

# Plasma-catalytic gas cleaning processes for the removal of model tar compound from biomass gasification

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**Abstract:** Non-thermal plasma technology has been regarded as a promising route for the conversion of biomass tar into clean fuels and value-added chemicals (e.g., H<sub>2</sub> and CO) at ambient conditions. Our recent work on the plasma reforming of model tar compound with or without catalysts will be discussed in terms of reactant conversion, yield of targeted product, and energy efficiency in the plasma process.

**Keywords:** plasma discharge, steam reforming, tar removal, plasma-catalysis

## 1. Introduction

Gasification of biomass wastes represents a major sustainable route to produce syngas (H<sub>2</sub> and CO) from a source which is renewable and CO<sub>2</sub>-neutral. However, one of the major challenges in the gasification process is the contamination of the product syngas with tar, particulate matter and other pollutants. The formation of tar causes major process and syngas end-use problems, including tar blockages, plugging and corrosion in downstream fuel lines, filters, engine nozzles and turbines [1]. Catalytic steam reforming of biomass tar offers one possible solution to produce a clean, high quality syngas from the gasification of biomass. Nickel-based catalysts mainly supported on alumina, have been extensively investigated for steam reforming of biomass tar because of its low cost, abundance and high initial activity. However, catalyst deactivation due to coke deposition is still a major challenge for this reaction [2].

Non-thermal plasma technology provides an attractive alternative to the conventional catalytic route for the conversion of hydrocarbons into value-added chemicals at a relatively low temperatures. In non-thermal plasmas, the overall gas temperature remains low, while the electrons are highly energetic, which is sufficient to break down most chemical bonds of molecules and produce highly reactive species: free radicals, excited atoms, ions and molecules for chemical reactions[3]. Moreover, the combination of plasma and solid catalysts (known as plasma-catalysis) has great potential to generate a synergistic effect, which can activate catalysts at low temperatures and improve the activity and stability of the catalysts, resulting in the remarkable enhancement of reactant conversion, selectivity and yield of end-products, the energy efficiency of the process [4].

The use of gliding arc discharge plasma for decomposition and reforming of biomass tar has attracted increasing attention due to its unique characteristics of high electron density and high volume capability. In this study, an AC gliding arc discharge plasma reactor has been developed for plasma steam reforming and plasma-catalytic reforming of model tar compounds [5]. Toluene and naphthalene were chosen as the model tar compound

since they represent the major stable aromatic products in the biomass tar. The effects of different parameters and catalysts were investigated in detail

## 2. Experimental setup

Fig.1 shows the overall schematic of the experimental setup. A laboratory scale flat GAD reactor was adopted as the plasma source. Nitrogen was used as the carrier gas in the reforming test. Model tar compounds toluene and naphthalene (C<sub>7</sub>H<sub>8</sub>, C<sub>10</sub>H<sub>8</sub>, purity >= 99%, Aldrich) were feed continuously by high-resolution syringe pumps (KDS Legato, 100) into a vaporization furnace heated to 300 °C, and then carried to the reactor by N<sub>2</sub> gas flow. For the plasma-catalysis system, the prepared catalyst was combined after the discharge region, leading to a plasma-assisted catalysis (PAC) system. The GAD reactor was supplied by a neon transformer with a maximum peak voltage of 10 kV and a frequency of 50 Hz. A cooling trap was placed at the exit of the plasma reactor to collect the condensable products in the effluent, which were analysed by a GC-MS (Agilent GC 7820A, MSD) and qualitatively identified. The gaseous products were analysed by a gas chromatography (Shimadzu, 2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

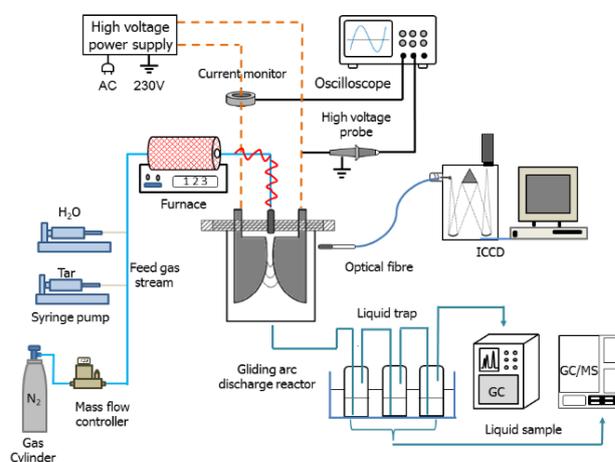


Fig.1. Schematic diagram of the experimental setup.

### 3. Steam reforming of toluene

The plasma conversion of toluene was carried out at a constant toluene flow rate of 4.8 ml/min and a discharge power of 43.5 W with and without steam, as shown in Fig. 2 [6]. Clearly, introducing steam into the plasma reaction significantly enhanced the toluene conversion from 5.4 % without steam to 41.6 % with steam, whilst the energy efficiency of the plasma process was increased by a factor of 8.

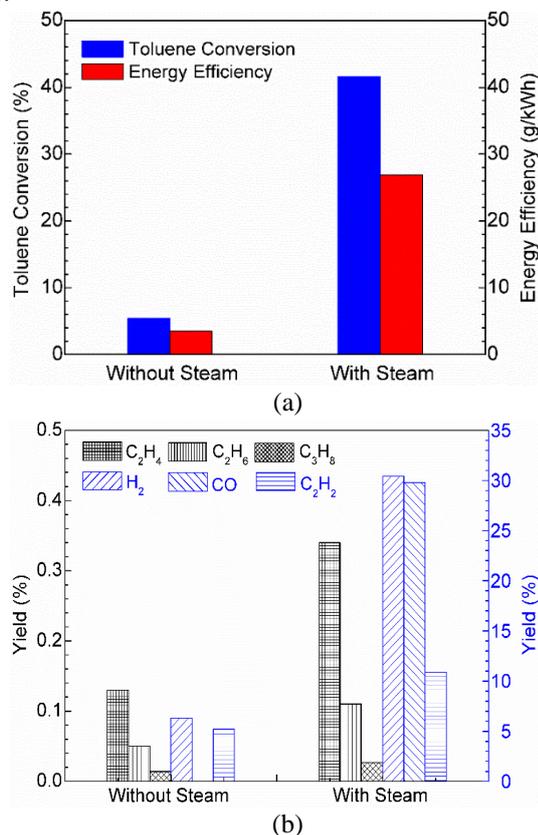


Fig. 2. Effect of steam on (a) toluene conversion and energy efficiency; (b) yields of primary gaseous products.

In addition, the presence of steam in the plasma conversion of toluene generated more gas products including H<sub>2</sub>, CO, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>. For instance, the yield of H<sub>2</sub> (6.3 %) was significantly increased by a factor of 5 when adding steam in this reaction. No CO was detected in the plasma toluene conversion without steam. However, a high yield of CO (29.8 %) was achieved in the plasma steam reforming of toluene, which suggests that water might play an important role in the stepwise oxidation reactions, eventually forming CO. It is also interesting to note that no CO<sub>2</sub> was detected in the gas products regardless of whether steam was used in the reaction, while CO<sub>2</sub> is a common by-product in the oxidation of toluene using air plasmas.

### 4. Steam reforming of mixture modal compounds

To assess the contribution of steam to the reduction of mixed tar compounds (toluene and naphthalene), the ratio of steam/carbon was varied between 0 and 3 to examine its

effect on the conversions of naphthalene and toluene at a total flow rate of 3.5 L/min and a discharge power of 59.4 W. As plotted in Fig. 3, the naphthalene conversion increased initially when increasing the steam/carbon ratio, reached a maximum of 63.0% at the steam/carbon ratio of 1. This value was significantly decreased when further increasing the ratio of S/C to 3. Similarly, the highest toluene conversion of 79.2% was obtained at an optimum steam/carbon ratio of 1.5, while changing the ratio of steam/carbon from 1.5 to 3 only slightly decreased the conversion of toluene. The formation of OH radicals when adding H<sub>2</sub>O to the GAD system, could create new reaction pathways for the step-wise oxidation of C<sub>10</sub>H<sub>8</sub>, C<sub>7</sub>H<sub>8</sub> and their fragments (R1 and R2), resulted in a boost of the destruction of tars in comparison to the plasma process with no steam. In the GAD plasma, OH radicals are mainly generated through water dissociation by electrons (R3 and R4) and excited nitrogen species (R5). The destruction of naphthalene and toluene can also be proceeded via the reaction with H radicals to form products such as styrene, xylene, and benzene.



where N<sub>2</sub><sup>\*</sup> represents excited N<sub>2</sub> species, which can be either N<sub>2</sub> metastable states N<sub>2</sub> (A<sup>3</sup>) or N<sub>2</sub> (a') [7].

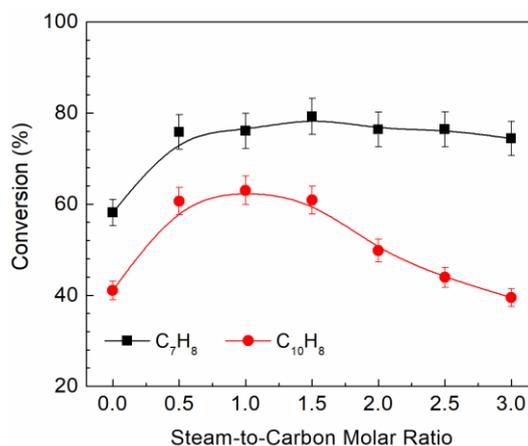
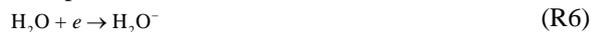


Fig.3. Influence of steam/carbon molar ratio on the conversion of naphthalene and toluene (C<sub>7</sub>H<sub>8</sub> content: 17.3 g/Nm<sup>3</sup>; C<sub>10</sub>H<sub>8</sub> content: 1.0 g/Nm<sup>3</sup>).

However, increasing steam content in the mixed stream did not always increase the conversion of naphthalene and toluene. Clearly, an optimal steam concentration can be found to reach the highest conversion of C<sub>10</sub>H<sub>8</sub> or C<sub>7</sub>H<sub>8</sub>. Although the presence of OH radicals could provide new reaction routes for tar cracking, electrons could also be consumed by water due to its electronegative characteristics (R6) especially at a higher steam content,

which in turn reduces the availability of electrons and reactive species for tar conversion.



The influence of  $\text{H}_2\text{O}$  on the destruction of  $\text{C}_{10}\text{H}_8$  or  $\text{C}_7\text{H}_8$  is thus dependent on the balance between these two opposite effects on the plasma reaction: i) enhanced tar conversion through additional oxidation routes due to the positive contribution of OH radicals and ii) reduced tar conversion resulted from the negative effect of electron attachment on water molecules.

#### 4. Plasma-catalytic reforming of modal tar compound

The plasma-catalytic reforming of biomass tar was investigated in a knife-shaped gliding arc discharge reactor at low temperatures and atmospheric pressure. The influence of different catalysts ( $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ , and  $\text{Ni-Co}/\gamma\text{-Al}_2\text{O}_3$ ) on the reaction performance of the plasma-catalytic reforming of toluene and naphthalene was evaluated. The catalyst pellets were placed below the tip of the electrodes shown in Fig. 1.

Fig. 4 shows the biomass tar conversion when using different catalysts. Obviously, toluene exhibits a remarkably higher conversion than naphthalene, indicating the toluene is easily destructible compared to naphthalene. This phenomenon should be related to the inherent molecular structure and stability of these molecules. The initiate reaction (H-abstraction) for tar destruction is more active in toluene due to the presence of methyl group in the molecule. The presence of the supported catalysts promote the conversion of tar. Integrating the 7.5Ni7.5Co catalyst into the GAD reactor exhibited the higher reaction performance than that using the 15Ni and 15Co catalysts. The highest conversion of toluene and naphthalene was 95.7% and 84.3%, respectively, in the presence of the 7.5Ni7.5Co catalyst, which were increased by 9.9% and 13.5% compared to these using the plasma-only process.

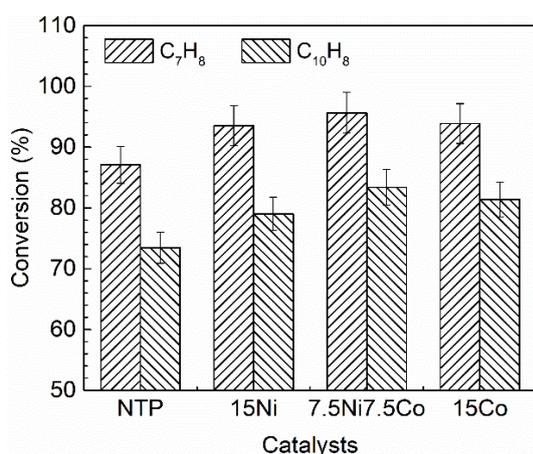


Fig.4. Effect of catalysts on the conversion of toluene and naphthalene ( $\text{C}_7\text{H}_8$  content:  $15.0 \text{ g}/\text{Nm}^3$ ;  $\text{C}_{10}\text{H}_8$  content:  $1.0 \text{ g}/\text{Nm}^3$ ; Discharge power: 75 W; Q: 3.5 L/min; S/C molar ratio: 1.5).

#### 5. Conclusions

In this study, plasma steam reforming of biomass tar model compounds were carried out in an AC gliding arc discharge reactor with and without catalysts. The results shown that adding steam into the plasma tar reforming system significantly improved the conversion of biomass tar, while increasing the formation of syngas and reducing the carbon deposition. Due to the electronegative characteristics of water molecule, an optimum steam/carbon molar ratio was observed for the highest conversion of the mixed biomass tar compounds. In addition, the introduction of alumina supported catalysts can further enhance the reaction performance and the type of the active metal in the supported catalysts also has a significant effect.

#### 6. Acknowledgements

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