Evolution properties of cellulose- and lignin-derived pyrolysis tars after interacting with coal chars

Zhen-Yi Du, Xia Wang, Zhi-Hua Zhang, Jie Feng*, Yu-Hong Qin, Bin-Bin Zhang, Wen-Ying Li*

Key Laboratory of Coal Science and Technology (Ministry of Education and Shanxi Province), Training Base of State Key Laboratory of Coal Science and Technology (Jointly Constructed by Shanxi Province and Ministry of Science and Technology), Taiyuan University of Technology, Taiyuan 030024, PR China

ABSTRACT

The reforming characteristics of biomass volatiles on anthracite chars were investigated by comparing the structural evolution of tars derived from cellulose and lignin as the major biomass components. In a two-stage quartz reactor, the pyrolysis volatiles of cellulose and lignin were produced in the first stage and then reformed in the second stage with or without the presence of anthracite chars between 600 and 900 °C. The results show that the presence of anthracite chars enhanced the destruction of volatiles of both feedstocks. Furthermore, the tar yields of lignin showed a slower decreasing trend with temperature than those of cellulose, suggesting that the lignin volatiles were more refractory to be reformed. The lignin tars had higher molecular weights and contained higher percentage of compounds with large aromatic ring systems ($\geq$3 fused benzene rings) than cellulose tars in the studied temperature range. Compositional analysis revealed that tars of both feedstocks experienced the transition from phenolic compounds to polycyclic aromatic hydrocarbons with increasing temperature. The surface areas of anthracite chars were reduced because of coke deposition after interacting with the volatiles of both feedstocks below 800 °C, above which the net gasification of chars took place.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Biomass/coal co-gasification has received growing interest recently due to several clear benefits associated with this technology. These two feedstocks can compensate for each other's weaknesses during the co-gasification process. On the one hand, coal with high carbon content increases the energy density of the mixed feedstocks and solves the seasonal fluctuation problems of biomass [1,2]. On the other hand, biomass is a renewable energy resource that can significantly reduce the CO_2 emission during coal utilization. More importantly, alkali and alkali earth metals in biomass were found to improve the gasification reactivities of the feedstocks and enhance the overall gasification rate during co-gasification [3–5]. However, tars, which have long been a tough issue in biomass gasification, still need to be addressed properly during the implementation of co-gasification [6]. Biomass is rich in volatiles while coal is rich in fixed carbon; therefore, biomass volatiles are finally released in the form of tars when they are not completely converted into gaseous products. The evolution of the biomass volatiles in the co-gasification process is depicted in Fig. S1. In brief, the biomass primary volatiles keep interacting with the coal char and are reformed into gases on the way out of the gasifier; and thus the amount and properties of tars are largely dependent on the reforming reactions on the coal char surface.

A number of studies have been carried out on the cracking/reforming reactions of volatiles on char surfaces as an effective way of *in-situ* tar destruction during lignite/biomass gasification [7–20]. In these works, chars with well-developed porous structures obtained from pyrolysis acted as a catalyst for the decomposition of volatiles at high temperatures (600–900 °C). Although the exact mechanism of the destruction reactions on char surface remains vague, some studies speculated that the oxygen-containing groups and inherent metallic species played important roles for the cracking/reforming reactions [21–23]. In addition, chars have also been used as a cheap and disposable catalyst support for tar reforming by loading various active metals, which turned out to be more effective in tar reduction than those without impregnated metals [24,25].

Lignocellulosic biomass is composed of three main components known as cellulose, hemicellulose, and lignin, whose structures

---

are significantly different from each other. Cellulose and hemicellulose are polysaccharides, while lignin is a polyphenolic macromolecule consisting of *p*-coumaryl, coniferyl, and sinapyl alcohols as the building blocks [26,27]. The different chemical compositions of biomass components cause their different thermochemical behaviors during pyrolysis/gasification. Yu et al. studied the characteristics of tar formation during cellulose, hemicellulose and lignin gasification and they found that lignin-derived tar was more stable and harmful [28]. Muley et al. compared the pyrolysis of cellulose and lignin, and the results indicated that cellulose bio-oil was rich in anhydrosugars, while lignin bio-oil was rich in phenols [29]. Thus, it is necessary to examine the behaviors of individual components, in order to have a better understanding of their specific roles when interacting with coal char during co-gasification.

In this paper, pyrolysis vapors of cellulose and lignin were subjected to interactions with anthracite chars to study the reforming reactivity of biomass volatiles with different chemical structures, i.e. more aromatic lignin volatiles versus less aromatic cellulose volatiles. The evolution of the structures and compositions of tars were obtained in the temperature range of 600–900 °C. The comparison of tar compositions between cellulose and lignin should shed new light on the tar evolution mechanism during co-gasification.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose and dealkaline lignin were purchased from Aladdin and TCI Shanghai, respectively. Although claimed as "dealkaline", the received lignin still had a high ash content of 15.7%; therefore it was washed with 2 mol/L HCl solution and deionized water in sequence to remove the minerals. The cellulose and purified lignin (hereafter denoted as lignin for simplicity) powders were then pelletized and crushed into particles within the desired sizes. Anthracite coal from the Shanxi Lanhua Coal Industry Group Co., Ltd., Jincheng, China, was used as the starting coal sample. The proximate and ultimate analyses of the starting materials are listed in Table 1. The char samples were prepared in the bottom stage of a two-stage reactor as shown in Fig. S2. Anthracite samples were preloaded in the bottom stage and then heated up at 10 °C/min to 900 °C, and then held at 900 °C for 30 min in 500 mL/min N_2 carrier gas. The samples used in the experiments were all sieved into the size range of 40–100 mesh.

2.2. Tar decomposition on anthracite char

The same two-stage reactor as shown in Fig. S2 was also used for studying tar evolution. The top and bottom stages were first independently heated up to their target temperatures. After purging the feeder with nitrogen gas for 30 min, the cellulose or lignin particles were fed at a rate of 10 g/h into the top stage (fixed at 500 °C) where the primary volatiles were generated. These volatiles were carried into the bottom stage (600–900 °C) by nitrogen gas into the bottom stage, where the bed is either empty or pre-loaded with 2 g anthracite chars. Steam (30 vol.% of total gas flow) was injected into the bottom stage by evaporation of water fed with a syringe pump. Each experiment lasted for 1 h, and stopped by leaving nitrogen flow until the furnace cooled down to room temperature. The residence time of the volatiles from the top stage passing through the char bed at 600 °C was 0.26 s.

2.3. Collection and analysis of tar, char and gaseous products

The char particles of cellulose or lignin in the wire mesh cup and the used anthracite chars in the bottom stage were collected and weighted after reaction respectively. The tarry products together with gaseous products left the reactor in the bottom and passed through 4 impinger bottles in series, which were immersed in icewater bath (the first and second traps) and ethanol/liquid nitrogen bath (the third and fourth traps). All the traps were thoroughly washed with methanol to guarantee the maximization of tar recovery. Tar was obtained after the removal of methanol in a rotary evaporator at 30 °C under vacuum. The non-condensable gaseous products were collected in a gas bag and subjected to GC analysis. All the product yields data are reported based on the fed amount of cellulose or lignin. All the experiments were carried out in duplicate and the average values were reported. The relative deviations of the yields of char, tar, and gases were less than 2.7%, 5.8% and 7.1%, respectively.

The tar samples were analyzed with a Gel permeation chromatography coupled with a diode array detector (GPC–DAD), where Waters styragel HT2 and HT3 columns were employed for analysis. The tar samples were all prepared at the same concentration in tetrahydrofuran (3.3 mg/mL). The molecular weight distribution was determined by setting the ultraviolet (UV) wavelength of the detector at 254 nm. Besides, DAD detector signals at different UV wavelengths can reflect the size of the aromatic clusters of tars. While all compounds with aromatic structures have absorbance at 254 nm, only those with at least three fused benzene rings absorb strongly at 350 nm [30–32]. Therefore, the integrated peak areas of GPC spectra at 254 nm ($\int UV_{254\,nm}dt$) on the basis of the same tar concentration can be used to compare the relative aromaticity of tars, and the ratio of the peak areas at 350 and 254 nm (i.e. $\int UV_{350\,nm}dt / \int UV_{254\,nm}dt$) reflects the relative concentration of the larger aromatic ring systems ($\geq$3 fused benzene rings) in the tars.

Gas chromatography/mass spectrometry (GC/MS, Agilent 7890-5977A) with a HP-INNOWAX column was used to identify and quantify the major light components in tars. The column effluent is split into two halves with a post-column splitter followed by a MS and a FID detector, used for qualitative and quantitative analysis,

Table 1
Proximate and ultimate analyses of the cellulose, acid-washed lignin and anthracite samples.

	Proximate analysis/wt.%, ad[a]				Ultimate analysis/wt.%, daf[b]				
	M[c]	A[d]	FC[e]	V[f]	C	H	O[g]	N	S
Cellulose	1.99	0.00	6.04	91.97	43.65	6.33	49.93	0.00	0.09
Acid-washed lignin	4.19	1.35	45.63	48.83	65.03	5.03	27.60	0.04	2.30
Jincheng anthracite	0.97	8.81	85.98	4.24	94.23	2.93	1.04	1.36	0.44

[a] ad = air dry basis.
[b] daf = dry and ash free basis.
[c] M = moisture.
[d] A = ash.
[e] FC = fixed carbon.
[f] V = volatile.
[g] Calculated by difference.