Hybrid plasma-catalytic steam reforming of toluene as a biomass tar model compound over Ni/Al$_2$O$_3$ catalysts

S.Y. Liu [a], D.H. Mei [a], M.A. Nahil [b], S. Gadkari [c], S. Gu [c], P.T. Williams [b], X. Tu [a,*]

[a] Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool L69 3GJ, UK
[b] School of Chemical & Process Engineering, University of Leeds, Leeds LS2 9JT, UK
[c] School of Chemical and Process Engineering, University of Surrey, Surrey GU2 7XH, UK

ABSTRACT

In this study, plasma-catalytic steam reforming of toluene as a biomass tar model compound was carried out in a coaxial dielectric barrier discharge (DBD) plasma reactor. The effect of Ni/Al$_2$O$_3$ catalysts with different nickel loadings (5–20 wt%) on the plasma-catalytic gas cleaning process was evaluated in terms of toluene conversion, gas yield, by-products formation and energy efficiency of the plasma-catalytic process. Compared to the plasma reaction without a catalyst, the combination of DBD with the Ni/Al$_2$O$_3$ catalysts significantly enhanced the toluene conversion, hydrogen yield and energy efficiency of the hybrid plasma process, while significantly reduced the production of organic by-products. Increasing Ni loading of the catalyst improved the performance of the plasma-catalytic processing of toluene, with the highest toluene conversion of 52% and energy efficiency of 2.6 g/kWh when placing the 20 wt% Ni/Al$_2$O$_3$ catalyst in the plasma. The possible reaction pathways in the hybrid plasma-catalytic process were proposed through the combined analysis of both gas and liquid products.

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1. Introduction

Biomass has great potential to make a major contribution to the low carbon economy and reaching COP21 targets. Biomass gasification has been regarded as a key thermochemical route for the production of a higher value syngas from a renewable and CO$_2$-neutral source [1]. The product gas or synthesis gas (a mixture of H$_2$ and CO) produced from biomass gasification can be used for generating electricity and heat by direct combustion in internal engines, while high quality synthesis gas can also be used as an important chemical feedstock for the synthesis of a variety of valuable fuels and chemicals. Clearly, biomass can make a significant contribution to all three key energy sectors: transport, heat and electricity [2,3].

However, one of the major challenges in the biomass gasification process is contamination of the product syngas with tar, which is a complex mixture of condensable hydrocarbons with molecular weight higher than benzene, some of which are carcinogenic. The content of tar in the produced syngas from biomass gasification varies from 1 g/m^3 up to 100 g/m^3, depending on the operating conditions of the gasification process [4]. The production of tars in biomass gasification process leads to major process and syngas end-use problems, including tar blockages, plugging and corrosion in downstream fuel lines, filters, engine nozzles and turbines, and has been a major barrier for the

development and deployment of biomass gasification process [3,4]. Considerable efforts have been focused on the removal of tars in product gas from biomass gasification using different processes, including thermal cracking [5,6], physical separation [7] and catalytic reforming [3,8–10]. Thermal cracking of tars requires very high reaction temperature (>800 °C) and thus cause a high energy input. Physical separation of tars could reduce the efficiency of the overall process and has great potential to cause secondary pollution. Along with the requirement for high temperature in thermal catalytic reforming process, rapid deactivation of catalysts due to coke deposition is the major challenge in thermal-catalytic reforming process.

The least researched, yet predicted to be the most attractive and effective, is the plasma gas cleaning process. Non-thermal plasma has been demonstrated as an effective solution for the removal of organic gas pollutants (e.g. volatile organic compounds VOCs) and synthesis of chemicals and fuels [11]. In non-thermal plasmas, the produced electrons are highly energetic (1–10 eV) and can break most chemical bounds of inert molecules, producing reactive species including free radicals, excited atoms, ions and molecules for a variety of chemical reactions. In addition, high reaction and fast reaching of a steady state in a plasma process allows rapid switch on and off the plasma process compared to other thermal processes, which significantly enhances the overall energy efficiency and provides a promising route for plasma process supplied by renewable energy (e.g. wind power or solar power) to act as an efficient chemical energy storage localized or distributed system at peak grid times [12,13].

* Corresponding author.
E-mail address: xin.tu@liverpool.ac.uk (X. Tu).

A more effective use of plasma is to integrate plasma process with heterogeneous catalysis, combining the advantages of fast and low temperature reaction by non-thermal plasmas and selective synthesis from catalysis. The combined plasma-catalytic process has great potential to produce a synergy, which can low the activation energy of catalysts and enhance the conversion of reactants, the selectivity and yield of desirable products, and the efficiency of the plasma process [11,14]. This novel hybrid process has attracted significant interest for gas clean-up, methane activation, CO_2 conversion, synthesis of carbon nanomaterials and catalysts [15]. However, very limited work has been focused on the use of non-thermal plasmas for the removal of tars from the gasification of biomass or waste. To the best of our knowledge, no work has been dedicated to the investigation of hybrid plasma-catalytic process for the removal of tars from biomass gasification. So far, a range of catalysts have been evaluated in thermal-catalytic reforming of tars at high temperatures, such as calcined rocks, clay minerals, ferrous metal oxides, activated alumina and supported-metal catalysts (e.g. nickel, cobalt and other noble metals) [16]. Nickel catalysts mainly supported on alumina, have been extensively investigated for thermal catalytic tar reforming because of its high initial activity, abundance and low cost. However, catalyst deactivation due to coke deposition remains a major challenge in catalytic reforming of tars. Our previous works showed that the coupling of plasma with Ni/Al_2O_3 catalysts can significantly reduce carbon deposition in plasma-catalytic reforming of biogas compared to thermal catalytic reactions [17]. However, it is not clear how a catalyst (e.g. Ni/Al_2O_3) present in the plasma process affects the reforming of tars or a tar model compound at low temperatures. Furthermore, previous studies mainly investigated the effect of different operating parameters on the performance of the plasma tar removal process [18,19], whereas few analyzed the by-products and intermediates in the plasma reforming of tar. In addition, a detailed understanding of the underlying reaction pathways and mechanisms in the plasma processing of tars is still missing. It is of primary importance to analyze both the gas and condensed liquid products in the plasma-catalytic steam reforming process to get new insights into the reaction pathways, which would provide valuable information for the further optimization of the hybrid plasma-catalytic process.

The present study aimed to demonstrate the effectiveness of the hybrid plasma-catalytic process for the removal of a tar model compound and provide an insight of toluene destruction pathways in the plasma-catalytic process. In this work, an in-plasma catalysis (IPC) system based on a coaxial dielectric barrier discharge (DBD) reactor was developed for the steam reforming of toluene, a typical model tar compound representing a major stable aromatic product in the tars formed in high temperature biomass gasification processes. The effect of $Ni/\gamma-Al_2O_3$ catalysts with different Ni loadings (5 to 20 wt%) on the plasma-catalytic removal of toluene was investigated in terms of toluene conversion, energy efficiency of the plasma-catalytic process and the distribution of gas products. The plasma steam reforming process without a catalyst was also carried out for comparison. Moreover, the possible reaction pathways involved in the plasma reactions were proposed and discussed through combined quantitative and qualitative analysis of gas and liquid products.

2. Experimental

2.1. Catalyst preparation

The $Ni/\gamma-Al_2O_3$ catalysts with different Ni loadings (5, 10 and 20 wt%) were prepared by the wetness impregnation method. The appropriate weight of $\gamma-Al_2O_3$ (1 mm diameter beads) was added to the metal precursor solution and impregnated for 12 h. The above solution was dried at 100 °C until most of water was evaporated. The obtained samples were heated at 100 °C for 24 h, followed by the calcination at 750 °C for 3 h.

2.2. Experimental setup

The experiments were carried out in a coaxial DBD reactor (Fig. 1). A 100 mm-long stainless steel (SS) mesh was wrapped over a quartz tube with an inner diameter of 18 mm and outer diameter of 21 mm. A SS rod with a diameter of 14 mm was used as an inner electrode and placed in the axis of the quartz tube. As a result, the length of the discharge region was 100 mm with a discharge gap of 2 mm. The inner electrode was connected to a high voltage output and the outer electrode was grounded via an external capacitor C_{ext} (0.47 μF). The DBD reactor was connected to an AC high voltage power supply with a maximum peak voltage of 30 kV and a frequency of 5–20 kHz. In this work, the frequency was fixed at 9 kHz. The applied voltage was measured by a high voltage probe (Testec, TT-HVP 15 HF), while the voltage on the external capacitor was recorded by a voltage probe (Tektronix P5100) to obtain the charge generated in the discharge. All the electrical signals were recorded by a 4-channel digital oscilloscope (Tektronix MDO 3024). The Q-U Lissajous method was used to determine the discharge power (P) of the DBD reactor. A homemade online power measurement system was used to monitor and control the discharge power in real time [20].

A total of 0.5 g of $Ni/\gamma-Al_2O_3$ catalyst was packed into the plasma region along the bottom of the quartz tube, partially filling the discharge gap and held by quartz wood. This partial packing method has shown to effectively enhance the interactions between the plasma and catalyst in a DBD reactor and consequently promoted the plasma-catalytic chemical reactions in our previous studies [21]. Before the reaction, the catalysts were reduced in a H_2 plasma at a discharge power of 60 W and a flow rate of 50 mL/min for 1 h in the same DBD reactor. Then, argon was used as a carrier gas with a flow rate of 150 mL/min. Toluene (C_7H_8, purity ≥ 99%, Aldrich) solution and deionized water were injected into the preheated pipe by high-resolution syringe pumps (KDS Legato, 100) at a flow rate of 0.2 mL/h and 0.6 mL/h, respectively. The steam-to-carbon molar ratio (S/C ratio) was fixed at 2.5 throughout the experiment. The mixed stream was heated to 160 °C in a copper pipe with an inner diameter of 4 mm (40 cm in length) controlled by a temperature controller system, to produce a steady-state vapour before flowing into the plasma reactor.

2.3. Methods of analysis and the definition of parameters

The gas products were analyzed by a two-channel gas chromatography (Shimadzu, GC-2014) equipped with a flame ionization detector (FID) for the measurement of C_1-C_4 hydrocarbons and a thermal conductivity detector (TCD) for the analysis of H_2, CO, CO_2 and CH_4. During the reaction, an ice trap was placed at the exit of the DBD reactor to condense liquid products. The collected liquid samples were analyzed by a gas chromatography– mass spectrometry (GC–MS, Agilent GC 7820 A, MSD) and qualitatively identified using the mass spectral library from National Institutes for Standards and Technology (NIST) [22]. All the measurements were performed after running the plasma reaction for around 30 min when the plasma reaction reached a steady-state.

In the plasma reforming reaction, the conversion of toluene $X_{C_7H_8}$, was calculated as the moles of carbon in the carbon-containing gas products (CO_2, C_2H_2, C_2H_4, C_2H_6 and C_3H_8) to the carbon in the input toluene:

$$X_{C_7H_8}(\%) = \frac{\text{Moles of carbon in the produced gas}}{\text{Moles of carbon in the feed}} \times 100 \qquad (2)$$

The yield of the products was defined as follows:

$$Y_{H_2}(\%) = \frac{H_2 \text{ produced(mol/s)}}{4 \times C_7H_8 \text{ input (mol/s)} + H_2O \text{ input(mol/s)}} \times 100 \qquad (3)$$

$$Y_{CO_2}(\%) = \frac{CO_2 \text{ produced (mol/s)}}{7 \times C_7H_8 \text{ input (mol/s)}} \times 100 \qquad (4)$$