

DECOMPOSITION OF TAR FROM BIOMASS GASIFICATION OVER CARBONACEOUS MATERIAL

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ABSTRACT Catalytic tar cracking is one of the promising tar removal methods. However, most of catalysts used so far have high cost and low resistant to deactivation. Using carbonaceous materials, e.g. biochar, is an alternative due to its catalytic ability for tar cracking, low cost and easily produced. In this study, the experiment of tar destruction over biochar was performed with the aim to explore the possibility of using biochar as catalyst and to study the effect of temperature on tar destruction over biochar. Naphthalene was selected as the model tar to represent polyaromatic hydrocarbons, which are abundant in biomass-derived tar and resistance to cracking. A commercial biochar was used as catalyst. All experiments were conducted in a fixed bed reactor. Naphthalene vapor was fed into the reactor system at 0.03 g/min. The experiment temperatures were 600-800°C with 100 minute reaction time. The thermal cracking experiment (without biochar) was also conducted under otherwise similar conditions for comparison. The blank experiments, i.e. no naphthalene fed, at corresponding temperatures were also conducted to establish the baseline for gas composition and char structure. The results showed that more naphthalene decomposed into gas and other cracking products as temperature was increased with or without the presence of biochar. Thermal cracking of naphthalene could be accelerated only at 800°C giving 44.1% conversion. With the presence of biochar, the maximum conversion of naphthalene was 82.8% at 800°C. The increasing trend of total gas and H₂ production with temperature were also observed and confirmed the enhanced cracking of naphthalene into gases. The decreased surface area and pore volume when compared to blank experiments at all temperatures tested suggests that naphthalene adsorption as well as the soot deposited on the internal surface of biochar occurred leading to the blocking of biochar pores.

1. INTRODUCTION

In recent years, interest in biomass gasification has been growing as a clean technology to produce energy. In gasification process, the main product is producer gas, which can be further used in various applications i.e. direct use in boilers, engines and gas turbines for heat and

electricity generation or as intermediates for fuels or chemicals. However, during gasification process, not only producer gas but also tar and particulates were produced. The formation of tar leading to some operational troubles in downstream equipment such as clogging or deposition on surfaces (Klinghoffer, et al., 2015).

Catalytic tar removal is considered as one of the efficient techniques for tar removal. One advantage of catalytic cracking is that the heating value of the gas is not reduced, as would be the case if the tars were thermally cracked at high temperature (Morris, 2004). In addition, the ability to increase the quantity of usable gases such as H₂ and CO in producer gas is quite high. There are several types of catalysts that have potential for tar removal. Ni-based catalysts have been found to be very effective for tar removal and increase the yields of CO and H₂. However, the weaknesses of Ni-based catalysts are their rapid deactivation, high concentration of tar in the feed and some are expensive. Carbon-based catalysts such as activated carbon and biochar have been widely used as catalyst or catalyst support for tar removal both inside the gasifier and in downstream process after gasifier. The attractiveness of biochar as a catalyst originates from its low cost material which can be produced within the gasification process and its high resistance to poisoning (Hosokai et al., 2008). The catalytic activity of biochar for tar reduction can be related to the pore size, surface area and ash or mineral contents in biochar.

So far, most studies investigated the catalytic activity of biochar for tar decomposition under reactive atmospheres, e.g. H₂, O₂, CO₂ and steam. Only a few studies were conducted under an inert condition, which may as well represent the other extreme of gas atmosphere. In typical producer gas from biomass air gasification, N₂ is the major component (around 40-55%) and for the remaining a combination of CO, H₂, CO₂, H₂O and other trace gases. This study therefore focused on investigating the catalytic activity of biochar for tar decomposition under pure N₂ under selected temperature range and also compared with thermal cracking experiment (without biochar). Naphthalene was chosen as the model tar to represent polyaromatic hydrocarbons, which are abundant in biomass-derived tar and resistance to cracking. The

spent biochars after the test with and without naphthalene were characterized in order to explore the possible mechanisms of naphthalene decomposition.

2. EXPERIMENT

2.1 Experimental Apparatus The schematic diagram of catalytic tar removal experimental setup is shown in Fig. 1. The system consists of three main parts: 1) a system for vaporization of naphthalene 2) a catalytic fixed-bed reactor and 3) a cold tar trap and gas collection unit. The reactor was made of a quartz tube with a diameter of 10 mm. Catalyst with 30 mm bed height was placed in the middle of heating zone inside the reactor and supported by quartz wool. The reactor was heated and controlled by an electrical furnace and the reactor temperature was measured by a K-type thermocouple.

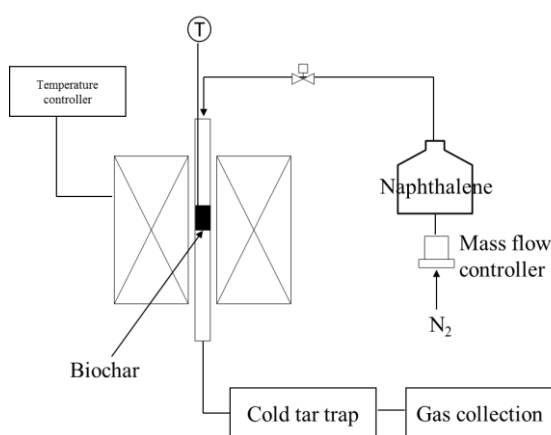


Fig. 1 Schematic diagram of catalytic tar removal experimental setup

The catalytic tar removal experiment was conducted at the temperature range of 600-800°C and holding time of 100 minutes. Naphthalene has been selected as a model tar instead of using a real tar to represent poly-aromatic hydrocarbons which are abundant in real biomass tar and resistant to cracking. A commercial biochar was used as catalyst in this study. The commercial biochar used was charcoal wood supplied from Gammaco Co., Ltd. in small cube shape with the particle size around 0.5-1 mm. The characteristics of commercial biochar used in this study including that from proximate analysis, ultimate analysis and elemental analysis of minerals are presented in Table 1. Carbon was the main element in the commercial biochar with concentration approximately 90%.

In each test, nitrogen was purged inside both the fixed bed reactor and naphthalene vaporization system to remove the remaining oxygen in the system. Then, the reactor was heated to the desire temperature. Naphthalene was vaporized at 140-150°C and nitrogen was used as carrier gas to flow naphthalene vapor through the reactor with the total outlet flow rate 100 ml/min. When the desired temperature was reached, the naphthalene vapor was passed through the reactor system with an average feed rate of 0.03 ± 0.001 g/min. The thermal cracking

experiment (without biochar) was conducted under otherwise similar same experimental conditions for comparison. For both types of experiment, analyses of collected (dry) gas and trapped tar were conducted. The blank experiments, i.e. no naphthalene fed, at corresponding temperatures were also conducted to establish the baseline for gas composition and char structure.

Table 1 Characteristics of commercial biochar.

Proximate analysis (% dry basis)					
Volatile matter		Fixed carbon		Ash	
9.59		79.70		10.71	
Ultimate analysis (% dry ash free basis)					
C	H	N	O		
			(by difference)		
90.72	0.93	0.38	7.87		
Elemental analysis (% dry ash basis)					
Si	Fe	Al	S	Ca	K
3.62	2.12	1.16	1.08	0.913	0.126

The conversion of naphthalene was calculated from the inlet and outlet amount of naphthalene as shown in Equation (1).

$$X = \frac{M_{in} - M_{out}}{M_{in}} \times 100 \quad (1)$$

where X is naphthalene conversion efficiency (%), M_{in} is the inlet amount of naphthalene (g) determined by the weight difference of naphthalene in the reservoir before and after the experiment, M_{out} is the outlet amount of naphthalene (g) determined using GC-FID for the concentration of naphthalene remaining in the trapped tar after experiment.

2.2 Analysis technique

2.2.1 Tar sampling and analysis. The cold tar trap method was applied for tar sampling in this experiment. The collection of tar was performed in a series of three impinge bottles. In the series of three impinge bottles, two were filled with isopropanol (IPA) and the remaining one was left empty. The first impinge bottle was heated at around 80°C to prevent condensation of naphthalene vapor. The other two left impinge bottles were laid in an ice bath filled with ice/salt mixture.

The concentration of naphthalene after reaction was quantitatively analyzed by a gas chromatograph (Shimadzu GC 2010) equipped with flame ionization detector. The GC column was HP-5 MS column, 30 m long, 0.25 mm diameter with a film thickness of 0.25 μ m and flow rate 1.2 mL/min. The column oven temperature was programmed from 45°C (held for 5 min) to 180°C at 5°C/min, then linearly increased from 180 to 300°C at 20°C/min, and held for 10 min.

2.2.2 Product gas analysis. The contents of H_2 , CH_4 , CO and CO_2 in the gas were determined. The CO was analyzed using GC-14B through a molecular sieve (MS-5A) column. Other gas species were analyzed using GC-

2014 through a Pora Plot Q (PPQ) column. Light hydrocarbons heavier than CH_4 were also measured but no significant concentrations were detected. The obtained gas composition was then corrected with that obtained from blank test.

2.2.3 Biochar characterization. The internal structure of biochars was analyzed in order to explore the possible mechanisms of naphthalene decomposition. The measured properties of biochar included BET surface area, pore volume and mean pore diameter. Surface area and porosity were determined from the corresponding nitrogen adsorption-desorption isotherms obtained at -196°C . The surface area was measured by the Brunauer-Emmet-Teller (BET) calculation method. The total pore volume was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $p/p_o = 0.99$.

3. RESULTS & DISCUSSION

3.1 Naphthalene conversion

The conversion of naphthalene as a function of temperature with and without biochar was calculated by Equation (1) and the results are presented in Fig. 2. Similar trend of naphthalene conversion was observed for both cases of experiment in which naphthalene conversion efficiency increased with increasing temperature. It was clearly observed that naphthalene is relatively stable at temperature 600 and 700°C as only around 9-14 % was converted into gases, other tar molecules and soot. In this study, the thermal cracking of naphthalene at 800°C gave maximum conversion efficiency at 44.05%. In the presence of biochar, the conversion efficiency of naphthalene was higher than the case without biochar at all temperature studied. The conversion efficiency of naphthalene in the presence of biochar at 600, 700 and 800°C was 33.28%, 59.52% and 82.23%, respectively. The increased conversion efficiency with the presence of biochar might be attributed to the high surface area and pore volume of biochar, which increase the availability of catalytic sites for tar cracking.

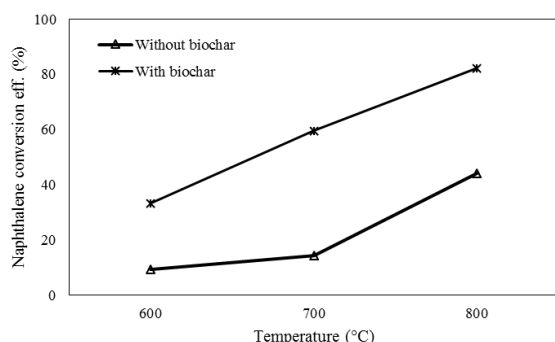


Fig. 2 Effect of temperature on naphthalene conversion without and with biochar at 600, 700 and 800°C .

3.2 Gas production

Product gases formed during the tests in the case with and without biochar at different temperatures were

analyzed and then corrected by those obtained from the blank test as mentioned in 2.2.2. The results are as shown in Fig. 3. A similar trend of gas production was observed for both cases of experiment in which total gas production increased with increasing temperature. This is because at higher temperatures, naphthalene loses its stability and has a greater chance to crack into gases. However, much smaller amount of gases was produced from thermal cracking of naphthalene when compared to catalytic cracking. Even at 800°C , only 0.4 mmol/g-naphthalene or 5.1% of naphthalene was thermally converted into gases. With the presence of biochar, total gas produced at 600°C was 0.62 mmol/g-naphthalene and increased to 1.15 mmol/g-naphthalene at 800°C . The increased gas yield confirms the positive effect of biochar catalyst for tar conversion into gases, which is enhanced at high temperatures.

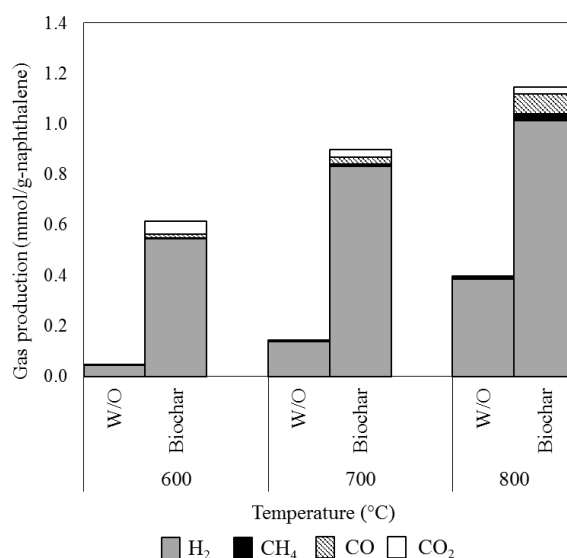


Fig. 3 Effect of temperature on gas production without and with biochar at 600, 700 and 800°C .

During thermal treatment, naphthalene converts into H_2 and smaller tar molecules than naphthalene. As shown in Fig. 3, H_2 was the main component of the gas produced at all conditions and had an increasing trend with temperature. Increasing temperature from 600°C to 800°C , the H_2 production from thermal cracking reaction increased by almost 10 times, i.e. from 0.04 to 0.39 mmol/g-naphthalene. However, this is still below the H_2 production at 600°C in the presence of biochar, i.e. 0.55 mmol/g-naphthalene. Increasing temperature to 800°C could even further increase H_2 production to 1.01 mmol/g-naphthalene. In the presence of biochar, the production of CH_4 , CO and CO_2 was significant albeit low. The concentration of CH_4 and CO increased with increasing temperature, while the CO_2 concentration decreased. The decreased CO_2 concentration at higher temperature could be explained by the reaction between the released CO_2 and naphthalene, which is favored by temperature and produce more CO at higher temperatures, especially at 800°C .

3.3 Characteristics of biochar The internal structure of biochar after the test with naphthalene at temperature 600-800°C are presented in Table 2 against the blank test (the case without naphthalene). Considering the internal structure of biochar from the blank tests, the BET surface area of all chars was relatively large, i.e. above 600 m²g⁻¹ close to that of activated carbon. The surface area and pore volume were found maximum at 700°C, while the mean pore diameter decreased throughout the range of temperatures studied. This observation is similar to the previous study by Guerrero, et al. (2008), in which the char surface area is maximised at 700°C when pyrolysing biomass at temperatures in the range of 600-900°C. It was reported that structural ordering and micropore coalescence during heat treatment are responsible for the decrease in the surface area values observed at temperatures over 800°C, resulting in a thermal deactivation of the chars and leading to a decrease in the number of active sites for reaction.

Table 2 Characteristics of biochar.

Biochar samples	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)
600°C – Blank	698.27	0.42	2.53
600°C – With tar	217.35	0.37	6.86
700°C – Blank	711.63	0.43	2.39
700°C – With tar	162.45	0.22	5.44
800°C – Blank	658.30	0.36	2.20
800°C – With tar	324.79	0.32	4.01

The surface area and pore volume of biochars obtained after catalytic reaction with naphthalene were significantly smaller when compared to the biochars from experiments without naphthalene. The decrease in the surface area and pore volume of biochar was probably due to the naphthalene adsorption as well as the possible soot deposition on the internal surface of biochar leading to the blocking of biochar pores. The largest difference was found at 700°C.

4. CONCLUSION

The effect of temperature on the decomposition of naphthalene over biochar under N₂ atmosphere was investigated in this study. Thermal cracking experiment of naphthalene (without biochar) was also conducted under otherwise similar conditions for comparison.

It was clearly observed that more naphthalene decomposed into gas and other cracking products as temperature was increased with or without the presence of biochar. Thermal cracking of naphthalene could be accelerated only at 800°C with 44.05% conversion. The presence of biochar promotes the conversion of naphthalene at all temperatures studied. At 600°C, naphthalene conversion was 33.38% and increased constantly to 82.23% at 800°C. The increasing trend of total gas and H₂ production with temperature were also observed and confirmed the enhanced cracking of

naphthalene into gases. The surface area and pore volume obtained after catalytic reaction with naphthalene decreased at all temperatures tested when compared to biochars from experiments without naphthalene, which suggests that naphthalene adsorption as well as soot deposition on the internal surface of biochar occur leading to the blocking of biochar pores.

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