Fuel Processing Technology 160 (2017) 34–38

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Catalytic cracking of 4-(1-naphthylmethyl)bibenzyl in sub- and supercritical water

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ARTICLE INFO

Article history:
Received 12 August 2016
Received in revised form 11 January 2017
Accepted 16 February 2017
Available online 23 February 2017

Keywords:
NMBB
Cracking
Supercritical water
Subcritical water
Ni/AC

ABSTRACT

The upgrading and reforming of coal-derived liquids are necessary for the application of high value-added liquid fuels, but the processing is difficult due to the amounts of impurities. In this paper, the catalytic cracking of 4-(1-naphthylmethyl)bibenzyl (NMBB) as a model reaction was studied deeply under sub- and supercritical water environment. Water might serve as a cheap and environmental H donor, which was more efficient than the supplied H_2 in the processing of coal-derived liquids upgrading. Meanwhile, sub- and supercritical water could provide a homogeneous reaction environment for NMBB cracking as special solvents. The NMBB conversion under subcritical water was much higher than that under supercritical water. Furthermore, for H_2 atmosphere, NMBB conversion was higher than that of N_2 atmosphere, indicating that the process of in-situ H_2 formation from subcritical water was more easily. Therefore, the cracking of NMBB under subcritical water and H_2 atmosphere could be regarded as a reasonable reaction condition.

1. Introduction

The coal and coal-derived liquids are widely selected as energy resources due to the abundant supply [1–5]. However, coal as a high-molecular weight material is composed of aromatic moieties connecting with ether or aliphatic linkages. It has ill-defined structures and coals reaction leads to large numbers of products even under mild conditions. Coal-derived liquids also contain high-molecular weight, S and N moieties. Therefore, the upgrading and reforming of coal-derived liquids are needed for the use of clean liquid fuels. In order to study the catalytic activity and products selectivity during the coal-derived liquids cracking process, a model compound is usually selected. Generally, developing model reaction for surrogates remains challenging. Chang et al. have investigated the reaction mechanisms of heavy oil cracking by using 1-phenyldodecane as a model compound [6]. The isomerization cracking of n-octane and n-decane has been studied over the regulated acidity Pt/WO_x-SO_4-ZrO_2 catalysts [7]. The *n*-octane catalytic cracking over alkali-treated MFI zeolites also has been studied for the research of acidity catalytic roles and pore structure [8]. The complexity of coal and coal-derived liquids obscure the nature of the interactions among them and makes it difficult to unravel the underlying reaction pathways, kinetics, and mechanism [9]. Thus, over the past few decades, 4-(1-naphthylmethyl)bibenzyl (NMBB) has been employed as a model compound of coal and coal-derived liquids for further upgrading with various catalysts, since it has an intriguing feature of the presence of five different potential cleavage sites C—C bonds (these bonds are denoted **a**–**e** in the structure shown) and several aromatic rings, as given in Fig. 1 [10].

A range of cracking technologies has been developed, including fluid catalytic cracking process, coking and hydrocracking. In our recent work on catalytic heavy oils and coal, we have found that water as addition has very strong promoting effect on catalytic hydrogenation of the reactants [11–13]. The physicochemical properties of supercritical water (critical point: $T = 374$ °C, and $P = 22.1$ MPa) are different from those of floating liquid water. Supercritical water has attracted great attention because of safe, non-toxic, readily available, inexpensive and friendly environmental, and it is also effective as a promising solvent for wide application, such as biomass gasification, effluent treatment, coal and heavy oil cracking [14–19].

Under N_2 or H_2 atmosphere, water addition indeed promotes coal conversions according to our previous studies [11,20]. In the sub- or supercritical water environment, hydrocarbons can be partial oxidized to supply CO for the continuously reaction. In this paper, the CO is formed from the reaction of sub- or supercritical water and hydrocarbons at first. Then, the produced in-situ H_2 from water gas shift reaction (WGSR, $CO + H_2O \rightarrow CO_2 + H_2$) with sub- or supercritical water will hydrocrack NMBB continuously [15,21,22]. In addition, the in-situ H_2 is more active than molecular hydrogen. Sato et al. have reported that coal derived liquid conversion increases because hydrogen atoms are provided by supercritical water [23].

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http://dx.doi.org/10.1016/j.fuproc.2017.02.014
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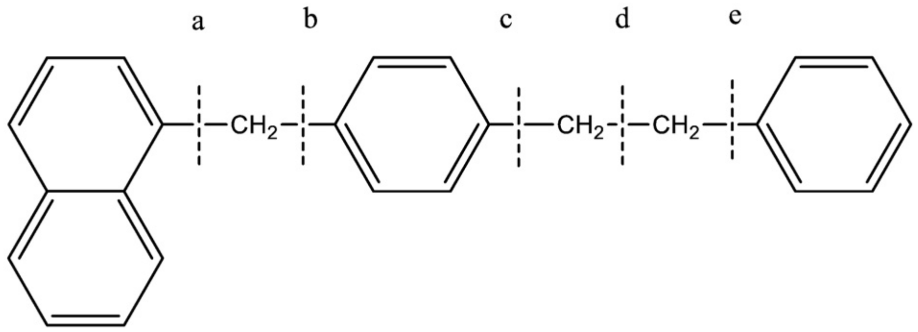


Fig. 1. Structure of NMBB and its five potential cleavage sites.

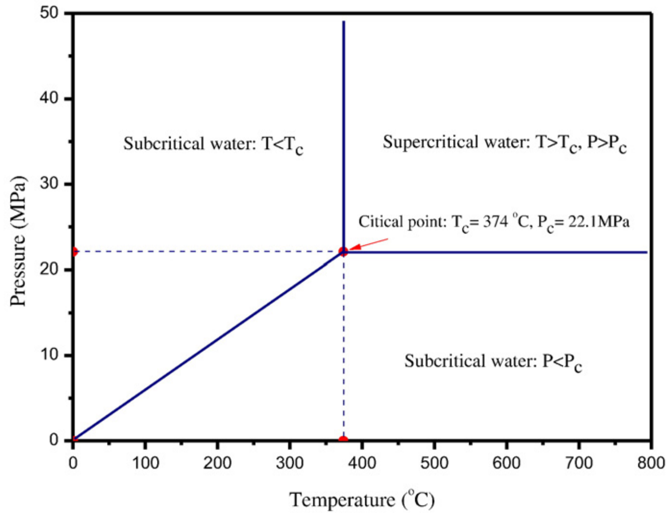


Fig. 2. Relationship between Subcritical water and supercritical water.

As we know that the condition of subcritical water is milder than that of supercritical water, it may be a promising method for coal derived liquid product upgrading in industrial application. In this work, the effect of sub- and supercritical water on the NMBB conversion and products selectivity has been discussed. The relationship between sub- and supercritical water is shown in Fig. 2.

2. Experimental

2.1. Catalyst preparation

The 5 wt% Ni-based catalyst with activated carbon (AC) as support was prepared by incipient wetness impregnation (IWI) method. Prior to impregnation, AC was pretreated at 120 °C for 4 h under vacuum condition. The wet catalyst was dried and calcined in N_2 at 400 °C. The calcined catalyst was reduced by H_2 at 400 °C and followed by passivation with 1% O_2 in N_2 atmosphere to obtain the final catalyst, denoted as 5%Ni/AC.

2.2. NMBB cracking reaction

Catalytic cracking of NMBB reaction was carried out in a 20 mL steel batch autoclave reactor (HASTELLOY alloy). As a typical run, 0.5 g of reduced Ni/AC, 3 g of NMBB (Tokyo Chemical Industry) and a certain amount of deionized water were placed in autoclave reactor using an electric furnace swinging. The reaction system was purged three times with 1 MPa H_2 or N_2 to remove the trapped air. After the purging, the reactor was pressurized with H_2 or N_2 to 3.0–6.0 MPa, and then the reactor system was heated up to 350 °C or 400 °C.

2.3. Products analysis

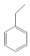
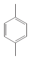
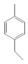
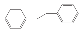
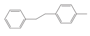
After reaction, the reactor was cooled down and then depressurized to atmospheric pressure. Water phase and oil phase products were separated by acetone as solvent. The liquid products were analyzed by a capillary chromatography (GC-14B, FID, Shimadzu, Japan). The solid products were first dissolved in toluene and filtered. The solids still remaining were placed on a petri dish, dried at 120 °C for 12 h and weighed. This toluene insoluble was defined as coke and spent catalyst [24].

(1) The conversion of NMBB was calculated by monitoring its disappearance:
Conversion (%) = [(the initial number of NMBB moles − the remaining number of NMBB moles) / the initial number of moles of NMBB] × 100%.

(2) The products distribution was denoted as:
Yield (mol%) = [product (mol) / the initial number of NMBB moles] × 100%.

(3) The formed coke was denoted as:
Weight of coke (g) = weight of insoluble solids (g) − weight of loaded catalyst (g).
Coke yield (wt%) = [weight of coke (g) / weight of loaded NMBB (g)] × 100%.

Table 1
Catalytic of NMBB under sub- or supercritical water in different atmosphere.

Run	Temp. (°C)	Atom sphere	Water state	Conv. (%)	Yield (mol%) of products										Coke (wt%)
															
1	350	N_2	Subcritical	23	0	0.07	0.04	0	0	0	4.51	0.22	0.42	6.41	27
2	350	H_2		44	0	0	0.17	0	0.13	0.48	8.21	0.33	0.71	14.3	22
3	400	N_2	Supercritical	55	0	0.53	0.12	0.62	0	0	18.6	0.90	2.61	18.3	31
4	400	H_2		58	0.38	2.00	0.70	1.00	0.25	0.25	22.4	1.24	3.71	27.8	28

Reaction conditions: NMBB, 3 g; H_2O, 11 g; 5%Ni/AC, 0.5 g; reaction time, 60 min; gas pressure, 3 MPa.