %, 20.98 % to 2.65 %, 5.91 to 2.39 % for upgraded heavy oil and (40.14 % to 24.20 %, 26.78 % to 15.43 %, 4.39 % to 3.13 % for upgraded vacuum residue. The increase in saturated hydrocarbons and the decrease of aromatics, resins, and asphaltenes in the products is due to the hydrothermal reactions. Previously it was reported [14] that thermal treatment of vacuum residue at 400 °C during 60 minutes led to decrease of density by 0.2 g/cm³ and remarkably improved the quality of product yields. After 1 hour of treatment, the fraction of asphaltenes decreased by 86 % and the aromatics increased from 20 to 63.3% [14].

Table. 4 Density and viscosity of upgraded products

| Sample               | Density, kg/m³ | Viscosity, mPa*s at 25 °C |
|----------------------|---------------|---------------------------|
| Tatarstan heavy oil  | 918           | 9.90                      |
| Vacuum residue       | 995           | 19.3                      |

Table. 5 SARA composition of the upgraded liquid products

| Nomination          | Saturate | Aromatic | Resins | Asphaltenes |
|---------------------|----------|----------|--------|-------------|
| Tatarstan heavy oil | 78.51    | 16.45    | 2.65   | 2.39        |
| Vacuum residue      | 57.24    | 24.20    | 15.43  | 3.13        |

*The viscosity of initial vacuum residue determined at 40 °C because of its solid state

Fig 2. The SARA fraction of upgrade oil
3.4. Analysis of Saturates fraction by Agilent Technologies 7890B GC Gas Chromatograph System

Fig. 3 presents the results of gas chromatographic analysis of saturates fraction before and after SCW treatment of heavy oil and vacuum residue. In the initial sample of heavy oil the saturated hydrocarbons from C_{19} to C_{27} were not detected, and other hydrocarbons as C_{28} to C_{30} were detected but in small amount. In the initial vacuum residue, the saturated hydrocarbons were detected from C_{21} to C_{31}. However, after upgrading, the both samples were enriched by new aliphatic hydrocarbons (dealkylation reaction of heavy components). In the product of the heavy oil after upgrading at 400 °C, a wide range of saturated hydrocarbons were detected from C_{11} to C_{29}, these increase of saturated hydrocarbons was due to thermal cracking reactions of resins and asphaltenes of heavy oil. In the liquid product of the vacuum residue after supercritical water treatment at 400°C, the saturated hydrocarbons concentration was considerably increased at C_{11}-C_{31} (fig. 3). The increase in concentration of saturated hydrocarbons is due to the intensification of conversion of vacuum residue under hydrothermal cracking in the supercritical water medium.
CONCLUSION

The process of upgrading of heavy oil and the vacuum residues at 400 °C and 60 min was carried out in this work. The composition and properties of upgraded products were compared with the initial samples. It was found that viscosity significantly decreased from 2073 to 16.6 mPa*s for heavy oil and from 26056 to 9.9 mPa*s for vacuum residues. At the same time the density increased from 971 kg/m³ to 918 kg/m³ for heavy oil and 1200 kg/m³ to 995 kg/m³). The conversion rate of heavy oil reached respective liquid products 85.6% and 64.7%, gases 3.1% and 21.6% and coke 11.3% and 13.7%. Also, the SARA fraction of crude oils (heavy oil and vacuum residue) was compared. The fraction of saturated hydrocarbons increased intensively in both products from 28.79 % to 78.51% and from 28.67 % to 57.24 %, while aromatics decreased from 44.32 to 16.45% and from 40.14 % to 24.20 % due to hydrothermal destruction and hydrogenation, the resins decreased from 20.98 % to 2.65 % and 26.78 % to 15.43 %. The asphaltenes, due to the supercritical effect of water decreased from 5.91% to 2.39% and 4.39% to 3.13%. The treatment of heavy oil and vacuum residue by supercritical water showed a very good performance on the conversion of heavy components into light liquid products and this technology can be perspective for industrial application.

Acknowledgments

This work was performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

REFERENCES

[1] R. M. Mills, *The myth of the oil crisis: overcoming the challenges of depletion, geopolitics, and global warming*. Greenwood Publishing Group, 2008.
[2] S. Akin, “Mathematical modeling of steam-assisted gravity drainage,” *Comput. Geosci.*, vol. 32, no. 2, pp. 240–246, 2006.
[3] Z.-M. Cheng, Y. Ding, L.-Q. Zhao, P.-Q. Yuan, and W.-K. Yuan, “Effects of supercritical water in vacuum residue upgrading,” *Energy & fuels*, vol. 23, no. 6, pp. 3178–3183, 2009.
[4] S. E. Moschopedis, J. F. Fryer, and J. G. Speight, “Investigation of asphaltene molecular weights,” *Fuel*, vol. 55, no. 3, pp. 227–232, 1976.
[5] O. N. T. of petroleum asphaltenes in Kozhevnikov, I.V.; Nuzhdin, A.L.; Martyanov and 217–222. supercritical water. J. Supercrit. Fluids 2010, 55, “Transformation of petroleum asphaltenes in supercritical water,” *J. Supercrit. Fluids*, vol. 55, no. 1, pp. 217–222, 2010.
[6] C. Ma, R. Zhang, and J. Bi, “Upgrading of coal tar in supercritical water,” *J. Fuel Chem. Technol.*, vol. 31, no. 2, pp. 103–110, 2003.
[7] C.-C. Zhu, C. Ren, X.-C. Tan, G. Chen, P.-Q. Yuan, Z.-M. Cheng, and W.-K. Yuan, “Initiated pyrolysis of heavy oil in the presence of near-critical water,” *Fuel Process. Technol.*, vol. 111, pp. 111–117, 2013.
[8] P. R. Filgueiras, C. M. S. Sad, A. R. Loureiro, M. F. P. Santos, E. V. R. Castro, J. C. M. Dias, and R. J. Poppi, “Determination of API gravity, kinematic viscosity and water content in petroleum by ATR-FTIR spectroscopy and multivariate calibration,” Fuel, vol. 116, pp. 123–130, 2014.

[9] M. T. Timko, A. F. Ghoniem, and W. H. Green, “Upgrading and desulfurization of heavy oils by supercritical water,” J. Supercrit. Fluids, vol. 96, pp. 114–123, 2015.

[10] L. Gao, Y. Liu, L. Wen, W. Huang, X. Mu, B. Zong, H. Fan, and B. Han, “The effect of supercritical water on the hydroconversion of Tahe Residue,” AIChE J., vol. 56, no. 12, pp. 3236–3242, 2010.

[11] N. Olukcu, J. Yanik, M. Saglam, M. Yuksel, and M. Karaduman, “Solvent effect on the extraction of Beypazari oil shale,” Energy & Fuels, vol. 13, no. 4, pp. 895–902, 1999.

[12] O. N. Fedyaeva, A. V Shatrova, and A. A. Vostrikov, “Effect of temperature on bitumen conversion in a supercritical water flow,” J. Supercrit. Fluids, vol. 95, pp. 437–443, 2014.

[13] M. Hosseinpour, S. Fatemi, S. J. Ahmadi, M. Morimoto, M. Akizuki, Y. Oshima, and E. Fumoto, “The synergistic effect between supercritical water and redox properties of iron oxide nanoparticles during in-situ catalytic upgrading of heavy oil with formic acid. Isotopic study,” Appl. Catal. B Environ., vol. 230, pp. 91–101, 2018.

[14] Y. Liu, F. Bai, C.-C. Zhu, P.-Q. Yuan, Z.-M. Cheng, and W.-K. Yuan, “Upgrading of residual oil in sub-and supercritical water: An experimental study,” Fuel Process. Technol., vol. 106, pp. 281–288, 2013.