

Article

A Study on the Hydrotreating of Coal Hydroliquefaction Residue and its Kinetics

Jue Huang, Xilan Lu, Dexiang Zhang and Jinsheng Gao *

Department of Chemical Engineering for Energy Resources, East China University of Science and Technology, Shanghai, China; E-Mails: huangj_edward@sina.com(J.H.); lxl@ecust.edu.cn(X.L.L.); zdx@ecust.edu.cn(D.X.Z.)

* Author to whom correspondence should be addressed; E-mail: gjs@ecust.edu.cn;
Tel.: +86 21 64252058.

Received: 19 August 2010; in revised form: 26 August 2010 / Accepted: 30 August 2010 /

Published: 09 September 2010

Abstract: Hydro-conversion of coal hydroliquefaction residue obtained from a 6t/day pilot plant of Shenhua Group in Shanghai was carried out under the hydrotreating condition. The coal hydroliquefaction residue and its product were extracted in sequence with *n*-hexane, toluene and tetrahydrofuran in a Soxhlet apparatus. The *n*-hexane soluble fractions increased with the increase of reaction temperature and time. Its amount increased from 14.14% to a maximum of 40.86% under the conditions of 470 °C and 30 min, which meant that moderate extension of coal residence time in the coal hydroliquefaction reactor is beneficial to the increase of oil yield. A 4-lumped kinetic model of coal hydroliquefaction residue hydro-conversion was performed using solubility-based lumped fractions. In the model, the tetrahydrofuran insoluble fractions were classified into two parts: easily reactive part and unreactive part. The kinetic parameters were estimated by a fourth-order Runge-Kutta method and a nonlinear least squares method, and the apparent activation energies were calculated according to the Arrhenius Equation. A large quantity of total catalyst consisting of remained liquefaction catalyst, part of the mineral from raw coal and additive Fe-based catalyst could considerably reduce the apparent activation energy of hydro-conversion for the toluene insoluble/tetrahydrofuran insoluble fractions to 36.79 kJ·mol⁻¹. The calculated values of the model coincided well with the experimental values.

Keywords: coal hydroliquefaction; residue; hydro-conversion; kinetics; recycle

1. Introduction

Due to the growing global energy demand and rising oil prices, coal hydroliquefaction (CHL) as a kind of clean coal technology which could replace crude oil imports by converting coal to liquids, has attracted increasing interest around the world, especially in China. The aim of CHL is to obtain as high an oil yield as possible under rational technological conditions. However, coal hydroliquefaction residues (CHLR), a by-product, usually account for 20%–30%, while the oil is just about 55% in a typical product distribution. Consequently, the efficient utilization of CHLR is vital from the viewpoint of improving coal liquefaction economy and environmental protection. Hitherto, the utilization of CHLR has been widely researched [1–5] in various applications, such as a feed stock for gasification, combustion or coking, as a asphalt pavement modifier or for making carbon microfibers, but all these require additional industrial infrastructure for the subsequent rework after the CHL process.

CHLR contains organic and inorganic matter. Preasphaltenes, asphaltenes and heavy distillate oil account for 40% to 60% in organic matter, and have a hydrogenation or hydrogenolysis potential, as reported in some articles [6–14]. The minerals from raw coal and the catalyst used in the hydroliquefaction process with their large content in inorganic matter are beneficial for optimizing CHL technology if CHLR is recycled as a CHL co-reactant, so it is absolutely necessary to study the liquefaction behavior of CHLR and its kinetics before designing any CHLR recycle process.

In order to figure out the possibilities and advantages of recycled CHLR as a co-reactant in CHL, the hydro-conversion behavior of CHLR was studied under moderate hydrotreating conditions and a kinetic model of this process was proposed using a 4-lumped kinetic model, considering the similarities and dissimilarities between CHL and CHLR hydro-conversion.

2. Result and Discussion

2.1. Hydro-Conversion of CHLR

The composition of the CHLR sample obtained by the sequential extraction is 14.14% *n*-hexane soluble fraction (HS), 35.00% *n*-hexane insoluble/toluene soluble fractions (A), 14.63% toluene insoluble/tetrahydrofuran soluble fractions (PA) and 36.23% tetrahydrofuran insoluble fraction (THFIS) on a dry and ash-free basis (wt. %, daf). Its proximate analysis and ultimate analysis data are listed in Table 1.

Table 1. Proximate analysis and ultimate analysis of Shenhua CHLR.

Proximate analysis/wt%			Ultimate analysis(daf)/wt%			
M _{ad}	A _d	V _{daf}	C	H	S	N+O
0	15.89	45.02	91.44	5.47	2.4	0.69

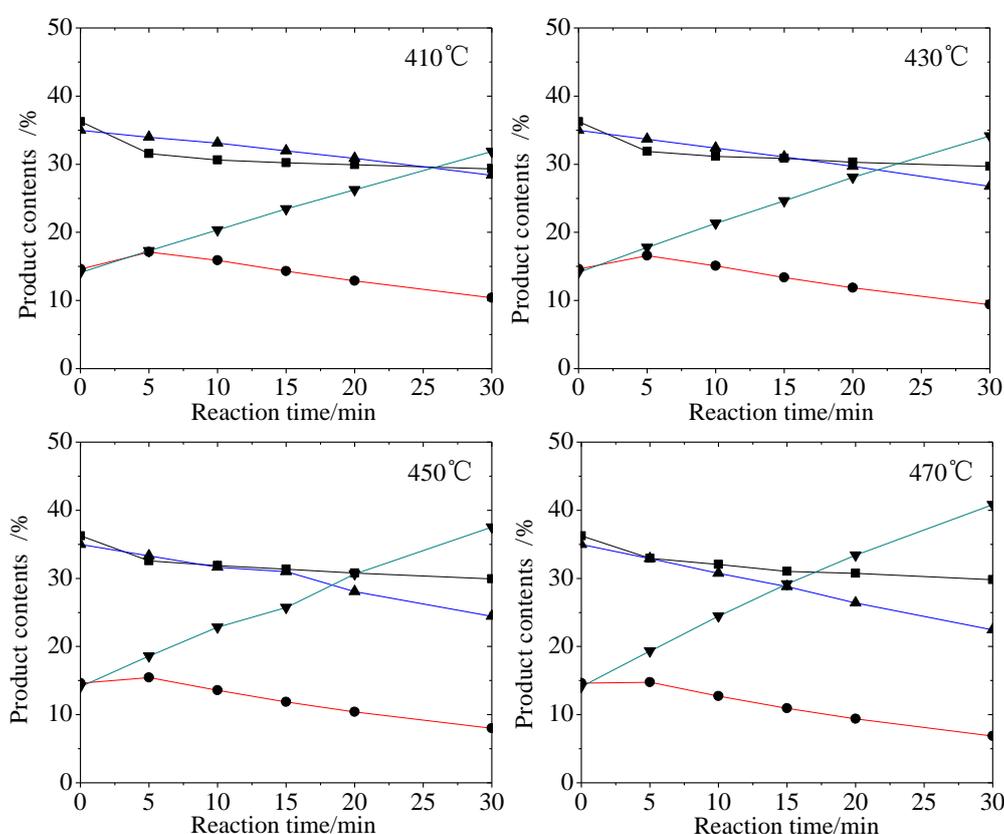
M_{ad}: Moisture content of sample on an air dry basis; A_d: Ash yield on a dry basis; V_{daf}: Volatile matter yield on a dry and ash-free basis.

The CHLR hydro-conversion experiments were carried out at four temperatures (410 °C, 430 °C, 450 °C and 470 °C), under an initial hydrogen pressure of 5MPa and at reaction times up to 30 min. CHLR hydro-conversion, like CHL, is a complicated process which involves a large number of competitive reactions, *i.e.* thermal decomposition, hydrogenation, dehydrogenation, dealkylation,

bond-breakage between simple structure units and the possible rupture of cyclic compounds. Once free radicals are formed, they are stabilized through hydrogenation to form lighter substances such as PA, A and HS or stabilized by each other to polymerize or condense to substances like THFIS. Unlike direct CHL, coke, PA, A and HS exist in the CHLR before the reaction. That is to say, PA and A are hydrogenated and cracked into oil or gas in the initial reaction stage.

Figure 1 illustrates the effects of reaction time on CHLR hydro-conversion. It was found that A decreased and HS increased continuously with reaction time increase at various temperatures. At 410 °C, A decreased from 35% to 28.38%, while HS increased from 14.14% to 31.88% after 30 min, which meant the conversion of A to the HS form is prolonged due to the increase of time.

Figure 1. Product contents of Shenhua CHLR hydro-conversions vs. time at various temperatures -■-, THFIS; -●-, PA; -▲-, A; -▼-, HS.

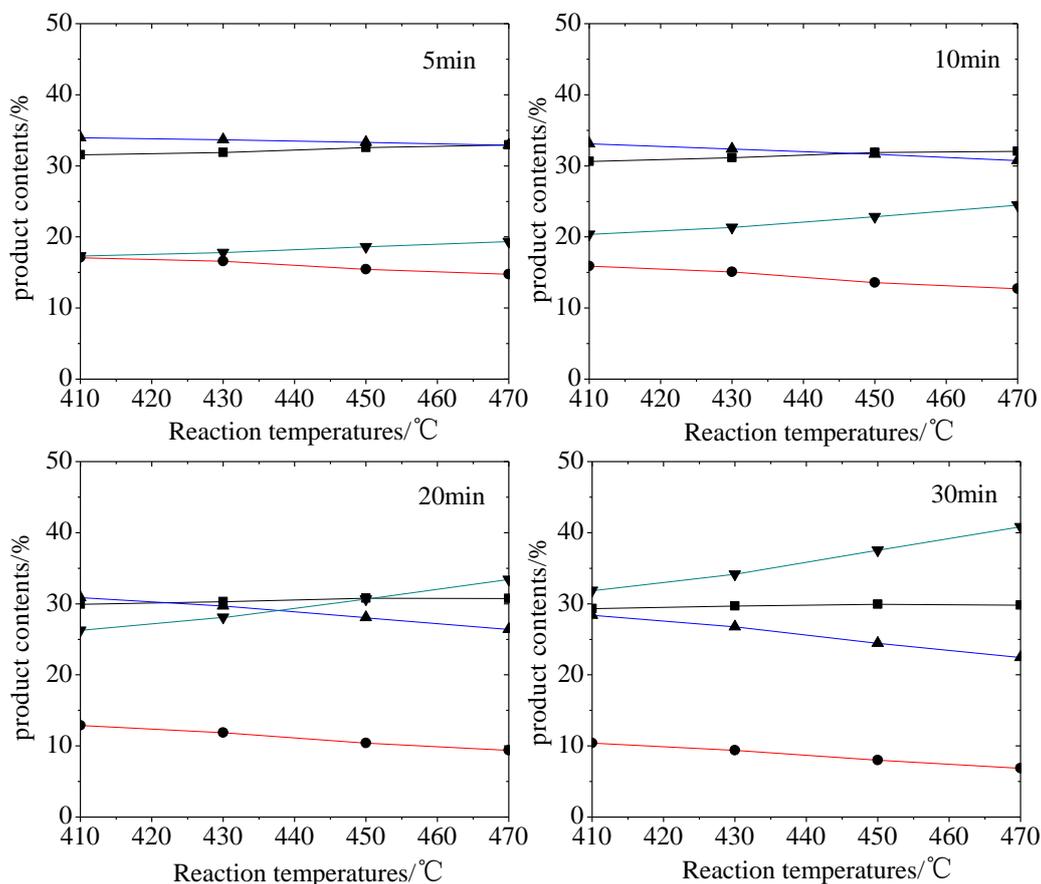


Apparently, extending of reaction time is beneficial for increasing the oil yield. THFIS decreased obviously during the initial reaction time (0–5 min) and slowly after 5 min at various temperatures, while PA increased during the initial time (0–5 min) and decreased after 5 min at various temperatures. At 430 °C, THFIS showed a sharp decrease from 36.23% to 31.91% in the first 5 min and a weak decrease from 31.91% to 29.68% in the final 25 min. PA showed an increase from 14.63% to 16.60% in the first 5 min and a decrease from 16.60% to 15.09% in the subsequent 5 min. It can be indicated that the formation of PA hydrogenated or cracked from THFIS is more active than condensation or hydrogenation of PA during the initial reaction time. As known from the literatures [6,15], THFIS with highly condensed poly-aromatic hydrocarbons and unreacted coal which experienced a long time of treatment during the typical CHL conditions, are impossible to convert to PA under moderate hydrotreating condition. However, there could be some mildly condensed PA and A contained in

THFIS, which were generated in the high-temperature separator of CHL process due to a lack of hydrogen. These condensed PA and A could easily depolymerized to PA again under the moderate hydrotreating conditions.

The temperature effects on CHLR hydro-conversion are described in Figure 2. THFIS increased slowly with the increase of reaction temperature at various times. During the initial 5 min, THFIS increased just from 31.58% to 32.95% when the temperature increased from 410 °C to 470 °C, indicating that the temperature has little effect on THFIS conversion. In all cases, both PA and A decreased with the increase of the reaction temperature, while HS increased with the increase of the reaction temperature. At 470 °C and 30 min, PA and A were at a minimum value of 6.86% and 22.44%, respectively, while HS was at its maximum value of 40.86%, suggesting an obvious increase in the total HS yield in CHL if CHLR is recycled as a co-reactant.

Figure 2. Product contents of Shenhua CHLR hydro-conversion vs. temperature at various times -■-, THFIS; -●-, PA; -▲-, A; -▼-, HS.



2.2. Hydro-Conversion Kinetic Model Establishment and Solution

Due to the complexity of CHLR and the diversity of CHLR hydrogenation products, it is difficult to describe the CHLR hydro-conversion process using a simple chemical kinetic reaction. The lumped kinetic model is the most effective method to reduce complexity. In this work, 4-lumped fractions have been defined on the grounds of different physico-chemical properties and solubility in different solvents as follows:

PA: the toluene insoluble/tetrahydrofuran soluble fractions

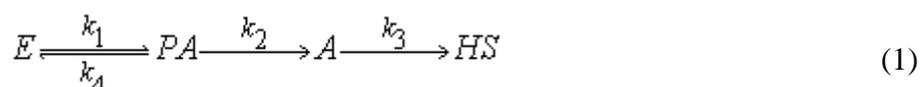
A: the *n*-hexane insoluble/toluene soluble fractions

HS: oil and gas

E: Easily reactive part in THFIS

According to some scholars' studies, THFIS with highly condensed poly-aromatic hydrocarbons and unreacted coal are hard to react under typical CHL conditions. But in this experiment, it was found that THFIS obviously decreased with time during the initial stage. This could be considered a result of the generation of some mildly condensed PA and A in the high-temperature separator of the CHL process. These condensed PA and A may easily depolymerize in a short time under the hydrotreating conditions, so in the kinetic model, we made an assumption that THFIS were classified into two parts: easily reactive part (E) and unreactive part (N). The experimental results indicated that the ratio of the converted E and produced E from the reverse reaction of PA was 2.39 at 470 °C and 5 min. Thus, the total converted E and produced E should be 25% of THFIS at 470 °C and 30 min based on the assumption that the ratio 2.39 was unchanged with the reaction time at 470 °C. Consequently, E was calculated as about 25% of THFIS and N was about 75% of THFIS.

Considering that the reaction temperature was not very severe and the catalyst had a moderate hydrogenation performance in the reaction, the polymerization and condensation of A and HS could be ignored while that of PA could not. Consequently, a reaction pathway as shown in Eq. 1 is proposed. All reactions in the pathway were based on serial and reverse reactions and assumed as first-order reactions. The influences of hydrogen pressure, particle size and mass transfer on CHLR hydrogenation were ignored.



According to the proposed reaction pathway, the time effect on CHLR hydrogenation is described by the following set of differential equations:

$$\frac{dE}{dt} = k_4 PA - k_1 E \quad (2)$$

$$\frac{dPA}{dt} = k_1 E - k_4 PA - k_2 PA \quad (3)$$

$$\frac{dA}{dt} = k_2 PA - k_3 A \quad (4)$$

$$\frac{dHS}{dt} = k_3 A \quad (5)$$

The objective function to be minimized was the sum of the squares of the difference between the experimental and the calculated values. The parameter estimation problem was mathematically formulated into the following nonlinear optimization program as described in Equation (6):

$$\min S = [(E_{\text{exp}} - E_{\text{pred}})^2 + (PA_{\text{exp}} - PA_{\text{pred}})^2 + (A_{\text{exp}} - A_{\text{pred}})^2 + (HS_{\text{exp}} - HS_{\text{pred}})^2] \quad (6)$$

where E_{exp} , PA_{exp} , A_{exp} , HS_{exp} are the experimental values of E, PA, A and HS, respectively, and E_{pred} ,

PA_{pred} , A_{pred} , HS_{pred} are the theoretically calculated values obtained from the derived model equations (2) through (5), respectively.

A program in MATLAB language based on the nonlinear least squares method was used to estimate the kinetic parameters in the proposed reaction pathway. Numerical solutions of the equations (2) through (5) were obtained by using a fourth-order Runge-Kutta method [16]. The kinetic parameters obtained for the model proposed are detailed in Table 2. All the kinetic constants calculated increase with temperature. The values of k_1 , k_4 at 470 °C are 2.8 times and 5.2 times of those at 410 °C, respectively. Temperature has a more severe effect on the reverse reaction of PA than hydro-conversion of THFIS, which indicates that the reverse reaction of PA is more active at a higher temperature.

The apparent activation energies were calculated from a semilogarithmic plot of $\ln k_1$, $\ln k_2$, $\ln k_3$ and $\ln k_4$ vs. $1/T \times 10^3$, as shown in Figure 3, using the Arrhenius Equation described in Equation (7):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (7)$$

where E_a is the apparent activation energy, A is the pre-exponential factor, R is the molar gas constant and T is the absolute temperature (K).

Figure 3. Arrhenius curve of the 4-lumped kinetic model for Shenhua CHLR hydro-conversion -■-, k_1 ; -●-, k_2 ; -▲-, k_3 ; -▼-, k_4 .

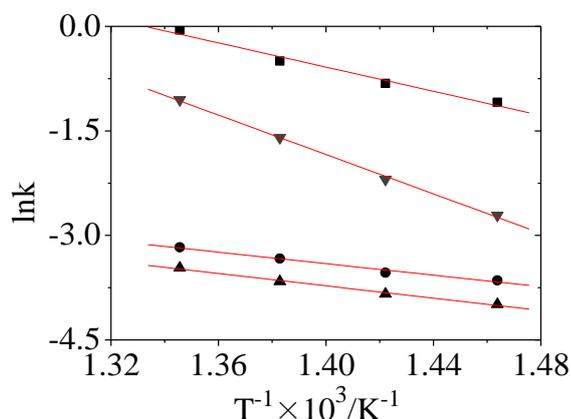


Table 2. Kinetic parameters of the 4-lumped model for Shenhua CHLR hydro-conversion.

Temperature/ °C	410	430	450	470	$E_a/\text{kJ}\cdot\text{mol}^{-1}$
k_1	0.3362	0.4406	0.6077	0.9472	72.13
k_2	0.0261	0.0292	0.0357	0.0420	34.29
k_3	0.0185	0.0215	0.0257	0.0312	36.79
k_4	0.0665	0.1112	0.2023	0.3489	117.49

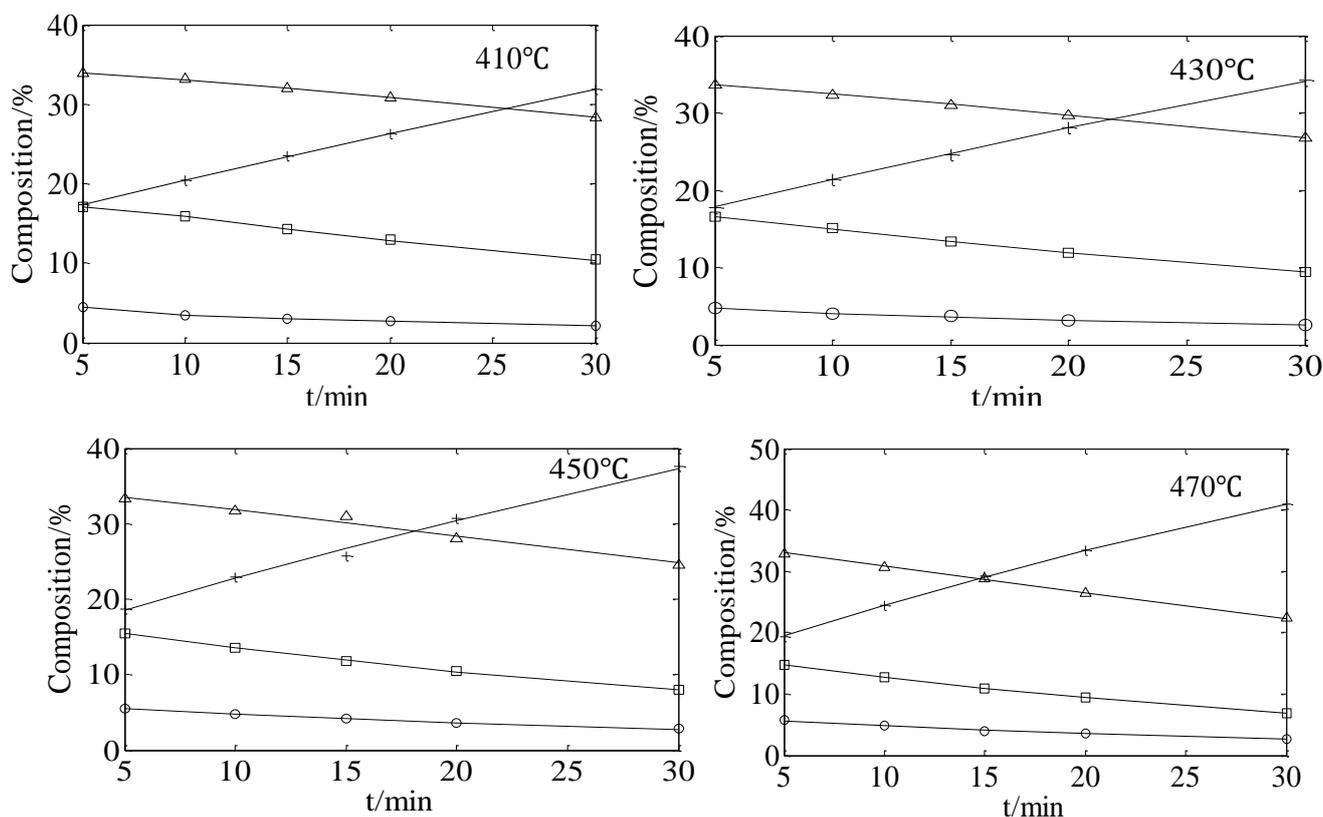
The apparent activation energy of depolymerization reaction for THFIS was much lower than that of PA formation reaction from coal in CHL [17], which proved that it was reasonable to make the assumption of classifying THFIS into E and N. Compared with the reported results of literature [6], the apparent activation energy of hydrogenation for A was much lower in this work and that for PA was low too. It could be considered as the result of the large quantity of total catalyst consisting of remaining liquefaction catalyst, part of the minerals from raw coal and the added Fe-based catalyst.

The large apparent activation energy of reverse reaction for PA could be explained by the fact that polymerization or condensation of PA needs higher temperatures, which are beneficial to the hydro-conversion of CHLR under the hydrotreating conditions. The reaction temperature of CHL was usually from 400 °C to 470 °C, which was almost identical to the hydrotreating conditions, indicating that there could be no severe polymerization if CHLR is recycled as a co-reactant in CHL.

2.3 Verification of the Model

Figure 4 gives the comparison results between calculated values of the model and the experimental data of CHLR hydrogenation catalyzed by Fe-based catalyst at four temperatures. It can be seen from Figure 4 that this model gives a satisfying fit between the calculated values from the model and the experimental data.

Figure 4. Comparison of kinetic model(lines) with experimental data (dots) of Shenhua CHLR hydrogenation at various temperatures -○-, E; -□-, PA; -△ -, P; -+-, H.



As reported, Benito *et al.* [6] found a decrease in asphaltenes, an increase in oil and gas and non-reaction of coke (toluene insoluble) with the increase of time and temperature in the hydro-cracking process. They proposed a simple model in which asphaltenes cracked to form gas and oil through two parallel reactions. However, in this experiment, a sharp decrease in THFIS under hydrotreating conditions was found and this result was not in accord with the kinetic model proposed by those authors. It could be viewed as the rational result of mildly condensed PA and A generated in the high-temperature separator of CHL process.

3. Experimental Section

The CHLR used was generated from a 6t/day CHL pilot plant of the Shenhua Group in Shanghai. The CHL reactor was operated at 455 °C and 18 MPa in the presence of Shenhua Fe-based catalyst (1 wt. % as Fe loading on daf coal basis). The CHL products were separated through high-temperature and low-temperature separators, followed by atmospheric and vacuum distillations. The CHLR discharged from bottom of a vacuum distillation column was cooled and then grounded to -80 mesh. To obtain different fractions of heavy liquids in the CHLR, the CHLR was extracted in sequence with *n*-hexane, toluene and tetrahydrofuran (THF) in a Soxhlet apparatus as commonly found in the literature [17,18]. The *n*-hexane soluble, *n*-hexane insoluble/toluene soluble, toluene insoluble/THF soluble and THF insoluble fractions obtained are defined as HS which consist of oil and gas (for samples after treatment), asphaltenes (A), preasphaltenes (PA) and THFIS, respectively. After each extraction step the insoluble materials collected in a thimble were carefully dried under vacuum and weighed to determine the extraction yield. The soluble materials were obtained by removing the solvent through rotary evaporation followed by drying under vacuum at 60 °C for 48 h.

The hydro-conversion experiment of CHLR was conducted in a 25 mL stainless steel micro-reactor. The reactor is a type of small autoclave, closed at the end with a plug which is provided with a valve for a gas inlet/outlet. The micro-reactor is furnished with a thermocouple for temperature measurement during the experiments. In a typical experiment, the reactor was charged with 4 g sample catalyzed by Fe-based catalyst (5 wt. % as catalyst loading on charged CHLR basis), purged and pressurized with hydrogen to an initial pressure of 5 MPa and rapidly heated to the reaction temperature of 410–470 °C by immersion in a preheated salt bath. The reaction time is defined as the residence time at the desired temperature neglecting the pre-heating periods. During the run, the system was continuously shaken vertically at 400 cycles/min. At the end of the run, the micro-reactor was quenched in a water tank to cool quickly. All the reactions were duplicated to ensure accuracy and the average errors were about ±2%. After the reactions, the micro-reactor was vented and the remaining materials were recovered by washing with *n*-hexane and then were extracted by the same solvent extraction procedure used for the CHLR fraction as above.

4. Conclusions

- (1) CHLR obtained from coal hydroliquefaction reactor could be converted to lighter fractions under moderate hydrotreating conditions. At 470 °C and 30 min, HS was enhanced from 14.14% to 40.86% suggesting that the total HS yield in CHL could increase if CHLR is recycled as a co-reactant in CHL. It also indicates that a moderate extension of coal residence time in CHL is beneficial to the increase of oil yield.
- (2) Reverse reactions of PA were not significant under the hydrotreating conditions and the temperature of CHL was almost identical with this hydrotreating condition, which indicated that there could be no severe polymerization caused by recycling of CHLR in CHL.
- (3) Unlike the highly condensed poly-aromatic hydrocarbons and unreacted coal contained in THFIS, mildly condensed PA and A generated in high-temperature separator of the CHL process could easily depolymerize in a short time under the hydro-conversion which was also proved by a kinetic study.
- (4) On the basis of the non-uniform constitution of CHLR, the moderate hydrotreating performance of

catalyst and the non-severity of temperature, the kinetics of the CHLR hydrogenation could be conveniently described by a 4-lumped kinetic model.

- (5) Our kinetic study of CHLR hydro-conversion shows that a large quantity of total catalyst consisting of remaining liquefaction catalyst, part of the minerals from raw coal and the Fe-based catalyst additive could considerably reduce the apparent activation energies of hydro-conversion for PA and A, which is beneficial to the recycling of CHLR in CHL.

Acknowledgements

This study was supported by Chinese National Programs for High Technology Research and Development (863 Program, 2006AA05Z314), National Basic Research Program of China (973 Program, 2011CB201304) and Shanghai Leading Academic Discipline Project (B506).

References and Notes

1. Chu, X.; Li, W.; Chen, H. Gasification property of direct coal liquefaction residue with steam. *Process Saf. Environ. Prot.* **2006**, *84*, 440–445.
2. Chu, X.J.; Li, W.; Li, B.Q.; Chen, H.K. Sulfur transfers from pyrolysis and gasification of direct liquefaction residue of Shenhua coal. *Fuel* **2008**, *87*, 211–215.
3. Zhou, Y.; Xiao, N.; Qiu, J.S.; Sun, Y.F.; Sun, T.J.; Zhao, Z.B.; Zhang, Y.; Tsubaki, N. Preparation of carbon microfibers from coal liquefaction residue. *Fuel* **2008**, *87*, 3474–3476.
4. Yang, J.L.; Wang, Z.X.; Liu, Z.Y.; Zhang, Y.Z. Novel Use of Residue from Direct Coal Liquefaction Process. *Energy Fuels* **2009**, *23*, 4717–4722.
5. Xiao, N.; Zhou, Y.; Qiu, J.S.; Wang, Z.H. Preparation of carbon nanofibers/carbon foam monolithic composite from coal liquefaction residue. *Fuel* **2010**, *89*, 1169–1171.
6. Benito, A.M.; Callejas, M.A.; Martinez, M.T.; Ana, M.B.; Maria, A.C.; Maria, T.M. Kinetics of asphaltene hydroconversion: 2. Catalytic hydrocracking of a coal residue. *Fuel* **1997**, *76*, 907–911.
7. Martinez, M.T.; Benito, A.M.; Callejas, M.A. Kinetics of asphaltene hydroconversion: 1. Thermal hydrocracking of a coal residue. *Fuel* **1997**, *76*, 899–905.
8. Sugano, M.; Ikemizu, R.; Mashimo, K. Effects of the oxidation pretreatment with hydrogen peroxide on the hydrogenolysis reactivity of coal liquefaction residue. *Fuel Process. Technol.* **2002**, *77*, 67–73.
9. Sugano, M.; Tamaru, T.; Hirano, K.; Mashimo, K. Additive effect of tyre constituents on the hydrogenolyses of coal liquefaction residue. *Fuel* **2005**, *84*, 2248–2255.
10. Sugano, M.; Onda, D.; Mashimo, K. Additive effect of waste tire on the hydrogenolysis reaction of coal liquefaction residue. *Energy Fuels* **2006**, *20*, 2713–2716.
11. Li, J.; Yang, J.L.; Liu, Z.Y. Hydro-treatment of a direct coal liquefaction residue and its components. *Catal. Today* **2008**, *130*, 389–394.
12. Wang, T.X.; Zong, Z.M.; Zhang, J.W.; Wei, Y.B.; Zhao, W.; Li, B.M.; Wei, X.Y. Microwave-assisted hydroconversions of demineralized coal liquefaction residues from Shenhua and Shengli coals. *Fuel* **2008**, *87*, 498–507.
13. Li, J.; Yang, J.L.; Liu, Z.Y. Hydrogenation of heavy liquids from a direct coal liquefaction residue

for improved oil yield. *Fuel Process. Technol.* **2009**, *90*, 490–495.

14. Wei, Y.B.; Zong, Z.M.; Xie, R.L.; Peng, Y.L.; Mou, J.; Ma, Y.M.; Zhou, X.; Huang, Y.; Wu, L.; Wei, X.Y. Solid Superacid-catalyzed Hydroconversion of Demineralized Shengli Coal Liquefaction Residue under Microwave Irradiation. *Energy Sources A* **2010**, *32*, 551–558.
15. Ikeda, K.; Sakawaki, K.; Nogami, Y.; Inokuchi, K.; Imada, K. Kinetic evaluation of progress in coal liquefaction in the 1t/d PSU for the NEDOL process. *Fuel* **2000**, *79*, 373–378.
16. Lange, T.; Kopsel, R.; Kuchling, T.; Klose, E. Hydrogenation behaviour of a German brown coal: 2. Non-isothermic kinetics. *Fuel* **1989**, *68*, 366–370.
17. Shui, H.F.; Chen, Z.X.; Wang, Z.C.; Zhang, D.X. Kinetics of Shenhua coal liquefaction catalyzed by SO₄²⁻/ZrO₂ solid acid. *Fuel* **2010**, *89*, 67–72.
18. Li, X.; Hu, H.Q.; Zhu, S.W.; Hu, S.X.; Wu, B.; Meng, M. Kinetics of coal liquefaction during heating-up and isothermal stages. *Fuel* **2008**, *87*, 508–513.

© 2010 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).