

研 究 主 論 文 抄 録

論文題目

重質油改質のための超臨界水中での炭化水素化合物の反応および金属錯体からの脱メタルに関する研究

Study on Reaction of Hydrocarbons and Removal of Metals from Metal Complexes in Supercritical Water for Upgrading Heavy Oil

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主論文要旨

《本文》

Chapter 1

This chapter contains the description of heavy oil including its recovery and upgrading processes. In addition, bottlenecks of conventional upgrading processes are critically discussed to explore new processes.

Chapter 2

This chapter includes complete understanding about sub and supercritical water (SCW) and its major properties. The SCW assisted upgrading process is critically reported.

Chapter 3

The objective of this chapter was to convert heptylbenzene (HPB), the simplest model compound of heavy oils, into low-molecular-weight hydrocarbons by suppressing side reactions that produced high-molecular-weight compounds and char. The dramatic variability in the ion product and the dielectric constant of water under supercritical conditions rendered supercritical water (SCW) an acid or a base catalyst. In this study, water was used without any catalyst. The reaction was carried out in an 8.8-mL batch

reactor fabricated from Hastelloy C-276. The ability of SCW to decompose HPB was studied at temperatures ranging from 425 to 475°C and pressures from 30 to 40 MPa. HPB was converted into light hydrocarbons such as ethylbenzene, propylbenzene, and butylbenzene, as well as heavy hydrocarbons and gases under the abovementioned conditions. The major liquids produced were toluene, ethylbenzene, unbranched phenylalkanes, branched phenylalkanes, phenylolefins, benzene, and naphthalene. HPB thermolysis followed first-order kinetics, with the following Arrhenius parameters: activation energy, 26.37 ± 1.21 kcal/mol; $\log(A, \text{s}^{-1})$, 10.81 ± 0.50 , where A is the pre-exponential factor. HPB pyrolysis in SCW followed almost identical kinetics, and SCW had negligible influence on the reaction path. A low water partial pressure was favorable for reducing the formation of heavier compounds, although the overall HPB conversion was close to 88% at a temperature of 450°C and a reaction time of 60 min. Char formation was drastically reduced in the SCW environment. These results suggested that water acts as a chemical reagent above its critical point (374°C and 22.1 MPa) and aids HPB decomposition.

Chapter 4

Naphthenic acid (NA) are present in crude oil and lead to corrosion problems within the oil refineries. The objective of this chapter is to reduce total acid number (TAN) from NA in an environmentally benign way, suppressing the solid deposition using supercritical water (SCW). The reaction was carried out in an 8.8 mL batch reactor fabricated from hastelloy C-276 with respective design temperature and pressure of 500°C and 50 MPa. The ability of SCW to reduce TAN was explored at temperatures from 400 to 490°C and water partial pressures (WPPs) from 0 to 45 MPa. Experimental results revealed that TAN removal was 82.53% at a temperature of 490 °C, WPP of 45 MPa and reaction time of 90 min. The TAN removal followed first order kinetics, with Arrhenius parameters of activation energy 15.83 kcal/ mol and a pre-exponential factor $1.4 \times 10^5 \text{ s}^{-1}$. Solid deposition was drastically reduced at WPP of 45 MPa. These results suggest that SCW is capable of reduction of TAN from NA with no use of catalyst or additives.

Chapter 5

Reaction kinetics and mechanisms of the decomposition of vanadyl etioporphyrin (VO-EP), the most common metal compounds present in heavy crude, were studied in supercritical water (SCW) in a toluene environment without the addition of any catalyst, H_2 or H_2S to remove vanadium. The aim of this chapter was to remove vanadium an

environmentally benign way from VO-EP at a high extent and in a short reaction time. The experiments were conducted in an 8.8 mL batch reactor fabricated from Hastelloy C-276. The capability of SCW to remove vanadium from VO-EP was discovered at temperatures of 410-490 °C and a water partial pressure (WPP) of 25 MPa. Experimental results revealed that the overall VO-EP conversion was 90.51 % at a temperature of 490 °C, WPP of 25 MPa and reaction time of 180 min. Under the same reaction conditions, approximately 80.26 % vanadium was removed by reaction with SCW. The global reaction followed first order kinetics, with Arrhenius parameters of activation energy 8.93 kcal/ mol and a pre-exponential factor 5.66 s^{-1} . A kinetic model of demetallation that well-fit the experimental results, was proposed. The reaction kinetics may be critically explained in terms of free radical mechanism. The obtained results suggest that SCW is capable of removing vanadium from VO-EP.

Chapter 6

In this chapter, reactions are described of nickelal porphyrin (Ni-P) in SCW in a toluene environment at temperature ranges of 450-490 °C and at water partial pressures (WPPs) of 25-45 MPa, all in the absence of catalyst and without the addition of hydrogen or hydrogen sulfide gas.

Ni-EP was proven reactive with SCW, which also acted as a hydrogen donor and a catalyst; SCW showed itself capable of removing nickel from Ni-EP. Experimental results revealed that WPP had a slight effect on SCW reaction with Ni-EP. A temperature of 490 °C, WPP of 25 MPa and reaction time of 180 min effected conversion of 95.02 % of Ni-EP to intermediate and final products. Under the same conditions, around 90.64 % of the nickel was removed by the action of SCW in the presence of toluene. The kinetics was consistent with first-order dependency on Ni-EP decomposition. Nickel was removed in two ways: first, nickel removal from the etioporphyrin ring was observed to occur by ring fragmentation phenomena where hydrogenation and hydrogenolysis reactions were involved; second, nickel was directly removed from the core of the complex by reacting with *OH* and ring fragmentation phenomena. Hydrogenolysis reactions occurred more rapidly than hydrogenation reactions. High WPP holds the potential to increase slightly the second hydrogenation step compare to low WPP. On the other hand, about 89.80% of the Ni-TPP was converted to intermediate and final products at a temperature of 490 °C, a pressure of 25 MPa and a reaction time of 90 minutes. Under the same conditions, around 65.63 % nickel was removed by the action of supercritical water. In addition, overall Ni-TPP conversion was basically invariant at the change of WPP from 25-35 MPa. Model

compound study revealed that nickel can be successfully removed from MP using SCW indicating that this non-catalytic process is applicable to removal of nickel from heavy oil in an environmental friendly way.

Chapter 7

This chapter aims to determine optimum reaction operating conditions of heptylbenzene (HPB) decomposition in supercritical water (SCW) using simulation software. The simulation was carried out with the help of a commercial simulator, Pro/II, using a plug flow reactor as a model reactor. To obtain kinetic data, all experiments were carried out in an 8.8 mL batch reactor fabricated from Hastelloy C-276 at temperatures of 425-475 °C and water partial pressure of 35 MPa. A decomposition equation was developed, and both activation energy and pre-exponential factor were then calculated. The obtained equation and values were input to the Pro/II simulator after creating the process. In this study, HPB is used as a model compound and water as a reaction medium without catalyst. The calculated results were compared with the experimental data, with different cases were studied to analyze the sensitivity of the process. The simulated results were seen to follow the experimental results. The obtained results suggest that the model is help to simulate heavy oil model compounds and to plan for large scale production.