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Research article

In-situ catalytic upgrading of coal pyrolysis tar on carbon-based catalyst in a fixed-bed reactor

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ABSTRACT

Coal pyrolysis tar was in-site upgraded in a fixed-bed reactor over char and activated carbon (AC) catalysts, and the effects of catalysts and temperature on tar upgrading were examined. The content of light tar with boiling point below 360 °C was improved over the catalysts despite the decrease of total tar yield. Compared with char catalyst, AC exhibited better upgrading performances, and the content of light tar increased with the temperature. The light tar yield over AC catalyst increased by 18% compared with that without catalysts at 650 °C. The variation in coal tar fractions suggested that upgrading is mainly from the conversion of the heavy components (pitch) in tar into light tar and gases. The role of carbon-based catalyst in upgrading process was also explored through the characterization by TG-DTG, FT-IR, N_2 adsorption and Raman spectroscopy. Compared with thermal cracking, adsorption on the catalysts and the minerals in char, high specific surface areas and relative more defects in the carbon catalysts seem to be the primary factor for upgrading tar.

1. Introduction

Coal pyrolysis, as one of the most promising technologies for energy sustainability, can produce liquid fuels, valuable chemicals and high heating value gas by mild conversion of coal. However, coal tar usually has high content of heavy fractions with boiling points above 360 °C up to more than 50% of total tar [1–3]. This heavy tar with high viscosity, easy pollution and low economic value usually leads to serious problems in the operation of industrial equipment and further processing of tar, which restricts the application of pyrolysis process in the industry.

To upgrade the coal tar, various methods were investigated including thermal cracking, hydrogenation and catalytic cracking for the decomposition of heavy components in tar. However, thermal cracking tends to result in insufficient decrease of heavy fractions even at high temperature and pressure, along with obvious loss of overall tar and energy inefficiency [4–6]. Hydrogenation of coal tar received substantial attention owing to remarkable improvement of tar quality and small-molecule gases yield, especially the content of BTX and their derivates [7], but some of heavy components (mainly pitch) are still difficult to be hydrocracked, and more hydrogen as an expensive gas is consumed and high pressure is utilized [8].

Catalytic upgrading presents a potential method for the conversion of heavy tar into light tar and pyrolysis gases by secondary reaction of tar precursors in the process of coal pyrolysis [9,10]. More studies are focused on the improvement of BTX and PCX contents [11,12]. Takarada et al. [13,14] found that the content of BTX on supported metal catalysts such as Co–Mo/Al_2O_3 was 5.8 (wt.% daf), which improved 30 times comparing with that on SiO_2 sample in a fluidized bed reactor for coal pyrolysis reaction. Deng et al. [15] investigated the catalytic upgrading over olivine and Co-olivine catalysts, and the heavy fraction (boiling points above 360 °C) was obviously reduced. Compared with the olivine as the catalyst, the pitch content over Co-olivine decreases by 17% at 550 °C. Sonoyama et al. [16] reported about 97 wt.% of initial heavy components in tar from pyrolyzing the Loy Yang coal at 500 °C were decomposed over iron-oxide catalyst with metal promoters. Öztaş et al. [17] believed that better catalytic effects were acquired by pyrolysis of Zonguldak bituminous coal mixed with $ZnCl_2$, $CoCl_2$ and $NiCl_2$. However, the metal catalysts including Ni and Ca are always subjected to some problems including sulfur poisoning, coke deposition and high cost despite their high activity for tar conversion.

Carbon-based catalyst such as char or activated carbon is considered to be a most potential for industrial application owning to low cost and easy availability [18–21]. Han et al. [18] studied the catalytic upgrading of coal pyrolysis tar over char-based catalysts, and found that light tar fraction (boiling points below 360 °C) increased by 25% with char compared with coal direct pyrolysis at 600 °C. Better upgrading effect was obtained at 500 °C when metal was supported over char. Gilbert et al. [22] investigated tar reduction of pyrolysis vapors from biomass over hot char in a fixed-bed reactor. The content of heavy fractions decreased to 18.4% at 500 °C and 8.0% at 800 °C. Although the properties of carbon-based catalyst, including specific surface area, pore volume, sulfur and carbon deposition resistance and containing metal oxides, will influence

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Table 1
Proximate and ultimate analyses of SM coal and carbon-based catalysts.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.% daf)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O*
Coal	1.76	8.16	35.77	71.40	4.42	0.65	0.25	23.38
Char	0.76	14.62	3.40	83.08	1.04	1.28	0.27	14.33
AC	1.22	2.10	3.98	94.16	0.64	0.29	0.00	4.91

* By difference.

tar upgrading, it is still unclear as to the upgrading mechanism. Zeng et al. [23] believed that tar could be absorbed on the surface of carbon-based catalyst when it existed down the pyrolysis coal, and large specific surface area promoted more tar to be dispersed on the surface, further leading to the enhancement of retention time for heavy tar upgrading.

To study the catalytic role of carbon-based catalyst in catalytic upgrading tar and the decrease of heavy tar components, in this work, two carbon-based catalysts, char and activated carbon, were used to upgrade the coal tar from coal pyrolysis in a fixed-bed reactor containing upper coal layer and lower catalyst layer. The effect of catalyst kinds and the temperature on the quality of coal tar was examined and the role in catalytic upgrading was also explored based on the experimental results and several analysis technologies.

2. Experimental section

2.1. Coal sample and carbon catalysts

Shenmu (SM) subbituminous coal was grounded and sieved below 0.15 mm and dried for the pyrolysis experiment. Two carbon-based catalysts were chosen for tar upgrading. One is the char prepared by pyrolysis of Shenmu coal at 850 °C for 3 h in N_2 on a fixed bed reactor; another is the commercial coconut shell activated carbon (AC). Their proximate and ultimate analyses of the coal and carbon catalysts were given in Table 1.

2.2. Apparatus and procedure

The upgrading of coal tar was carried out in a vertical fixed-bed reactor with an inner diameter of 18 mm and a length of 150 mm. In each run, the reactor was charged with upper coal sample (5 g) and lower carbon-based catalyst (1 g), and some quartz wool was placed between them for separation. After the reactor was purged with high-purity N_2 for approximately 10 min to remove the air before the reaction, it was heated to the desired temperature within less than 10 min by a moving preheated furnace, and maintained for 30 min for pyrolysis and upgrading in the N_2 flow rate of 100 ml/min. The volatile vapors during the coal pyrolysis were carried through upgrading zone of the tar by high-purity nitrogen, upgraded and collected by a cool trap. Long isotherm zone of the furnace kept the coal pyrolysis and upgrading of the resultant pyrolysis tar in the same temperature. The non-condensable gases were collected and the solid char and catalyst were removed from the reactor for analysis after the experiment.

2.3. Analysis of tar and gases

Tar plus water was separated according to ASTM D95-05^{e1} (2005) using toluene as solvent. The tar yield (Y_{tar}) and light tar yield ($Y_{light\ tar}$) in dry ash-free base are calculated as follows:

$$Y_{tar} = \frac{W_{tar}}{W_o \times (1 - A_{ad} - M_{ad})} \times 100\%$$

$$Y_{light\ tar} = Y_{tar} \times w_1\%$$

where, W_{tar} and W_0 are the weight of tar and coal sample; A_{ad} and M_{ad} are the ash and moisture contents of coal; and $w_1\%$ is the light tar content. The results presented are the mean values of at least 3 equivalent experiments, and the estimated error of tar yield is within ±0.2%, indicating good repeatability.

The components analysis of coal tar was conducted by simulated distillation (ASTM D-2887) according to boiling points of fractions listed in Table 2. The light tar content ($w_1\%$) herein refers to the fractions with a boiling point below 360 °C including light oil, phenol oil, naphthalene oil, wash oil and anthracene oil. Before the analysis, the tar was first dissolved in carbon disulfide, and then Na_2SO_4 was added to adsorb the water in tar. After filtration to remove Na_2SO_4, the tar with carbon disulfide was concentrated by distillation and used for analysis.

Pyrolysis gases were analyzed by an on-line gas chromatography (GC7890II) equipped with a thermal conductivity detector packed with 5A molecular sieve and a flame ionization detector with GDX502 packed column.

2.4. Characterization of catalysts

TG/DTG experiments of carbon-based catalysts were performed using a Mettler Toledo TGA/SDTA851^e thermogravimetry analyzer. About 20 mg sample was heated from 25 °C to 850 °C with a heating rate of 10 °C/min using argon as the carrier gas at a constant flow rate of 60 ml/min. The surface analysis of carbon-based catalyst was measured by FT-IR on an EQUINOX55 spectrometer using KBr pellet technique. N_2 adsorption of the fresh and spent catalysts was measured on the physical adsorption apparatus (ASAP 2420) at −196 °C. The samples were outgassed at 300 °C for 4 h prior to adsorption. The parameters on the pore structure were obtained by using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods. Raman spectra of carbon catalysts were recorded on a Thermo Scientific DXR Microscope using the 532 nm line of solid state laser. The laser was focused to about 150 μm in diameter at a power of 1 mW in order to prevent thermal degradation. Raman spectral from 800 to 1800 cm^{-1} were measured with a spectral resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Effect of carbon catalysts on the upgrading of coal tar

Two kinds of carbon catalysts were used to in-situ upgrade the coal tar from pyrolysis at different temperatures. To acquire the distribution of tar fractions, simulated distillation was used to analyze the tar compositions from pyrolysis at 650 °C, and the curves in Fig. 1 referred to

Table 2
Simulated distillation fractions of tar from pyrolysis at 650 °C.

Catalyst	Fraction (wt.%)					
	Light oil (<170 °C)	Phenol oil (170–210 °C)	Naphthalene oil (210–230 °C)	Wash oil (230–280 °C)	Anthracene oil (280–360 °C)	Pitch (>360 °C)
–	2.8	5.6	5.4	15.6	15.0	55.6
Char	4.3	7.3	5.6	16.5	16.4	49.9
AC	8.9	15.5	8.8	23.8	18.5	24.5