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## Catalytic hydrogenation of Low temperature coal tar into jet fuel by using two-reactors system

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## ABSTRACT

The experiment of the jet fuel fraction through hydrogenation was investigated via hydrogenation in two-stage fixed beds reactor filled with hydrofining catalyst and hydroisomerization catalyst with low-temperature coal tar (LTCT) distillate ( $< 360^\circ\text{C}$ ) as the feedstock. The reaction of coal tar on the catalyst was studied through analyzing the yield of product, the saturation performance, the carbon number distribution and the chemical components of the jet fuel fraction. In current study, the experimental conditions included the temperature at  $340\sim 400^\circ\text{C}$ , the pressure of  $6\sim 12\text{ MPa}$  and the liquid hourly space velocity (LHSV) of  $0.4\sim 1.0\text{ h}^{-1}$ . The results showed that at a fixed pressure (10 MPa), reaction temperature ( $380^\circ\text{C}$ ), LHSV ( $0.8\text{ h}^{-1}$ ) and the  $\text{H}_2/\text{oil}$  ratio of (1600:1), the yield of the jet fuel fraction and the content of saturated hydrocarbons in the products were 58.0% and 60.7%, respectively. Finally, by GC-MS analysis, cyclanes and i-alkanes were dominant components in the jet fuel fraction, approximately accounting for 63.08% and 20.25%, respectively.

### 1. Introduction

Until now, petroleum is still an important part of the energy structure. Petroleum is all over the corners of life, and it can be said that oil has promoted the development of modern civilized society. According to the BP Statistical Review of World Energy 2016, petroleum accounts for 32.7% and 32.9% of the global primary energy consumption in 2014 and 2015, respectively [1]. Taking China as an example, petroleum consumption has reached 498 million tons, while the rate of self-sufficiency has fallen to 41.9% in 2013 [2]. In addition, in the next ten to fifteen years, oil demands and supply capacity is expected to reach a level of 750–800 million tons per year in China [3]. Therefore, the development of various new energy sources to meet the energy demand has attracted more and more attention in the world [4,5]. In this respect, many efforts have been made to develop alternative energy sources such as coal-derived liquid, bio-oil, and shale oil. However, there are always some problems that limit the spreading of these alternative energy sources [4,5]. In contrast, the reserve of coal resources is rich, accounting for 92.6% of the gross reserves of exploitable fossil energy resources, which can produce over 10 million tons of coal tar every year in China [3,5,6].

Coal tar, as a brown byproduct of coal pyrolysis, accounts for 2.5%–4% of the raw material [5]. The production of coal tar is huge,

reaching more than 10 million tons per year in China [4,6]. Therefore, if it can be converted into clean liquid fuel, the benefit will be inestimable. However, coal tar is a very complex mixture, containing a large number of alkanes, cycloalkanes, aromatics and heterocyclic compounds, especially some polycyclic aromatic hydrocarbons (PAHs) [7,8]. Regrettably, about 500 kinds of compounds can be identified, at present [8]. Moreover, due to the poor fluidity and thermal stability of coal tar, which has led many researchers to mainly rely on a pure model compound to study the transformation rules and reaction pathways of coal tar components such as phenanthrene [9,10], naphthalenes [11,12], phenols [13], and so on, rather than a real fraction. However, the composition of models is so pure in research that it can not effectively reveal the reaction path of each component in coal tar and the rules of influence among the component, leading to a gap between laboratory research and real reaction [4,5].

The catalyst is the core of the whole hydrogenation reaction and one of the most important steps in the entire reaction system. The hydrogenation catalyst with SAPO as support can significantly improve the quality of oil products. For example, Zhang et al. [14] found the isomeric selectivity of two kinds of materials could reach over 90% under high conversion rate with n-heptane and n-tetradecane as feedstock on the SAPO-11 catalyst. The isomer yield of n-hexadecane was higher with weaker cracking reaction due to the weaker acidity of SAPO-11

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catalyst [15]. Campelo et al. [16,17] concentrated on the hydroprocessing of n-hexane, n-heptane and n-hexadecane on Pt/SAPO-11 catalyst. The data showed the isomeric selectivity of three feedstocks was higher. The conversion of n-dodecane was 70%, while the isomeric selectivity reached 87%. Condensation point of straight-run diesel decreased from 0 °C to –28 °C, while the yield of diesel was 96% engine by Wei Xiaoming et al. [18]. Ke Ming et al. [19] studied the catalytic mechanism of n-octane of over Ni-W/SAPO-11, realizing that the conversion rate was 70%, while isomeric selectivity was 80%.

Therefore, the previous studies were mostly based on the model compounds over SAPO molecular sieve. The study on the catalytic mechanism of coal tar as raw materials on SAPO molecular sieve has not been received as much attention. In order to further understand this process, in the study, the catalytic mechanism and reaction path for the preparation of the jet fuel on the SAPO catalyst were studied via fixed bed reactor with low temperature coal tar as raw materials.

## 2. Experimental

### 2.1. Feedstock

The LTCT as a byproduct of brown coal pyrolysis was obtained from North of Shaanxi Province, China. Coal tar contains a large number of heavy components such as asphaltenes, which had difficult being hydrogenated, resulting in blocking the pipeline and even an accident. Therefore, in the experiment, the distillate fraction that the boiling point was lower than 360 °C was selected as feedstock [5,20–23]. Its main physicochemical properties were exhibited in Table 1. As shown in Table 1, the content nitrogen and sulfur were 0.43 wt% and 0.15 wt %, respectively. Furthermore, the H/C molar ratio of raw material was 1.248, revealing feedstock has a large number of unsaturated hydrocarbon [4,24]. In addition, the major composition and content of LTCT were obtained by gas chromatography/mass spectrometry (GC/MS) in Fig. 1. The contents of indene, PAHs and alkylnaphthalene were relatively lower, indicating that feedstock was lighter.

### 2.2. Catalysts

Two commercial catalysts were used in this experiment with namely Ni-W/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-W/SAPO-11, respectively. Main physicochemical properties of the catalysts were given in Table 2. In addition, there was a secrecy agreement with the catalyst suppliers, the remaining properties and the model number of the catalysts could not be published for the time being.

### 2.3. Hydrogenation system

The hydroprocessing was carried out via two-stage fixed beds reactors. The schematic diagram of the device was shown in Fig. 2. And the device was divided into the reactant feeding part, the reaction part

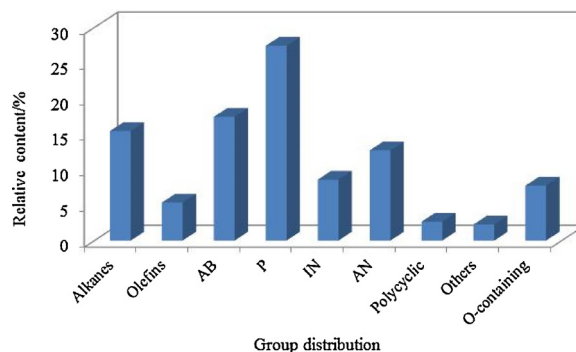
**Table 1**

The basic properties of feedstock.

Properties	Unit	Value
Density(20 °C)	g/cm <sup>3</sup>	0.9982
Viscosity(50 °C)	mm <sup>2</sup> /s	13.71
Distillation range		
IBP <sup>a</sup>	°C	174
30%/50%	°C	245/295
70%/90%	°C	321/357
FBP <sup>b</sup>	°C	371
H/C	/	1.248
Nitrogen	wt%	0.43
Sulfur	wt%	0.15

<sup>a</sup> Initial boiling point.

<sup>b</sup> Final boiling point.



**Fig. 1.** Distribution of group components in feedstock.

**Table 2**

The composition and textural properties of catalyst.

Properties		Ni-W/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Ni-W/SAPO-11
Composition/ wt%	Ni	2.44	3.15
	W	21.92	17.41
S <sub>BET</sub> , m <sup>2</sup> /g		253	205
Pore volume, ml/g		0.53	0.2
Pore diameter, nm		4.74	3.92
Acidity/mmol·g <sup>-1</sup>	Weak	1.81	0.11
	Medium and strong	0.37	0.04

and the separation part. The reaction system mainly contained the refined reactor and the isomeric reactor. Each reactor tube was made of 316 stainless steel with 17 mm in internal diameter, 1120 mm in length, which was filled the 30 ml porcelain balls with 4 ~ 5 mm in diameter, then the 30 ml refining catalyst (Ni-W/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), and finally the 30 ml porcelain balls which were acted as disengaging part to guarantee homogeneous distribution between liquid and gas in the refined reactors. According to the above method, isomeric catalyst (Ni-W/SAPO-11) and porcelain balls were filled in the second reactor (the isomeric reactor). The reaction temperature in reactors was mensurated via thermocouples with the external diameter of 6 mm which were placed into metal canul with the internal diameter of 0.25 in. h. Raw material was fed radially at the top of reactors, while the products were out-flowed radially at the bottom of reactors. In addition, the reactors were sealed via fluorine rubber ring.

Both reactors were heated though electric heating furnace. Each reactor had three stages of electric heating with an independent temperature control to monitor the bed temperature by a K thermocouple. The first stage of the reacting furnace was the preheating section with the length of 200 mm and the power of 1.5 kW. The second stage belonged to the constant temperature section with the length of 200 mm and the power of 1.5 kW. Thermal insulation part was the third section with the length of 150 mm and the power of 1.0 kW.

In the reactant feeding system, there were mainly high pressure hydrogen supply and feedstock supply that was sealed by low pressure nitrogen. High pressure hydrogen was obtained via the compressor. Furthermore, all the liquid pipelines were enlaced by heating belts to avoid oil condensation. The separation section mainly contained separators, a cooler and so on.

Before the reaction, the catalysts were activated with 2 wt% CS<sub>2</sub>. The presulfiding process was carried out at 360 °C, 10 MPa and 1.0 h<sup>-1</sup> for 6 h. After presulfiding, the experimental parameters were set as follows: the temperature of 340 ~ 400 °C, the pressure of 4 ~ 10 MPa, the LHSV of 0.4 ~ 1.0 h<sup>-1</sup> and the H<sub>2</sub>/oil ratio of was kept at a fixed level of 1600:1. Hydrogen and liquid feedstock were mixed at the top of the reactor and then entered the reactor for reaction. The device was kept for 7 h that the products were emptied in the first three hours, while the remaining products were collected in the next four hours after it was stable. In addition, the liquid products were divided into the

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