

A study on catalytic conversion of toluene by modified oak char

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ABSTRACT

In order to study the effect of catalytic conversion of biomass gasification tar model compound (toluene) by oak char, a fixed bed test system was used to test the conversion efficiency of toluene, the liquid phase composition was detected by GC-MS. The results show that the conversion efficiency of toluene does not exceed 57.27% at 600 and 700 °C, but it increases significantly at 800 °C, up to 93.07% of KMnO₄ modified char. The content of the liquid phase product of the catalytic conversion of toluene is related to the temperature and whether the char is modified. Moreover, most of liquid phase product are aromatic compounds. Among them, bibenzyl is an important intermediate product in the catalytic conversion of toluene.

Keywords: gasification, oak char, catalytic conversion, toluene

NONMENCLATURE

Abbreviations

GC-MS Gas chromatograph-Mass spectrometer

Symbols

η_{tar} The toluene conversion efficiency, %.

M_{tar} The mass of toluene, g

M_1 The total mass of the gas scrubber filled with isopropanol, deionized water and silica gel before the experiment, g

M_2 The total mass of the gas scrubber filled with isopropanol, deionized water and silica gel after the experiment, g

1. INTRODUCTION

As one of the most attractive and promising options for biomass thermochemical conversion technology,

Selection and peer-review under responsibility of the scientific committee of the 12th Int. Conf. on Applied Energy (ICAE2020).

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there are universally commercial applications of biomass gasification in power supply, thermal energy production, chemical synthesis, metal smelting and other fields. In the process of biomass gasification, it is decomposed into three parts with gasification agent at high temperature: synthesis gas, tar and solid residue composed of char and/or ash [1]. However, tar could block and corrode downstream pipelines, filters and other equipment, which causes a waste of its own energy. It limits the applications of biomass gasification technology. Therefore, the purification treatment of gasified tar is of great significance.

At present, catalytic conversion is considered to be the most promising technology for purifying tar due to its high tar removal efficiency and relatively mild operating conditions [2], and it is also one of the most effective methods to convert tar into useful synthesis gas. As a by-product in the process of biomass gasification, char accounts for 12% to 30% of the total amount in initial biomass, and is cheap and easy to obtain [3]. The conditions of char as a catalyst due to its porous structure, the existence of O-containing groups on surface, structure of the carbonaceous matrix, and the inherent alkaline (earth) metals (K, Na, Mg, Ca, etc.). Gilbert P et al. [4] detected that the conversion efficiency of pyrolytic wood char to tar was 66% at 800 °C, which was mainly due to the presence of alkaline (earth) metals. Bhandari et al. [5] found that higher removal efficiency for toluene of activated char. Some scholars [6] studied loading alkali (earth) metals, loading iron, copper, nickel and other metals, and electrochemical methods and other modifications. Wang et al. [7] found that the char by KMnO₄ modified successfully carried manganese oxide particles, increased the number of oxygen-containing groups, and also enhanced the adsorption performance. However, KMnO₄ modified

char is mostly used to remove heavy metal ions, and it has not been reported to remove tar. It is necessary to study the feasibility of this modification for removing tar. At present, there are few studies on gasified biomass char as a catalyst for removing tar.

In this paper, oak gasification char (unmodified and modified) is selected as the catalyst, and the biomass gasification tar model compound (toluene) is used as the research object to study the effects of catalytic conversion efficiency and liquid phase product by modified oak char. It hopes to provide a reference for the research and preparation of more efficient and economical tar removal catalysts.

2. MATERIALS AND METHODS

2.1 Preparation and treatment of oak char samples

Table 1 Ultimate and proximate analysis of oak and oak char

Sample	Ultimate analysis (wt. %)					Proximate analysis (wt. %)			
	S _{t,d}	C _d	H _d	O _d	N _d	M _{ad}	A _d	V _{daf}	FC _{ad}
Oak	0.04	48.41	5.62	45.54	0.15	5.90	0.24	85.79	13.34
Oak char	0.04	90.01	1.1	3.14	0.22	1.90	5.48	4.29	88.75

Note: S_{t,d} — total sulfur on dry basis, d — dry basis, ad — air dry basis, daf — dry ash-free basis

2.2 Activity test of samples

The efficiency test system for the catalytic conversion of toluene by oak char is shown in Fig.1. It consists of three parts: gas supply system, catalytic conversion system, and collection system. The catalytic conversion system includes a fixed bed reactor and catalyst bed. The collection system consists of a water bath and a gas scrubber, and the gas scrubber is filled with isopropanol. The collection system needs to create a low temperature environment, so an ice water bath is used to collect the liquid phase product as much as possible. The carrier gas is N₂, the flow is 50 mL min⁻¹, and toluene is added to 0.05 mL min⁻¹ through a micro-injection pump (LSP01-3A, China). Each group of experiments is 20 minutes, and each group of experiments is repeated 3 times. The toluene conversion efficiency (denoted as η_{tar}) is defined as:

$$\eta_{tar} = \frac{M_{tar} - (M_2 - M_1)}{M_{tar}} \times 100\% \quad (1)$$

Where: M_1 and M_2 are the total mass of the gas scrubber filled with isopropanol, deionized water and silica gel before and after the experiment, g; M_{tar} is the mass of toluene used in the experiment, g; η_{tar} is the tar model compound (toluene) conversion efficiency, %.

The oak selected in this article is produced in Europe and is resistant to wear. Made it to block with a size of 1-2.5 cm for reserving. The experiment of preparing oak char by gasification in a fixed-bed quartz tube reactor system. To ensure fully gasify, the flow efficiency of N₂ and CO₂ are 70 mL min⁻¹ and 330 mL min⁻¹ (the mass of oak is 5g), respectively, and keep 30 minutes at 800 °C. The ultimate analysis and proximate I analysis of oak and gasified oak char are shown in Table 1. In the experiment, oak char was modified with KMnO₄ solution: Mixing 2 g of oak char with 10 mL of 0.2% KMnO₄ solution and stir for 4 hours. After drying, it is placed in a muffle furnace and calcined at 300 °C for 1 hour, then rinsed with deionized water, and then dried (KMnO₄-Treated). A group of gasified oak char without any treatment (Untreated) was added as a control.

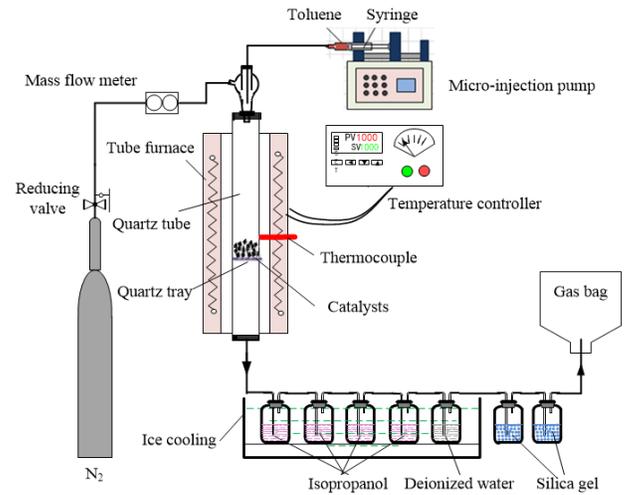


Fig. 1 Test experimental system of catalytic conversion efficiency for toluene by oak char

2.3 The detection of liquid phase product

The solution containing the liquid phase product in the four gas scrubbers was poured into the beaker, and clean the pipes and gas scrubbers with isopropanol for 2-3 times. The cleaned solution was still poured into the beaker, and then remove the possible water in the solution through anhydrous Na₂SO₄. The solution through a 45 μm filter to obtain the test liquid, which would be detected by gas chromatography-mass spectrometry (GC-MS, Trace ISQ, China).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Activity evaluation of oak char samples

In order to prove that char is catalytic on toluene, a blank experiment of thermal cracking was done by Al_2O_3 as the bed material, and then catalytic conversion experiment would be done by oak char as the bed material. The thermal cracking conversion efficiency of toluene at different temperatures and the catalytic conversion efficiency of oak char samples to toluene were obtained. As shown in Fig.2, the efficiency of thermal cracking and catalytic conversion for toluene both increase with the increase of temperature. It shows that the main conversion reaction of toluene is an endothermic reaction [8].

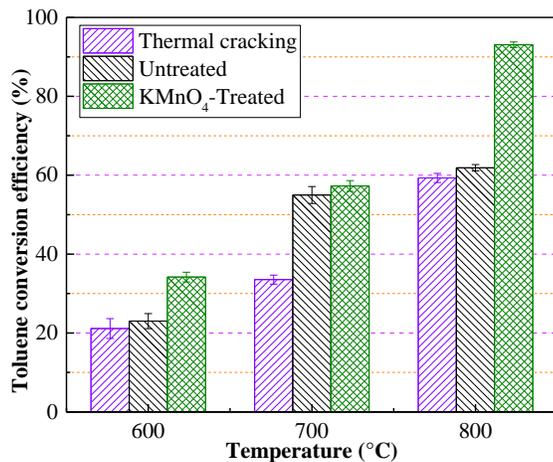


Fig.2 Toluene conversion efficiency by thermal cracking and oak char samples at different temperatures

The thermal cracking conversion efficiency of toluene is 21.12% at 600 °C, and the conversion efficiency of Untreated is not much gap from one of thermal cracking. The η_{tar} of KMnO_4 -Treated were 34.18%, indicating that the activity of KMnO_4 -Treated is higher than that of Untreated at low temperature (600 °C). It could be seen that the degree of toluene cracking is very low at 600 °C, which is similar to the results of Li et al. [9]. At 700 °C, the conversion efficiency of toluene increased to a certain extent. The efficiency of Untreated and KMnO_4 -Treated increased by 31.96% and 23.09%, respectively, compared with that at 600 °C. But the highest η_{tar} does not exceed 57.27% (KMnO_4 -Treated). At 800 °C, the efficiency of thermal cracking and Untreated are 59.31% and 61.89%, respectively, which are equivalent to the test results of Mi et al. [10]. The efficiency of KMnO_4 -Treated is higher than that at lower temperatures, reaching 93.07%, and the degree of toluene catalytic conversion is very high. Therefore, in

terms of efficiency, the char with this modification method is feasible to remove tar.

3.2 Analysis of liquid phase product

In this experiment, GC-MS analysis was performed on the liquid phase product obtained from the catalytic conversion of toluene from Untreated and KMnO_4 -Treated at 700 °C. Although the peak area of the spectrum obtained by GC-MS analysis cannot determine the actual content of the test liquid sample, if the quality of the tested samples is the same, the corresponding peak area could be compared between different tested samples in relative content [11]. The GC-MS analysis results of the liquid phase product obtained by catalytic conversion of toluene from char samples at 700 °C are shown in Table 2.

Table 2 Liquid phase product of catalytic conversion for toluene by GC-MS analysis at 700 °C

	RT/min	Composition	Relative content/wt.%	
			Untreated	KMnO ₄ -Treated
1	4.60	Benzonitrile, m-phenethyl-	—	2.65
2	5.60	Ethylbenzene	7.85	8.68
3	5.78	Benzene, 1,3-dimethyl-	3.71	4.12
4	6.27	Styrene	8.35	12.88
5	16.94	Cyclohexasiloxane, dodecamethyl-	3.21	9.90
6	18.26	Biphenyl	—	2.56
7	19.41	1,1'-Biphenyl, 4-methyl-	15.57	5.19
8	20.73	2,2'-Dimethylbiphenyl	13.79	15.89
9	21.30	Bibenzyl	16.03	14.41
10	21.43	Benzene, 1-methyl-3-(phenylmethyl)-	4.17	3.02
11	22.70	1,1'-Biphenyl, 3,4'-dimethyl-	13.99	7.18
12	22.91	3,3'-Dimethylbiphenyl	6.89	6.78
13	23.77	Cyclooctasiloxane, hexadecamethyl-	3.23	—
14	25.01	cis-Stilbene	3.21	4.96
15	26.37	Phenanthrene	—	1.78

The liquid phase product exist in the form of light aromatic hydrocarbons and monocyclic alkanes. Most of the liquid phase product is aromatics. The toluene used in the experiment was only one-ring aromatic hydrocarbons. However, a large amount of two-ring aromatic hydrocarbons were detected in the product, and three-ring aromatic hydrocarbons (phenanthrene) were also detected in KMnO_4 -Treated. It is because more energy is required for the cracking of such substances,

which is also one of the main reason that toluene cannot be completely cracked [8]. Tar would be cracked into coke, CO, CH₄ and other gases in the cracking reaction, and many reactive free radicals will also be produced. Most of the reactive free radicals are aromatic, which will polymerize into aromatics at lower temperature

According to the research from Huang et al. [12] on the thermal cracking mechanism of toluene, the initial mechanism of toluene thermal cracking could be shown in Fig.3. When the thermal cracking temperature of toluene reaches about 500 °C, reaction path 1 is supported. Toluene is first thermally cracked into benzyl radical and hydrogen radical, and then into bibenzyl. As the temperature increases (800 °C), reaction path 2 is supported, and the proportion of reactions that produce benzene radicals would be greater than the proportion of benzyl radicals. Among the liquid phase product of the catalytic conversion for toluene listed in Table 2, bibenzyl accounts for a large proportion of the product, reaching 14.40% and above, while biphenyl (without methyl) is only in KMnO₄-Treated is detected, indicating that at 700 °C, the Untreated supported reaction path 1, no path 2, and KMnO₄-Treated supported both path 1 and 2 occurred, indicating that the sample can catalyze the thermal cracking reaction (≥ 800 °C) at 700 °C. Bibenzyl is one of the important intermediate product in the catalytic conversion of toluene, and then undergoes a series of cracking, dehydrogenation and condensation reactions into other organic compounds [13].

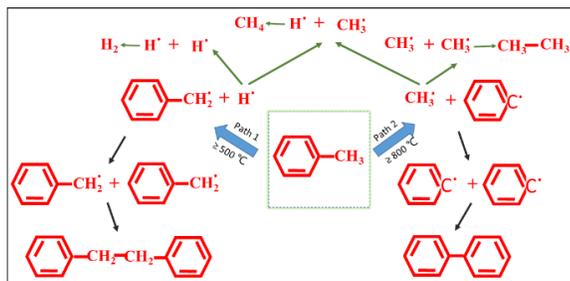


Fig.3 Schematic diagram of the initial mechanism for toluene thermal cracking

4. CONCLUSIONS

The toluene conversion efficiency is low at 600 and 700 °C, and the highest is only 57.27% (KMnO₄-Treated). The conversion efficiency increased significantly, especially for the KMnO₄-Treated, as high as 93.07%. The liquid phase product of the catalytic conversion of toluene is mostly aromatic compounds. The temperature and modification is influential on the initial cracking path

of toluene, and then the relative content of the product components.

ACKNOWLEDGEMENT

This work was supported by the Natural Science Foundation of Shaanxi Province (2019JM-277) and Research Project of Guangdong Special Equipment Inspection and Research Institute (2020CY-2-07).

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