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Novel findings in conversion mechanism of toluene as model compound of biomass waste tar in molten salt

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ABSTRACT

Molten salt owning large specific heat capacity and thermal conductivity coefficient is a promising reaction medium for catalytic pyrolysis/gasification of biomass waste. The understanding of tar conversion mechanism in molten salts is of great importance and needs to be clarified. The present study investigated the interactions between ternary carbonate eutectics ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) and main tar model compounds during pyrolysis and CO_2 gasification process. The results showed that the molten salt could dramatically suppress the gas productivity (H_2 and CH_4) of toluene. A high molar ratio of CO_2 in molten salt gasification would further inhibit the H_2 yield, probably through the reverse water gas shift reaction. Meanwhile, a tendency towards polycyclic aromatic hydrocarbons (PAHs) formation was identified by examining liquid product in both molten salt pyrolysis and gasification process. And the formation of PAHs was likely correlated to the consumed H radical pool via its reaction with CO_3^{2-} and/or CO_2 . Tar-containing alcohols and carboxylic acids could provide with free radicals and effectively inhibit the PAH generation. Meanwhile, the OH radical could react with CO_3^{2-} to generate less active carbonate radical and hydroxyl, resulting in more fused liquid product. Introducing OH and H containing substance was recommended to enhance the decomposition of aromatics in molten carbonates.

1. Introduction

With increasing concern about global warming issue and energy crisis, seeking alternative technology for sustainable replacement of fossil fuel is among the major challenges facing most countries [1]. Abundant biomass waste is one of the renewable primary energy sources, offering the potential to produce carbon neutral fuels [2]. Pyrolysis/Gasification is considered to be an innovative option for upgrading low value biomass waste to syngas for further syntheses or the ready-to-use biofuel [3,4]. During such process, the waste can be flexibly converted into tar, char or gas [5] through optimizing the thermochemical condition. Besides, lower emissions of CO_2 and other flue gases, such as SO_2 and NO_x can be obtained in the absence of air [6].

More recently, an integration of pyrolysis/gasification and molten salt presents advancement in biomass waste utilization and attracts attention from researchers worldwide [2,3,7,8]. Molten salts owning large specific heat and thermal conductivity coefficient [9] are commonly known as heat storage medium in solar power generation. Besides, as reaction medium, molten alkali cations are able to implement catalytic cracking of carbonaceous compounds [10], e.g. solid waste, biomass and coal. And the catalysis has proved to be enhanced with

temperature increasing, which usually exceeds $600\text{ }^\circ\text{C}$ [11]. The catalytic mechanism is explained by electron transfer and oxygen transfer theories correlated to vacancies in molten salt's structure [10]. Meanwhile, the sulfide and chloride contents produced during the thermochemical process, such as H_2S and HCl , can be in situ captured in the salts [12,13]. The impact on environment and the cost of gas clean equipment can be reduced consequently. Therefore, by combining the above advantages molten salt pyrolysis/gasification of biomass waste is a promising solution for waste-to-energy. Nevertheless, it should be noted that tar conversion pathway could be altered in the presence of molten salt, which plays a significant role in sufficient utilization of such technology.

Lab-scale experiments focused on thermochemical conversion in molten salt have been conducted in the past thirty years. Yeboah et al. [14] evaluated different eutectic salt mixture catalysts for CO_2 gasification of coal in a fixed-bed bench scale reactor. The result demonstrated that ternary alkali eutectics showed better catalytic activity than binary or unary salts. And carbonates were more effective than nitrates. Moreover, Hathaway and co-workers [15] studied the kinetics of pyrolysis in a bath of ternary carbonate eutectic blend. Arrhenius rate expressions proved that the molten salt could increase the

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rate of pyrolysis by 74% and act as both catalyst and heat transfer media. With respect to gas production, molten salts could raise not only the total useful gas yield but also the proportion of hydrogen [16]. In the meantime, secondary products in the form of condensable tar were reduced significantly [3,15,16].

Regarding the tar yield, similar result was found in Zhang's study that the presence of carbonates considerably accelerated the tar decomposition into gaseous products [17]. In addition, it is evident that alkali salts would change tar composition derived from biomass waste pyrolysis [18]. Umeki et al. [19] observed reduction on primary tar production during devolatilization stage of sawdust with K impregnation and promotion on light tar degradation. Contradictory to the above findings, molten carbonate salts could also enhance the tar yield. Rizkiana et al. [12] employed eutectic mix of alkali carbonate salts to assist pyrolysis of low rank coal. The results showed that molten carbonate salts would significantly increase the liquid production yield. Unfortunately, the interaction mechanism remained unclear. Consequently, a more detailed tar conversion mechanism needs to be clarified for the sufficient utilization of molten salt technology.

In the present work, the tar cracking and reforming in ternary carbonate eutectics ($\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$) were conducted at 650, 750 and 850 °C. Toluene, methanol, ethanol and acetic acid were adopted as tar model compounds. The gas phase and liquid phase product was detected by gas chromatography (GC) and gas chromatography-mass spectrometer (GC-MS). A general conversion mechanism of tar model compounds during molten salt pyrolysis/gasification of biomass waste was proposed.

2. Experimental

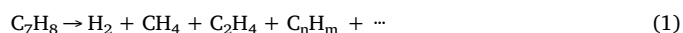
The ternary carbonate eutectics were prepared by firstly mixing individual lithium carbonate (32.1 wt.%), sodium carbonate (33.4 wt.%) and potassium carbonate (34.5 wt.%). Then, the mixture was heated at 800 °C in a muffle furnace for 6 h and cooled to ambient temperature. At last, the solid eutectic mixture was ground in an agate mortar and dried at 105 °C to remove the moisture.

Since toluene was one of the major tar components derived from biomass waste pyrolysis/gasification [20], it was adopted as tar model compound, representing light aromatics. Fig. 1 showed the schematic of experimental facilities. The toluene was injected into a nebulizer and mixed with the carrier gas (N_2 , purity $\geq 99.999\%$) to acquire aerosol. Afterwards, the pre-heater set at 250 °C evaporated the aerosol and the toluene vapor was introduced into the bottom of the cylindrical reactor downstream through 8 pin holes ($\Phi 2$ mm). After reaction in molten

salts, the liquid and gaseous product was collected by condenser and gas bag, respectively. To avoid undesirable condensation, the exhaust pipe was also heated up to 250 °C.

To acquire fast kinetics and avoid thermal decomposition of the molten salts, the temperatures were set 650, 750 and 850 °C. Before experiments, the reactor was heated to target temperature and purged with argon for 30 min. to exhaust the air. The injection pump feeding rate was fixed at a constant rate of 0.05 mL/min and each run lasted for 60 min. CO_2 , typically employed/formed in biomass waste pyrolysis/gasification, was introduced (35.84 vol.%) to estimate its influence on tar conversion in molten salt. Since tar content in producer gas generally varied from 0.5 to 100 g/ Nm^3 [21], the total flow rate was controlled at 558 SCCM by mass flowmeters and the tar concentration was maintained at 76.1 g/ Nm^3 consequently. In the experimental groups, 56.779 g molten eutectics was sent into the reactor to establish a 5.5 cm high bed. Methanol, ethanol and acetic acid as tar-containing alcohol and carboxyl model compounds were mechanically pre-mixed with toluene (volume ratio = 1:3). Gas chromatography (GC) and gas chromatography-mass spectrometer (GC-MS) were adopted to determine the product compositions. The main reactions (Eqs. (1) and (2)) and side reactions (Eqs. (3)–(5)) that could take place in the reactor were demonstrated below.

Cracking reaction



Dry reforming



Reverse water-gas shift reaction



Boudouard reaction



Methanation reactions



To evaluate the efficiency of toluene cracking into gas (H_2 , CH_4 and CO), gas productivity (%) was defined as Eq. (6). The actual gas production (mL) was detected and calculated by GC. The theoretical gas production (mL) corresponded to experimental conditions. For cracking in N_2 atmosphere, it's assumed that per mole of C_7H_8 would completely cracking (Eq. (1)), producing 4 mol of H_2 and 7 mol of carbon. For

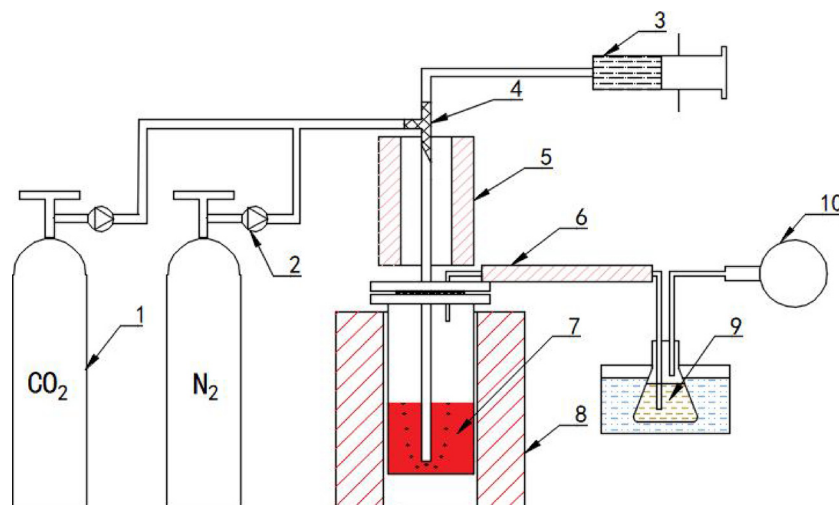


Fig. 1. Schematic diagram of experimental facilities: 1, gas vessel; 2, mass flowmeter; 3, injector; 4, nebulizer; 5, pre-heater; 6, heating jacket; 7, molten carbonate salt; 8, infrared furnace; 9, cold trap; 10, gas bag.

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