CO-HYDROGENATION PERFORMANCE OF PINE SAWDUST AND HEAVY COMPONENTS OF COAL TAR

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ABSTRACT

Making the heavier components of coal tar into lighter components, which are the raw material for fuel and the chemicals, will improve the economy of pyrolysis. To promote the hydrogenation of heavy components, the co-hydrogenation of heavy components and pine sawdust (PS) was extensively studied in this work. The addition of PS significantly promoted the hydrogenation of heavy components which improved the yield of n-hexane soluble matter from 66.63 wt% to 75.46 wt%. The results of synchronous fluorescence showed that the product has a significant degree of lightening. Addition of biomass increased the aliphatic hydrogen content as evidenced by Fourier transform infrared spectroscopy.

Keywords: Medium-low temperature coal tar, heavy component, hydrogenation, pine sawdust

NONMENCLATURE

Abbreviations	
PS	Pine sawdust
CTP	Coal tar pitch
YNS	Yield of n-hexane soluble matter
THN	Tetrahydronaphthalene
Symbols	
H_{ar}	Aromatic hydrogen
H_{al}	Aliphatic hydrogen
H_{ar}/H_{al}	The ratio of aromatic hydrogen to aliphatic hydrogen

1. INTRODUCTION

Medium- and low-temperature coal tar is an important part of coal pyrolysis accounting for 5%-10% of total coal pyrolysis products. This tar has heavy components for around 50%[1]. Effective utilization of heavy quality resources is helpful to realize the clean and efficient utilization of coal[2]. The heavy components (mainly polycyclic aromatic hydrocarbons) are difficult to be processed and transformed due to their high viscosity and condensation degree [3, 4]. Heavy oil is currently processed by delayed coking, visbreaking, catalytic cracking and hydrogenation. Delayed coking and visbreaking belong to the thermal processing process, and are used to process all types of residual oil[5]. However, the quality of liquid products is poor and the coke yield is high. Catalytic cracking and hydrogenation could produce the quality oil however the catalysts used in these processes are highly vulnerable to heteroatom poisoning [6].

Biomass, as a renewable energy, plays an increasingly important role in the current energy structure. As a potential hydrogen-rich energy source, it is often used for co-conversion with other energy sources. There are a large number of alkali metals that play a key role in promoting cracking reaction. At the same time, the biomass, during the thermal conversion process, will produce a large number of oxygen-containing compounds, which are believed to promote the cracking of macromolecules[7, 8]. In addition, using biomass rather than the catalysts solve the problem of catalyst's easy deactivation.

Therefore, co-hydrogenation dealing with biomass was discussed here. Briefly, the proper utilization of

Table 1 Proximate and elemental analysis of PS

Sample	Proximate Analysis (wt%, ad)				Elemental Analysis (wt%, daf)				
	M	A	V	FC	C	H	O[a]	N	S
PS	2.41	1.09	81.78	14.72	52.41	6.58	40.78	0.09	0.14

[a] By difference. M-moisture, A- ash, V-volatiles matter, FC-fixed carbon.

Table 2. Material balance of hydrogenation reaction between PS and CTP

Sample	Reactants (g)					Products			YNS[b]
	PS	CTP	THN	H_2	Σ_1	Gas[a] (m^3)	Oil (g)	Water (g)	(%)
1	5.01	10.01	35.62	0.74	51.38	1.01×10^{-2}	46.95 (1.61 wt%)[c]	1.91	75.46
2	5.09	-	25.34	0.74	31.17	1.03×10^{-2}	26.73 (1.36 wt%)	1.76	27.27
3	-	10.01	10.45	0.74	21.20	1.00×10^{-2}	17.12 (1.28 wt%)	1.02	66.63

[a] Detect by Raman Laser Gas Analyzer, mainly including CO, CO_2, CH_4, C_2H_6, C_3H_8.
[b] Yield of n-hexane solvent. [c] The ratio of water in oil.

biomass renewable energy was accomplished with the promotion of lighter components[9]. By using the biomass mixed with other polymers, the rate and quality of liquid oil product will be improved[10]. Catalysis is always used in the upgrade process of heavy coal tar, high temperature is used as well, which causes the high cost in business. Therefore, the mixture of biomass and waste plastic can reduce the severity of reaction[11]. In addition, it is observed that the addition of waste tyres to the feedstock blend is significantly decreasing the amount of aldehydes and phenolic compounds, which is beneficial for improving the stability of the new bio-oils [12]. As for the reaction system of the mixture by heavy components and biomass, the synergies will be used to improve the lightening process of heavy components, which is rarely reported. This study is focus on the effect of the addition of biomass.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Pine sawdust (PS, Proximate and elemental analysis of PS was in Table 1.) was crushed to the size pf 40-60 mesh and dried at 105 °C for 12 h. A high-pressure reaction kettle with 150 mL capacity was used to carry out co-hydrogenation.

2.2 Preparation of heavy components

Rectifying tower (DEA-JB-30) was used in the distillation experiment. The heavy components of coal tar with a boiling point over 350 °C were obtained by vacuum distillation at 4 kPa. Then, the obtained components were hydrogenated.

2.3 Hydrogenation experiment

The heavy component and PS were mixed together with THN and stirred. This mixture was transferred into the quartz liner and kept in the reactor which was then sealed. After confirming that the reactor is leak free, 6 MPa hydrogen gas was filled in the reactor. The rotation speed was adjusted to 300 r/min, and the temperature was increased to 400 °C. The heating rate was 5 °C /min, and the residence time was 60 minutes. After the reaction, the reactor was taken out of heating furnace and cooled it to room temperature 30 °C. Experimental conditions were recorded during the reaction, and the products were collected after the reaction for characterization.

2.4 Hydrogenation product analysis

The gaseous product was analyzed by Raman Laser Gas Analyzer (produced by Atmosphere Recovery Inc.). The relative contents of H_2, CH_4, CO, CO_2, C_2H_6 and C_3H_8 were normalized to obtain the gas composition for the subsequent calculation.

The liquid products were obtained from the extraction of solid and liquid mixtures by Soxhlet extractor using hexane as the solvent at 80 °C for 24 h.

3. RESULTS AND DISCUSSION

3.1 Analysis of hydrogenation products

Hydrogenation experiments were carried out for three raw materials (Sample 1-3 were PS+CTP, PS, CTP). Material balance of hydrogenation reaction of three samples were established in Table 2. The addition of PS significantly promoted the hydrogenation of heavy

components which improved the yield of n-hexane soluble matter from 66.63 wt% to 75.46 wt%.

3.2 Analysis of hydrogenation products by gel permeation chromatography (GPC)

According to the working principle of gel permeation chromatography (GPC), the substance with large molecular weight is detected first [13]. Fig. 1 shows that there are two obvious peaks around 12 and 22 min for heavy components, but only one peak appears at 22.5 min after hydrogenation. The shift of peaks from the later time is aroused by the change of lightening process. This indicates that conversion of heavy components to lighter components could be achieved under this condition (without catalyst). However, the liquefaction of biomass can also produce oil products. Fig.1 shows that the hydrogenation products of biomass are also concentrated at 22.5 min. To prove the influence of PS addition on the lighter components, supporting evidences are mandatory.
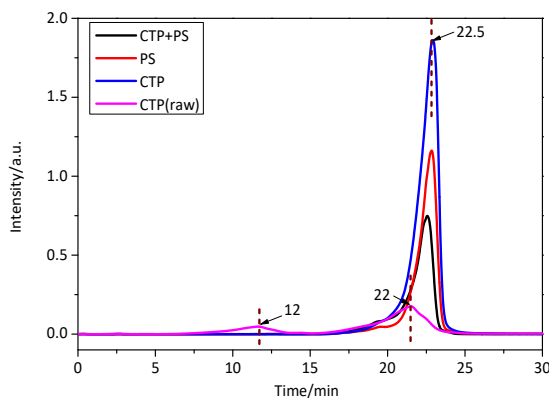

Fig 1. GPC of heavy components

3.3 Analysis of hydrogenated liquid products by synchronous fluorescence spectroscopy (Sy-F)

Ultraviolet fluorescence spectra are used to detect the mixtures having conjugated structures. There is a corresponding relationship between the peaks and the rings of polycyclic aromatic hydrocarbon[14]. Fig. 2 (a) evidences the increase of lighter components with the addition of PS. While the parent liquefied products of PS are appeared at 350 and 450 nm, the peaks of parent heavy components product are noted at 470 nm and 520 nm. On the other hand, the product obtained from co-hydrogenation are observed at 420, 450 and 470 nm. The product of co-hydrogenation is lighter than the liquefied product of biomass and hydrogenation product of heavy components. It is clear that the addition of pine sawdust promotes the lightening of heavy components.
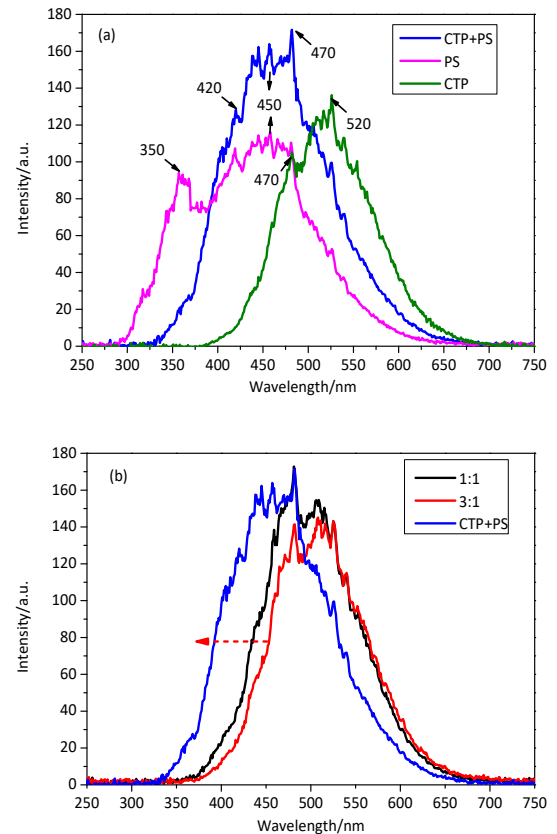

Fig. 2 Sy-F spectra of products from pine sawdust and heavy components

Under the optimized conditions, the obtained oil yield of biomass is 1/4. The raw material is mixed with PS (1/3). Then, the contribution rate of direct liquefaction oil production from PS in the reaction products is about 1/12. Therefore, the product results from 1/4 and 1/2 proportions are compared with the mixed product showing the synergistic promotion effect of the two processes. The two groups of experimental results are configured into tetrahydrofuran solution (1 mg/mL) in the same proportion as the above experiment. Fig. 2 (b) shows that the mixture (mixed CTP and PS with the ratio 2/1 before the reaction) is indeed lighter than the mechanical mixture of two products.

3.4 Analysis of liquid product of Fourier transform infrared spectroscopy

The content of aromatic hydrogen (H_{ar}) is determined by the intensity of wave number at 3030-3060 cm^{-1}[15]. The content of aliphatic hydrogen (H_{al}) is
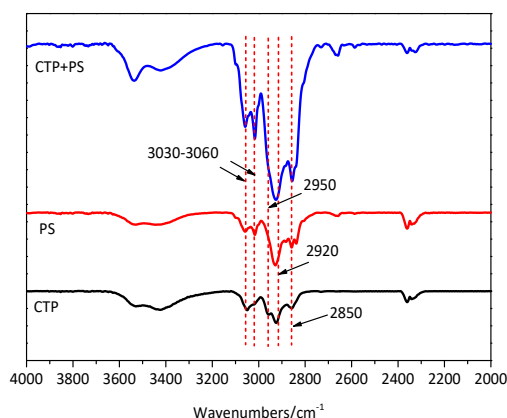
Fig. 3 FT-IR analysis of products from pine sawdust and heavy components

determined by the strength of the peak noted at 2920 cm^{-1}. The results of the study are integrated by the peak fitting method as Fig. 3. H_{ar}/H_{al} ratio is obtained by the area. The value of H_{ar}/H_{al} (CTP) is 0.42, H_{ar}/H_{al} (PS) is 0.28, and H_{ar}/H_{al} (CTP mixed with PS) is 0.24. It is shown that the content of aliphatic hydrogen has increased significantly after the co-hydrogenation.

3.5 Conclusions

For the hydrogenation and lightening process of heavy components, the addition of biomass has been found significantly useful，and the main content that promote the process is probable to be the lignin[12, 16]. Therefore, through this experiment, it is proved that there is a synergistic effect between biomass and heavy components during co-hydrogenation conversion that promotes lighter components.

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