



## Research article

# The catalytic reforming of tar from pyrolysis and gasification of brown coal: Effects of parental carbon materials on the performance of char catalysts



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## ABSTRACT

The carbon structure of char as catalysts is very crucial as it greatly governs the catalytic activity of char for tar reforming reactions. More importantly, the char structure also plays an important role in affecting the interactions between the inherent metal species and carbon atoms, thus affecting the catalytic performances. This study aims to investigate the effects of char structure on the reforming of tar derived from the gasification and pyrolysis of Shengli brown coal. Chars prepared from five kinds of acid-washed carbonaceous materials, including biomass, brown coal, bituminous coal, anthracite and graphite, were used as tar reforming catalysts in this work. The different effectiveness of H-form char catalysts from the different ranking carbon materials have clearly shed light on the effects of char structure on tar reforming. Results show that the chars from biomass and low rank coals featured obviously higher catalytic activity than those from high rank fuels. The variation in char structure that was revealed by FT-Raman has greatly exerted impacts on tar yields as well as tar compositions. Interestingly, the supply of steam (in the gasification condition) did not always see the reduction in tar yields, very much depending on the type of char catalysts used in the experiments.

## 1. Introduction

Gasification of coal or any other carbonaceous materials under moderate reaction conditions can improve the cold-gas efficiency as well as save capital and maintenance costs, especially for small scale systems which features high surface/volume ratio and thus significant heat loss. Besides the syngas (mainly H<sub>2</sub> and CO), tarry materials as the undesirable products will be inevitably generated from the gasification process [1,2], particularly at medium reaction temperatures and pressures. The tar contents in product gas are higher when lower rank fuels (e.g. brown coal or biomass) are used as feedstocks due to the high yields of volatile that are tar precursors. Tar elimination has been and will continue to be a very hot research area because it can somehow determine the feasibility and competency of newly-developed gasification technologies.

Wet scrubbing is a widely adopted approach to condense the tar components from hot gas mixture at the outlet of gasifier [3,4], of which oil is a better absorbent than water as tarry materials are largely hydrophobic. However, wet scrubbing produces large amounts of waste

liquid containing poisonous and even cancerous chemicals. With increasingly stringent requirements on environment protection, people now become more reluctant to utilize the wet scrubbing method to remove tars from gasification system. Thermal cracking has also been intensively examined to decompose the large hydrocarbons, which normally requires temperatures above 1200 °C (even higher) to achieve satisfied effects. Besides, coke formation is always a concurrent process during the thermal reactions of tar [5]. Introducing oxygen to oxidize/destroy the tar compounds has also been considered as another option. Ahrenfeldt et al. [6] reported that the primary tar from the pyrolysis of wood pellets in a two-stage gasifier could be effectively converted into small molecules and PAHs. The tar reduction by oxidation had to be at a cost of the decrease in syngas heat value, and thus reducing cold gas efficiency. Catalytic reforming has received a great attention for removing tar from both pyrolysis and gasification of coal, biomass and other carbonaceous materials [7–9]. A variety of catalysts such as dolomite, olivine and Ni-Al<sub>2</sub>O<sub>3</sub> for tar reforming have been tested under various experimental conditions [10–12]. Natural minerals such as dolomite and olivine are cheap and easily accessible, but with relatively

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poor catalytic activity and weak strength. Ni-based synthesized inorganic catalysts showed very excellent catalytic performance for tar reforming. It was suggested that Ni based catalysts could not only effectively eliminate tar, but also show activity for water gas shift reactions (thus adjusting the ratio of H<sub>2</sub> and CO) [13,14]. However, the weak strength and easy deactivation by coke formation were the fatal disadvantage that prevented the Ni based inorganics from being used as catalysts for tar reforming in a commercial scale.

Chars derived from pyrolysis and gasification of coal and biomass have seen a very promising future as a candidate for catalytic tar reforming [7,15,16]. Chars as tar reforming catalysts have been well demonstrated in both fundamental and pilot-scale studies [7,16,17]. It is economically viable and could be prepared on site. The most striking feature is that the spent char catalyst could be recycled to the reactor to be gasified, leaving zero environmental footprints. Activity of char as catalysts is attributed to its inherent catalytic AAEM (alkali and alkaline earth metallic) species as well as the defected carbon structural units in chars [1,17,18]. The carbon structure including O-containing functional groups would not only show catalytic activity themselves, but also largely govern the roles and fates of AAEM species and thus its catalytic performance. Therefore, it is of paramount importance to investigate the effects of carbon structure on chars' catalytic performance for tar reforming. As the first step, the effects of carbon structure should be determined without the disturbances from AAEM species, which will provide very basic and fundamental information for this series of studies. Different carbonaceous materials (i.e. biomass, different ranks of coals and graphite) were used in this study so as to formulate different char catalysts with various carbon structures. The raw carbon materials were acid-washed to remove AAEM species before being used for preparing char catalysts.

Therefore, the objective of this work was to examine the effects of the structures of char on its activity for reforming tar that was generated from pyrolysis/gasification of Shengli brown coal in a bench scale quartz reactor. Chars prepared from five kinds of acid-washed carbon materials were used as catalysts. The results indicate that the difference in carbon structure (and thus catalytic reactivity) has apparently led to the variations in tar yields and tar compositions, as well as has interestingly changed the role of steam on tar reforming.

## 2. Experimental

### 2.1. Coal samples

A Chinese brown coal from Shengli mining site was used as feedstock to generate volatile (tar precursors) in a two-stage quartz reactor in this work. It was ground and sieved to obtain the particles ranging from 98 to 150  $\mu\text{m}$ , and its proximate and ultimate analyses are listed in Table 1.

### 2.2. The catalyst preparation

The different ranks of carbon materials including wood (Natural oak chips), brown coal (Shengli), bituminous coal (Datong), anthracite (Jincheng) and commercial graphite (99.99%) were firstly milled to prepare the samples with the particle sizes of 98–150  $\mu\text{m}$ . To remove the AAEM species, approximately 30 g of each sample was soaked in acid mixture of HCl (38.0 wt%) and HF (40.0 wt%) (1:1 by volume) for

**Table 1**  
Proximate and ultimate analyses of Shengli brown coal.

Proximate analysis (wt%)				Ultimate analysis (daf, wt%)				
M	A <sub>d</sub>	V <sub>daf</sub>	FC <sub>daf</sub>	C	H	N	S	O*
4.11	7.99	46.26	53.74	64.39	4.50	1.21	0.42	29.48

daf-dry ash free; d-dry basis; \*-by difference.

**Table 2**

Moisture contents and ash yields of carbon materials before and after acid washing.

Sample	Before washed		After washed	
	Moisture/wt%	Ash/wt%	Moisture/wt%	Ash/wt%
Wood	8.44	2.38	2.65	0.68
Brown coal	7.39	11.50	5.80	2.56
Bituminous coal	1.28	6.57	1.66	1.86
Anthracite	0.15	12.93	1.67	1.53
Graphite	Purity:99.99%			

8 h. The samples inside the solution were then filtered out and washed using double-distilled water before evaporating the water in oven at 70 °C for 24 h. The moisture contents and ash yields of the different ranks of carbonaceous materials before and after acid washing are summarized in Table 2. The impurity of graphite was negligible, and thus was not subjected to the acid washing process. After the acid washing treatment, the ash yields for all the carbon materials were in the range of 0.6–2.6 wt%. The remained inorganics were not dissolvable in acids and generally inert.

The dried sample (H-form raw materials) was further sieved to ensure that its size distribution was within 98–150  $\mu\text{m}$ , which was then sealed and stored in a fridge.

To prepare H-form char catalysts, 10 g of each H-form raw material was loaded into the bottom section of the two-stage quartz reactor as is shown in Fig. 1.1 L/min argon was continuously supplied into the reactor via its bottom to maintain the inert atmosphere. The reactor was then quickly dropped into the electrically-heated hot furnace at 900 °C and held for 30 min for a complete devolatilization. Subsequently, 15% steam in argon was provided into the reactor so as to activate the char for 10 min. At the end of experiments, the reactor was lifted out of the furnace and naturally cooled down to room temperature with the constant argon flow to maintain the inert atmosphere. The prepared chars were then collected and ready to be used as tar reforming catalysts.

### 2.3. Tar reforming

Tar reforming experiments were also conducted in the same two-stage quartz reactor. Brown coal as feedstock to generate tar was always dried in an oven at 70 °C overnight. To begin with, 1 g char catalyst prepared above was evenly distributed on the top quartz frit. The reactor with char catalysts was then heated up in the furnace to 800 °C under the protection of argon (0.65 L/min). After the temperature was stabilized, 1.8 g brown coal was fed into the bottom stage at a feeding rate of 180 mg/min through a water-cooled probe with further 10 min holding time. Therefore, the volatile released during heating up was forced to pass through the char catalyst bed, hence being catalytically reformed in situ by the catalyst. Blank experiments in the absence of char catalysts were also carried out for the purpose of comparison. The pyrolysis or gasification conditions were realized by supplying only argon or adding 15% steam in argon, respectively, via the bottom tube of the quartz reactor shown in Fig. 1.

### 2.4. Tar collection and analysis

During the feeding time, four washing bottles connected in series were used for capturing tar vapor (Fig. 1, Part II) at the exit of quartz reactor [7]. Dry ice was inserted into the first two bottles to condense the majority of tar and all the steam. In the meantime, the organic solvent mixture (analytically pure chloroform and methanol with volume ratio of 4:1) was loaded into the latter two bottles to ensure no escape of organic vapors. The volume of the blended solvent in each bottle was 50 mL. A dry ice bath was used to accommodate the four bottles to guarantee the low temperature inside the bottles. After

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