Fuel Processing Technology 118 (2014) 49–54

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Co-pyrolysis of heavy oil and low density polyethylene in the presence of supercritical water: The suppression of coke formation

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ARTICLE INFO

Article history:
Received 3 February 2013
Received in revised form 29 July 2013
Accepted 6 August 2013
Available online xxxx

Keywords:
Coking
Co-pyrolysis
Heavy oil
Polyethylene
Supercritical water

ABSTRACT

At 693 K and water density of 0.30 g/cm^3, the co-pyrolysis of heavy oil and low density polyethylene (LDPE) in the presence of supercritical water (SCW) was investigated with the emphasis on the coking mechanism involved. The co-pyrolysis in SCW was found to have the significant advantages of the decreasing yield of coke and the increasing yield of aromatics over the pyrolysis of heavy oil alone in SCW. With the increase in the loading of LDPE, the suppression of condensation in co-pyrolysis is gradually intensified, suggesting the essential role of LDPE as an external H-source in co-pyrolysis. Only in the continuous SCW phase can the H-donation between the pyrolysis networks of heavy oil and LDPE be effectively accomplished, by which the condensation of light oil fractions to heavy oil fractions and the deep condensation of asphaltenes to coke are partly suppressed.

1. Introduction

The reserve of heavy oil worldwide is more than twice that of conventional light crude oil, making up an increasing proportion of the feedstock for refineries. Oil refining technologies available, such as catalytic cracking and hydrocracking, have already shown limitation to the processing of heavy oil of inferior quality. Because of the unique solubility and diffusivity properties of hydrocarbons in supercritical water (SCW, $T_c = 647$ K, $P_c = 22.1$ MPa, $\rho_c = 0.32$ g/cm^3), the upgrading of heavy oil via pyrolysis in SCW has been extensively investigated in academia since the 1990s [1–5].

Essentially, the pyrolysis of heavy oil is an H-deficient process. Once it was believed that H atoms could be transferred from SCW or superheated steam into the pyrolysis product of heavy oil. According to the upgrading of asphalt with and without partial oxidation in SCW, Sato et al. deduced that hydrocarbon radicals can be capped by H-abstraction from SCW [6]. Zhao et al. also considered SCW as an H transfer agent in the upgrading of vacuum residue in SCW [7]. However, the isotopic tracing of ^{2}H and ^{18}O in the pyrolysis of polyethylene in SCW indicated that SCW might participate in pyrolysis through hydration with low olefins rather than through H-abstraction with hydrocarbon radicals [8,9]. Density functional theory calculation further denied the thermodynamic feasibility of the H-abstraction between hydrocarbon radicals and water even water is in the supercritical state [10]. Provided that the pyrolysis of heavy oil in SCW follows primarily the free radical mechanism, SCW thus can hardly be an effective H-source for pyrolysis.

Now there is a growing awareness that the introduction of additional H-sources is inevitable for the upgrading of heavy oil in SCW. With the aid of molecular or in-situ produced H_2, Cheng et al. studied the hydrocracking of heavy oil in SCW. The formation of coke was found to be effectively suppressed, together with an increasing yield of maltenes [11,12]. Recently, Bai et al. attempted the co-pyrolysis of heavy oil and low density polyethylene (LDPE) in SCW [13]. The suppression of coke formation, which was attributed to the H-donation between the pyrolysis networks of heavy oil and LDPE, was also observed. Furthermore, the efficiency of H-donation was confirmed to be sensitive to the applied thermodynamic state of SCW. By the consideration that recycled polyolefins might be used as an alternative H-source, the upgrading of heavy oil via the co-pyrolysis with polyolefins in SCW has the remarkable advantages of low cost and simple operation over the hydrocracking of heavy oil in SCW. Nevertheless, an in-depth study on the co-pyrolysis of heavy oil and polyolefins in SCW is still necessary for the future application.

In this work, the co-pyrolysis of heavy oil and LDPE as well as the pyrolysis of heavy oil alone in the presence of SCW was investigated with the focus on the coking mechanism involved. On the basis of experimental results, the possible pathway of the H-donation responsible for the suppression of coke formation in co-pyrolysis was proposed. Then, the influence of SCW on the H-donation was further discussed. In what follows, “co-pyrolysis” means in particular the thermal cracking

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http://dx.doi.org/10.1016/j.fuproc.2013.08.007

of heavy oil accompanied by LDPE, while “pyrolysis” is the thermal cracking alone of heavy oil or LDPE.

2. Experimental

2.1. Apparatus and reaction run

All experiments were applied in a Parr 4598-HPHT autoclave with a capacity of 0.1 L. The autoclave made of SS316L steel is equipped with flat paddles whose stirring rate was kept at 800 rpm during reaction. Both co-pyrolysis and pyrolysis were performed at a fixed temperature of 693 K and a water density of 0.30 g/cm^3.

In a typical run for co-pyrolysis, 20 g of heavy oil, 30 g of water and a certain amount of LDPE were loaded into the autoclave first. After being purged with N_2 of high purity, the reactor was sealed. Then, the reactor was heated to 693 K at a slope of 10 K/min. The reaction lasting 30 to 60 min finally was terminated by subjecting the reactor into forced air cooling. Basically, the procedure of pyrolysis was similar to that of co-pyrolysis except that no LDPE was loaded into the autoclave.

2.2. Product separation and analytical procedures

After the reaction, the autoclave was washed thoroughly with toluene to collect products. According to a standard procedure which can be seen elsewhere, the collected product was separated into saturates, aromatics, resins, asphaltenes and coke [13]. The mixture of saturates, aromatics and resins is referred to as maltenes.

The yield of liquid oil fractions (Y_i) or coke (Y_c) was evaluated by

$$Y_i = m_i/(m_{raw} + m_{LDPE}) \times 100\% \tag{1}$$

$$Y_c = m_{coke}/(m_{raw} + m_{LDPE}) \times 100\% \tag{2}$$

where m_i denotes the weight of any liquid oil fraction and m_{coke} is that of coke. m_{raw} and m_{LDPE} are the weights of the loaded raw heavy oil and LDPE.

The mass balance (M-B), hydrogen balance (H-B) and carbon balance (C-B) in each run were evaluated by

$$M-B = \left(\sum m_i + m_{coke}\right)/(m_{raw} + m_{LDPE}) \times 100\% \tag{3}$$

$$H-B = \frac{\sum m_i \cdot \dfrac{H/C_{oil}}{H/C_{oil}+12} + m_{coke} \cdot \dfrac{H/C_{coke}}{H/C_{coke}+12}}{m_{raw} \cdot \dfrac{H/C_{raw}}{H/C_{raw}+12} + m_{LDPE} \cdot \dfrac{1}{7}} \times 100\% \tag{4}$$

$$C-B = \frac{\sum m_i \dfrac{12}{H/C_{oil}+12} + m_{coke} \dfrac{12}{H/C_{coke}+12}}{m_{raw} \dfrac{12}{H/C_{raw}+12} + m_{LDPE} \cdot \dfrac{6}{7}} \times 100\% \tag{5}$$

where H/C_{oil} and H/C_{coke} are the H/C ratios of oil and coke products. H/C_{raw} is the H/C ratio of the raw heavy oil. It was assumed that the H/C ratio of LDPE is 2.

The elemental analysis of oil and coke samples was applied on a vario EL III element analyzer. The morphology of coke samples was observed on a NanoScope IIIa MultiMode AFM microscope with the accelerating voltage of 15 kV. The NMR spectra of oil samples were analyzed on a Bruker AVANCE 500 MHz NMR spectrometer during which deuterated chloroform and tetramethylsilane were used as the solvent and the internal standard for calibrating chemical shift. Protons in oil were classified as aromatic H (H_{Ar}), α-alkyl H (H_α), γ-alkyl H (H_γ) and other alkyl H (H_β). Carbon atoms were classified as aromatic C (C_{Ar}), alicyclic and paraffinic C (C_{N+P}) [14,15].

The distributions of H and C of different definitions in oil samples were evaluated by

$$\%H_i = \left(A_iH/\sum A_iH\right) \times 100\% \tag{6}$$

$$\%C_i = \left(A_iC/\sum A_iC\right) \times 100\% \tag{7}$$

where subscript i denotes anyone of the defined H or C atoms. A_iH and A_iC are the peak areas of different H and C atoms on the ^{1}H NMR and C NMR spectra.

The average number of H atoms bonding directly with an aromatic C atom (H_m), an indication of the polycyclic degree of oil samples, was given by

$$H_m = H/C_{oil} \times (\%H_{Ar}/\%C_{Ar}). \tag{8}$$

By the analytical methods mentioned above, the measured properties of the raw heavy oil are listed in Table 1. LDPE used in this work has a density of 0.92 g/cm^3 and a melting point between 378 and 388 K. The weight average molecular weight of LDPE is 1.25 × 10^5 Da.

Each experimental run was repeated three times and the maximum errors of the product distribution fell within a reasonable range of ±5%. Only the average data were reported in the figures hereinafter. For simplicity, the values of balance evaluation and the measured H/C ratios were attached in the corresponding figures.

3. Results and discussion

3.1. Coking mechanism in pyrolysis of heavy oil in SCW

Before discussing the coking behavior of the co-pyrolysis in SCW, it is better to clarify the coking mechanism in the pyrolysis of heavy oil in SCW first. The pyrolysis of heavy oil in SCW then was performed at 693 K and water density of 0.30 g/cm^3, with the product distribution at the reaction time ranging from 30 to 60 min illustrated in Fig. 1.

With the extension of reaction time, the yield of asphaltenes decreases from 7.2 to 3.1 wt.% and that of aromatics decreases from 39.9 to 33.6 wt.%. Meanwhile, the yields of saturates and resins fluctuate around 4.0 wt.% and 16.0 wt.%, respectively. Evidently, the quality of the liquid pyrolysis product is improved since an increasing H/C ratio from 1.39 to 1.48 and a decreasing proportion of asphaltenes from 10.8 to 5.5 wt.% can be obtained. However, such an improvement is at the cost of undesired condensation. Not only the yield of coke increases from 18.3 to 29.3 wt.%, but also the yield of maltenes decreases from 59.4 to 52.4 wt.%. In fact, the yield of coke at the reaction time of 45 min is already higher than the content of asphaltenes in the raw heavy oil, which means that part of light fractions is lost via condensation. Since the formation of coke with a decreasing H/C ratio is always accompanied by the production of H-rich gases, the hydrogen balance is gradually worsened from 81% to 74%. However, the mass balance and carbon balance nearly keep unchanged.

NMR analysis of the liquid pyrolysis product was subsequently performed, with the results listed in Table 2. As the reaction goes on,

Table 1
Properties of the raw heavy oil.

ρ (g/cm^3)	H/C ratio	SARA fractions (wt.%)			
		Saturates	Aromatics	Resins	Asphaltenes
0.98	1.27	10.5	42.1	25.5	21.9
H distribution (%)				C distribution (%)	
H_{Ar}	H_α	H_β	H_γ	C_{Ar}	C_{N+P}
9.1	16.8	58.6	15.5	17.2	82.8