PE04

The kinetics of the upgrading of heavy oil in supercritical methanol

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ABSTRACT

The crude oil upgrading was conducted in supercritical methanol(scMeOH) using batch reactors. The influence of temperature (653 to 693 K), reaction time (0 to 120 min) on product distribution was investigated and FTIR analysis of maltene was conducted.

At all temperature, maltene yield decreased over time. Asphaltene yield increased at the beginning and then decreased while coke yield increased slowly and then increased sharply from the point of maximum asphaltene. It shows that asphaltene was converted to coke rapidly after the maximum asphaltene peak and the kinetics from asphaltene to coke varies greatly with the fraction of asphaltene. Also, from the maltene analysis, the crude oil was upgraded into the light oil with more saturate and less aromatic, resin in scMeOH. FTIR analysis of raw maltene and product maltene showed that scMeOH are presumed to participate in the form of methoxy radical in scMeOH upgrading. The results of the FTIR quantitative analysis indicated that the crude oil turned into a lighter crude oil.

To understand the crude oil upgrading process in scMeOH, four lump kinetic model including maltene, asphaltene, coke, and gas was proposed and kinetic parameters were estimated from the experimental data. The calculated rate constants and activation energies showed that the decomposition of asphaltene is the most dominant reaction in the upgrading of crude oil while the generation of coke is suppressed.

INTRODUCTION

The reserves of heavy crude oil are more than twice those of conventional light crude oil. With the development of petroleum engineering and the decrease of conventional light oil reserves, the production of heavy crude oil has increased significantly around the world but there are many problems to utilize heavy crude oil. Heavy crude oil has high viscosity, density, and high concentrations of heteroatoms such as sulfur, nitrogen, nickel, and vanadium because of its high molecular weight compounds such as asphaltene. To utilize heavy crude oil, it is necessary to remove high molecular weight compounds like asphaltene.

Since the 1990s, there have been many challenges to decompose high molecular weight

compounds using supercritical water (SCW, Tc= 647.5 k, Pc=22.05 MPa). SCW has high diffusivity with favorable transport properties and low polarity dissolving the organic compounds. SCW participates in the reaction of decomposing the large molecules as a reaction medium, solvent, reactant or even catalyst.

Recently, there are many studies to upgrade the crude oil or its components in the supercritical fluid. SCW is promising reaction solvent for the upgrading of crude oil. It has been found that the amount of light components increased while the amount of heavy components decreased in SCW upgrading, proposing that upgrading is dominated by free radical reaction based on thermal cracking. Also, there have been several studies on the upgrading of crude oil using scMeOH, which show that scMeOH is much more effective in reducing heavy components and increasing light components than SCW.

In this study, scMeOH was used as a solvent to upgrade the crude oil. The effect of the reaction variables including the reaction temperature and time on the upgrading of the crude oil was evaluated by measuring the product distribution. And the structure change of product was investigated using FTIR. Also, four lump kinetic model using maltene, asphaltene, coke, and gas was proposed and estimated from the experimental data.

MATERIALS AND METHODS

The experiments were carried out using custom-built batch reactors in the molten salt bath with an electric shaker. The reactor was made of SUS316 steel with the volume of 22 mL. The molten bath was composed of $NaNO_3/KNO_3/Ca(NO_3)_2$ in a ratio of 46:24:30.

The reactor was loaded with 3.3g crude oil and 3.3g methanol (oil:solvent = 1:1, w/w). Afterward, the sealed reactor was immersed in the molten salt bath at pre-set designed reaction temperature while constantly shaking. After the reaction, the reactor was removed from the molten salt bath and quickly quenched to the room temperature by immersing in a cold water bath. The designed reaction temperatures and retention time were 653, 673, 693 K, and 5, 15, 30, 60, 120 min, respectively. The density of solvent was kept at 0.15g/ml for all experiments, and the reaction pressure was in the range of 31.8–38.4 MPa. At each temperature and time, it experimented twice for reproducibility.

The processed products were fractionated into five components such as saturate, aromatic, resin, asphaltene: SARA, and coke as described in Figure 01.

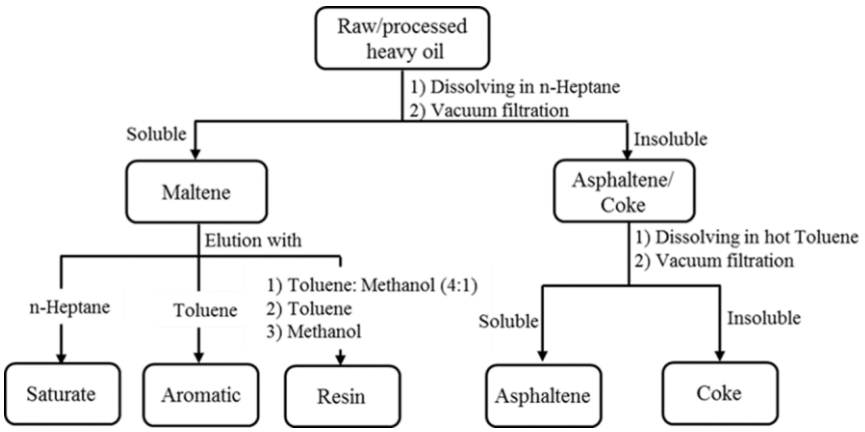

Figure 01. SARA and coke fractionation procedure for raw and the products

The FTIR analysis of maltene was analyzed in a Nicolet 6700 model in the resolution of 8 cm^{-1} and 32 scans in the wavelength range of 4000-650 cm^{-1}. The determination of peak intensities with deconvolution and calculation of integrated area were performed using the Omnic software from Nicolet.

RESULTS

The product distribution of crude oil upgraded in scMeOH are listed in Figure 1. The experiments were carried out at the temperature of 653, 673, 693 K with the reaction time of 5, 15, 30, 60, 120 min and with an oil-methanol ratio of 1:1.

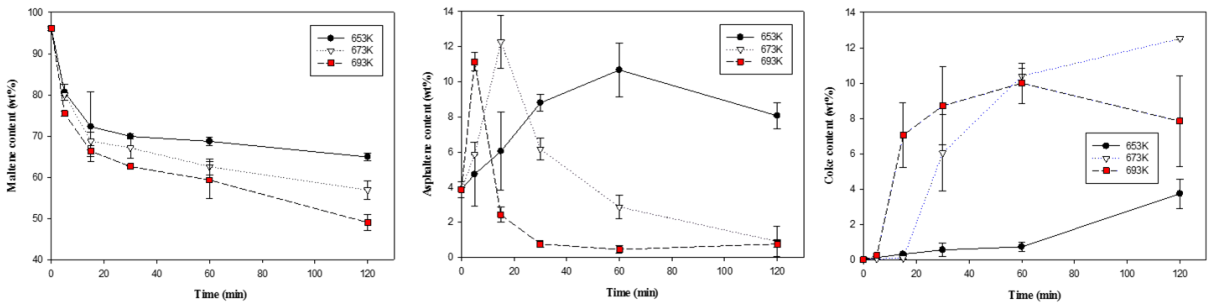

Figure 02. Influence of the temperature and time on maltene, asphaltene, coke in the product

The maltene components of crude oils upgraded in scMeOH were analyzed using SARA fractionation, and the results are listed in Figure 2.

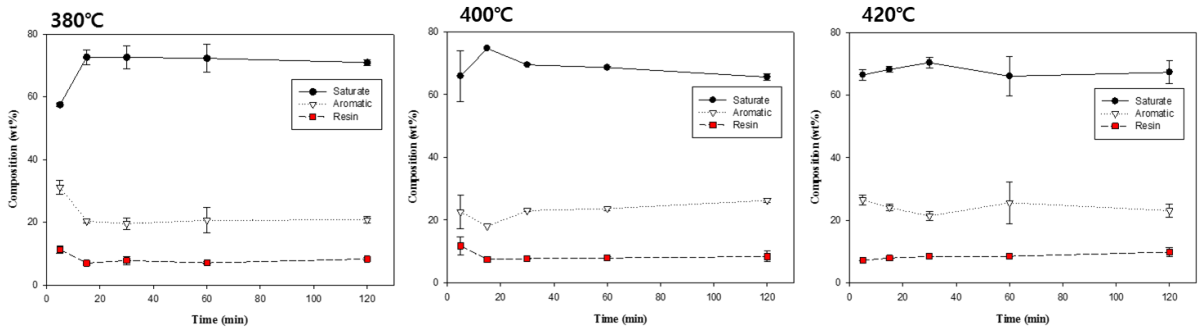

Figure 03. Maltene analysis of crude oil upgraded in scMeOH at (a) 653K, (b) 673K, (c) 693K.

To understand the upgrading of crude oil in scMeOH, four lump kinetic model including

maltene, asphaltene, coke, and gas for the crude oil upgrading in supercritical water was suggested. Compared to previous studies in which asphaltene is decomposed into maltene, the reaction model including the reaction pathway from asphaltene to maltene was developed.

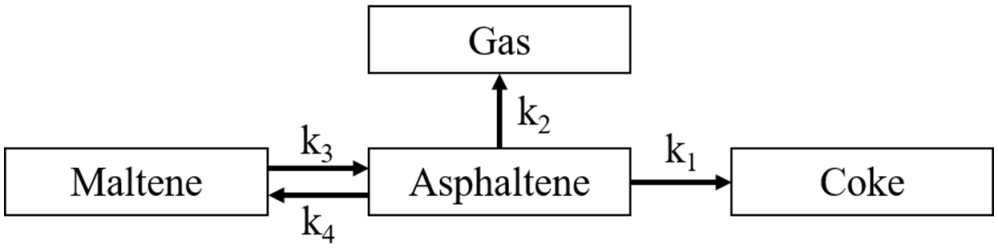

Figure 04. Four lump kinetic model for the upgrading of crude oil in scMeOH

As many previous studies have shown that decomposition of asphaltene or other transformations between lumps usually follow the first-order kinetics, it is assumed that all the reaction pathways in the kinetic model follow the first order reaction.

From this four lump kinetic model, the rate constants in the kinetic model were calculated by function for the minimization of constrained nonlinear multivariable and fourth order of Runge-Kutta method with global optimization toolbox of Matlab R2016b. The optimal value of the rate constant in the model was determined by solving the nonlinear least-square problems of minimizing the residual sum of squares (RSS) criterion. The rate constants, activation energies, and pre-exponential factors are listed in Table 1.

Table 01 Parameters of the four lump kinetic model for the upgrading of crude oil in scMeOH

$k_i(min^{-1})$	Temperature (k)			E_i(kJ/mol)	$A_i(min^{-1})$	R^2
	653	673	693			
k_1	0.0020	0.0113	0.0330	264.2	8.022E+18	0.9862
k_2	0.0219	0.0306	0.1084	149.5	2.943E+10	0.8881
k_3	0.1295	0.5434	0.7793	169.8	1.144E+13	0.9038
k_4	0.7417	3.4475	8.2530	227.2	3.178E+18	0.9804

To evaluate the kinetic model presented above, the parity plot for the yield of maltene, asphaltene, coke, and gas was presented in Figure 5. R^2 was about 0.9349, and it shows that four lump kinetic model for the upgrading of crude oil in scMeOH is reasonable.

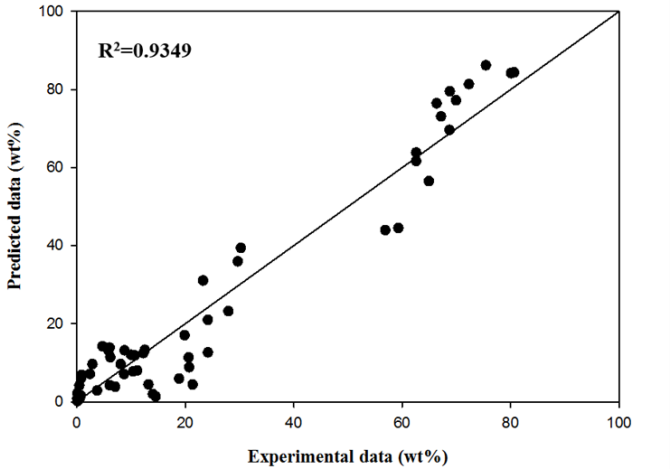

Figure 05. Parity plot of the product yield predicted by kinetic model versus experimental value

To check the effect of the scMeOH upgrading on the specific functional group, the maltene component of the raw material and the maltene component of the product were compared using FTIR. Among the products, the product reacted at 673 K for 1 hour was selected and analyzed. The FTIR results of the maltene of raw material (Arabian heavy oil) and the maltene of upgraded product are shown in Figure 06.

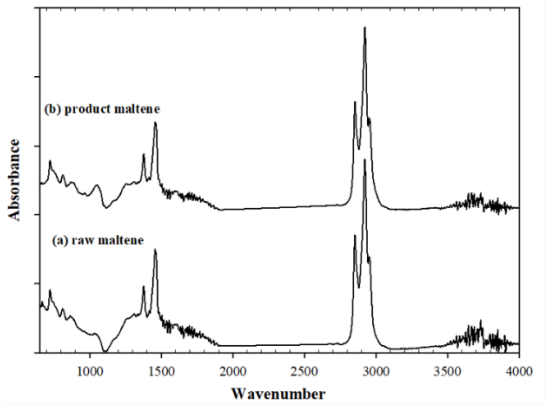

Figure 06. FTIR spectrum of raw maltene and product maltene

Significant differences in the results appeared in the region of 1000-1100 cm^{-1}. There is a distinct peak in the product maltene, whereas the peak does not appear in the raw maltene. The absorption bands at 1000-1100 cm^{-1} can be indicated by stretching vibration of C-O-C stretch in ether, C-O stretch in alcohol, carboxylic acid and C-C stretch in ketone. However, there were no apparent peaks of O-H stretching vibration common to alcohol and carboxylic acid or peaks of C=O stretch. It is assumed that C-O-C ether group were generated by the scMeOH upgrading.

For quantitative comparison of major functional groups in crude oil, the integrated area of peaks and the intensities of specific wavelength were investigated. The maltene of crude oil reacted in scMeOH shows lower ratio of R, higher ratio of I_1 and I_2 than the maltene of raw crude oil, which means the shorter side chain of aliphatic substituents and more amount of aliphatic and aromatic groups. It shows that raw crude oil turned into a lighter crude oil in

scMeOH.

CONCLUSION

The crude oil upgrading in supercritical methanol was studied at the temperature of 653, 673, 693 K and at the reaction time ranging from 0 to 120 min. The effect of the reaction variables which include the reaction temperature and reaction time on the upgrading of the crude oil in scMeOH was evaluated by measuring the product distribution. FTIR peaks of raw maltene and product maltene showed that scMeOH are presumed to participate in the form of methoxy radical in scMeOH upgrading. The results of the FTIR quantitative analysis indicate that the crude oil has turned into a lighter crude oil.

To understand the upgrading process in scMeOH, four lump kinetic model using maltene, asphaltene, coke, and gas was proposed and kinetic parameters were estimated from the experimental data. From the rate constants and activation energies, it was inferred that the decomposition of asphaltene is the most dominant reaction in the upgrading of crude oil while generation of coke is suppressed.

ACKNOWLEDGEMENTS

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