



Research article

Pilot-plant study of upgrading of medium and low-temperature coal tar to clean liquid fuels



Rui Wang, Donghui Ci, Xin Cui, Yu Bai, Congyun Liu, Deting Kong, Shuai Zhao, Yinhua Long, Xiaofen Guo *

National Institute of Clean-and-Low-Carbon Energy, Beijing 102209, China

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ABSTRACT

Clean liquid fuels can be obtained from hydrogenation of middle and low-temperature coal tar at hydrogen pressure of 10MPa using three serial fixed-bed reactors on a pilot scale. The hydrodemetallization catalyst in the first-stage reactor provides the high capacity of metal removal and asphaltenes conversion as well as the low removal of sulfur and nitrogen, protecting the highly active downstream catalysts from poisoning by carbon and metal deposition. The second-stage hydrotreating catalysts exhibited the high activity for the deep removal of sulfur and nitrogen, which was affected by reaction temperature and liquid hourly space velocity. The excellent hydrocracking activity can be obtained with a desirable distribution of liquid products under the feed nitrogen of below 100 ppm and optimized conditions. The product composition is also correlated with the reaction behaviors occurred on the different catalyst surface. The results of this work show that the whole-fraction MLTCT could be upgraded through moderate-pressure hydrogenation to produce high-quality clean fuels.

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1. Introduction

With the environmental concerns and the depletion of crude oil is on the rise, many efforts have been made to develop alternative energy sources such as coal-derived liquid, bio-oil and shale oil [1,2]. China has abundant coal reserves and coal-based chemical industry has grown substantially. Over 10 million tons of coal tar is produced every year from coal gasification and carbonization [3]. As an alternative to petroleum, middle and low-temperature coal tar (MLTCT) can be considered as a suitable feedstock to produce transportation fuels via hydroprocessing, which has attracted much attention and been commercialized in China. In order to achieve the high conversion efficiency, high yield of liquid fuels and reduce operation cost, extensive industrial researches have focus on the process technology aspects such as reactor and catalyst type, process parameter and feedstock pre-treatment [4]. On the other hand, the chemical complexity of coal tar has also driven fundamental studies to mainly focus on reaction networks and kinetics on the pure model compounds [5,6] or simulates using several compounds with different functional groups [7]. Therefore, there is always a gap between fundamental studies in lab and real reaction behaviour of coal tar occurred during the industrial operations. The interaction between real coal tar and catalyst surface during industrial process and its influences on catalyst and product composition is not clear yet. Moreover, coal tar is typically hydrogenated in fixed-bed reactor under rigorous conditions over 12 MPa and even higher for the whole-fraction coal

tar, due to its high viscosity and complex composition [8,9]. It is recently reported that [10,11] after removing the heavy distillates, coal tar distillate (<360 °C) could be hydrogenated to produce clean liquid fuels at mild hydrogen pressure of 8MPa. However, the hydrogenation of whole-fraction coal tar under mild conditions has not been reported yet. The hydroprocessing performance can be influenced greatly by process variables, catalyst type and feed properties [12,13].

In the present work, three-stage hydrogenation of whole-fraction MLTCT was performed under mild conditions at hydrogen pressure of 10 MPa in fixed-bed reactors at a pilot-plant scale. The effects of catalyst type, process parameters and feed properties on chemical compositions of the products are also studied. The aim of this work is to upgrade whole fraction MLTCT via moderate-pressure hydrogenation to produce clean liquid fuels during the long-term running. We also try to bridge the gap between industrial and fundamental researches by the correlation between the pilot-plant products composition and catalytic reaction mechanisms.

2. Experimental

2.1. Feedstock

A commercial whole-fraction MLTCT sample was used as the feedstock, which was obtained from an industrial coal carbonization process at 600–800 °C (Shenmu, Shanxi province, China). The main properties of the feedstock are listed in Table 1. Compared with petroleum crude oil, MLTCT contained higher levels of oxygen (8.71%), Fe and Ca

* Corresponding author.

E-mail address: guoxiaofen@nicenergy.com (X. Guo).

Table 1
Main properties of middle and low-temperature coal tar (MLTCT).

Properties	Value
Density, g/cm ³	1.0752
Viscosity, 50 °C, mm ² /s	218.81
C, wt.%	80.97
H, wt.%	7.52
O, wt.%	8.71
S, wt.%	0.18
N, wt.%	0.68
H/C molar ratio	1.11
Aromatic carbon ratio, %	66.61
C ₇ asphaltenes, wt.%	22.58
Toluene insoluble, wt.%	1.14
Quinoline insoluble, wt.%	0.28
Fe, mg/kg	117
Ca, mg/kg	103
Ni + V, mg/kg	<0.3
Distillation range, °C	
IBP	185
10%	254
50%	385
90%	480

impurities (220 ppm). A low H/C atomic ratio of 1.11 indicates that the aromatics are much more abundant in MLTCT [14].

2.2. Catalyst preparation and characterization

The Mo-Ni/ γ -Al₂O₃ hydrodemetallization (HDM) catalyst was prepared using the molded γ -Al₂O₃ as the support. The support was impregnated in an dissolving solution containing required amounts of metal salts (NH₄)₆Mo₇O₂₄·4H₂O, Ni(NO₃)₂·6H₂O and (NH₄)₂HPO₄. The resulting precursor was dried in an oven at 120 °C for 24 h and then calcined at 500 °C for 2 h. Commercial hydrotreating (HDT) and hydrocracking (HDC) catalyst were used in this study, and the properties of all catalysts are listed in Table 2. The business information of the commercial catalysts cannot be provided stipulated by a signed confidential agreement with the catalyst suppliers.

BET surface area and pore size were measured using the nitrogen adsorption isotherm method (Quanta Chrome Instrument NOVA 2000). The samples were degassed at 250 °C for 6 h before analysis. The elemental compositions of catalysts were determined by a ZSX Primus II X-ray fluorescent spectrometer (Rigaku, Japan). The SEM-EDS characterization was conducted by a Nova Nano SEM 450 and Oxford X-max 50 EDS.

2.3. Test procedure

The pilot-plant test of MLTCT hydrogenation was carried out in three-stage, 3 * 500 ml fixed-bed reactors. As shown in Fig. 1, the entire reaction system consists of the reactant feeding unit, hydrogenation reactors and the product separation and collection unit. The reactant feeding unit consists of a tar supply line and a high-pressure hydrogen supply line. The hydrogenation unit consists of three fixed-bed reactors in series, including hydrodemetallization (I), hydrotreating (II) and hydrocracking (III) reactors. The product separation and collection unit includes a stabilizer, a three-phase separator, H₂S Scrubber and so on. Hydrogen and feedstock mixture were fed from the top of the reactor after preheating and premixing. Liquid product samples were collected after the device reached a stable state. The liquid products were distilled into gasoline (<180 °C), diesel (180–350 °C) and residue oil (>350 °C) fractions for analysis.

Before reaction, the catalysts were in-situ presulfided at 360 °C using a temperature-programmed procedure. The presulfiding agent was 1.5% carbon disulfide in kerosene, with a liquid hourly space velocity (LHSV) of 1.0 h⁻¹ and H₂/oil ratio of 1000. After the presulfiding, all the operation parameters were set at their desired values as follows:

H₂ pressure of 10 MPa, H₂/oil ratio of 1000 or 1500, temperature of 370–400 °C and LHSV of 0.2–1.0 h⁻¹. Normally, one of these variables was changed with the others kept constant.

The conversion of HDS (hydrodesulfurization), HDN (hydrodenitrogenation) and HDM is defined as:

$$\% \text{ Conversion} = \frac{(C_{\text{feed}} - C_{\text{product}})}{\text{wt.\% of sulfur content in feed}} \times 100$$

where C_{feed} is the initial concentration of sulfur, nitrogen and metal in the feedstock while C_{product} is the final concentration of the product.

The residue conversion of hydrocracking is defined as:

$$X_c = \frac{(\text{wt.\% of } 350 \text{ } \hat{A}^+ \text{ materials in feed} - \text{wt.\% of } 350 \text{ } \hat{A}^+ \text{ materials in product})}{(\text{wt.\% of } 350 \text{ } \hat{A}^+ \text{ materials in feed})} \times 100.$$

2.4. Analysis method of feedstock and product

Elemental analysis of C/H/O/S/N was carried out using an Elementar EA3000 and EA500 (Leeman, German). Metals were analyzed using an inductively coupled plasma-atomic emission spectroscopy SPECTRO ARCOS (ICP-AES, SPECTRO, Germany). The distillation range was determined by simulated distillation using a GC (Agilent 7890A). The properties of oils were determined for: (i) density using a DM40 (Mettler Toledo, Swiss); (ii) viscosity using a DMA 5000 (Anton Paar, Austria); (iii) research octane number (RON), cetane number (CN) using a SX-100 K, ASTM D613.

The hydrocarbon types of the feedstock and products were analyzed by a GC-MS (Agilent 7890A/5975 GC-MS) with standard test method SH/T 0606-2005 (Chinese standard test method for hydrocarbon types in middle distillates by mass spectrometry), which is a modified version of the ASTM D2425-04. Samples were pre-separated with SPE (solid phase extraction) cartridges into saturated and aromatic components, and then subjected into GC-MS to get the hydrocarbon type information.

3. Results and discussion

3.1. Investigation of hydrodemetallization catalyst

Catalysts used in the heavy feedstock upgrading processes typically use an association of several kinds of catalysts, each of them playing a specific and complementary role, which can be tailored according to the nature of the feeds and the target products. As shown in Table 1, MLTCT contained the high viscosity and high content of C₇-asphaltenes. Hence, in the present work, hydrogenation of MLTCT was conducted in three serial fixed-bed reactors loaded with HDM, hydrotreating and hydrocracking catalysts.

The activity test of the HDM catalyst in the first-stage reactor was performed at 280 °C, H₂ pressure of 10MPa, LHSV of 0.5 h⁻¹ and H₂/oil ratio of 1000. The properties of the catalyst and product before and after HDM are shown in Table 3. It is seen that HDM catalyst had a high surface area (106 m²/g) and pore volume (0.47 cm³/g), and contained a pore structure of 1.3% micropore, 63.7% mesopore and

Table 2
Properties and chemical compositions of catalysts.

Catalyst	Type	Shape	Active metal, wt.%			S _{BET} , m ² /g	Pore volume, cm ³ /g	Pore diameter, nm
			Mo	W	Ni			
Mo-Ni/ γ -Al ₂ O ₃	HDM	Ring	5	-	1.2	106	0.47	15.7
Mo-Ni/ γ -Al ₂ O ₃	HDT	Lobed	10	-	3	215	0.42	7.8
W-Ni/USY	HDC	Bar	-	16	5	324	0.39	4.8

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