Article:

Liu, SY, Mei, DH, Nahil, MA et al. (2017) Hybrid plasma-catalytic steam reforming of toluene as a biomass tar model compound over Ni/Al_2O_3 catalysts. Fuel Processing Technology, 166. pp. 269-275. ISSN: 0378-3820

https://doi.org/10.1016/j.fuproc.2017.06.001

Hybrid plasma-catalytic steam reforming of toluene as biomass tar model compound over Ni/Al_2O_3 catalyst

Shiyun Liu[a], Danhua Mei[a], Mohamad A Nahil[b], Siddhath Gadkari[c], Sai Gu[c], Paul T. Williams[b] and Xin 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*

*** Corresponding Author**

Dr. Xin Tu
Department of Electrical Engineering and Electronics,
University of Liverpool,
Liverpool, L69 3GJ,
UK
Tel: +44-1517944513
E-mail: xin.tu@liverpool.ac.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) reactor. The effect of Ni/Al_2O_3 catalysts with different nickel loadings (5-20 wt. %) on the performance of the plasma-catalytic gas cleaning process was evaluated in terms of toluene conversion, yield of gas products, 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 catalysts significantly enhanced the toluene conversion, hydrogen yield and energy efficiency of the plasma process, whilst significantly reduced the formation of organic by-products. Increasing the 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_2O_3 catalyst in the plasma. The possible reaction pathways in the plasma-catalytic process were proposed through the combined analysis of both gas and liquid products.

Keywords: non-thermal plasma; dielectric barrier discharge; plasma-catalysis; biomass gasification; tar removal;

1. Introduction

Biomass has great potential to make a major contribution to low carbon pathways in the UK and globally, contributing to the UK's goal of reducing its greenhouse gas emissions by 80% by 2050 and the international mitigation target of a maximum 2 degrees Celsius temperature rise. The gasification of biomass represents a major thermochemical route to produce a high energy value syngas from a source which is renewable and CO_2-neutral [1]. The product gas or synthesis gas (a mixture of H_2 and CO) produced from gasification can be used for the generation of electricity and heat by direct combustion in internal combustion engines, while high quality synthesis gas can also be used as an important chemical feedstock for the synthesis of a wide range of valuable fuels and chemicals. Clearly, biomass can make a significant contribution to all three key energy sectors: electricity, heat and transport [2].

However, one of the major challenges in the biomass gasification process is contamination of the product syngas with tar. Tar is a complex mixture of condensable hydrocarbons with molecular weight higher than benzene, some of which are carcinogenic. The concentration 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 [3] . 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, and had been a major barrier for the development and deployment of biomass gasification process [1-3]

Considerable efforts have been devoted to the removal of tars in product gas from biomass gasification using different processes, including thermal cracking [4, 5], physical separation [6] and catalytic reforming [7-10]. Thermal cracking of tars requires very high reaction temperature (>800 ºC) 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 steam reforming process, rapid deactivation of catalysts due to coke deposition is another major challenge in thermal-catalytic process.

So far many types of catalysts have been reported for tar conversion, such as calcined rocks, clay minerals, ferrous metal oxides, activated alumina and supported-metal catalysts (e.g. nickel, cobalt and other noble metals) [11]. Nickel 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 [12, 13]. However, the metal catalysts may suffer from deactivation due to sintering, coke deposition and poisoning with sulphur and chlorine. Coke deposition is one of the most serious issues in catalytic reforming of hydrocarbons, especially for aromatic hydrocarbons [3].

The least researched, yet predicted to be the most attractive and effective, is the plasma gas cleaning process. Non-thermal plasma has been demonstrated to be effective for the removal of low concentration gas pollutants (e.g. volatile organic compounds VOCs) and the synthesis of fuels and chemicals at atmospheric pressure and low temperatures [14]. In non-thermal plasmas, there is a significant difference between the electron temperature and the temperature of heavy particles, known as the non-equilibrium character. The overall gas kinetic temperature in such a plasma can be as low as room temperature, while the produced electrons are highly energetic (1-10 eV) and can break most chemical bounds, producing a cascade of chemically reactive species including free radicals, excited atoms, ions and molecules for the initiation and propagation of chemical reactions. In addition, high reaction rate and fast attainment of steady state in a plasma process allows rapid start-up and shutdown of the plasma process compared to other thermal processes, which significantly reduces the overall energy cost and offers a promising route for plasma process powered by renewable energy to act as an efficient chemical energy storage localized or distributed system at peak grid times [15, 16].

A more effective use of plasma is possible by exploiting its inherent synergetic potential through the combination of plasma with heterogeneous catalysts, which can activate the catalysts at low temperatures and improve their activity and stability, resulting in the remarkable enhancement of reactant conversion, selectivity, and yield of target products, as well as the energy efficiency of the plasma-catalytic process [14, 17]. This novel hybrid process has attracted tremendous interest for environmental clean-up, methane activation, CO_2 conversion, synthesis of carbon nanomaterials and catalysts [18]. However, very limited work has been focused on the use of non-thermal plasma 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 cleaning of tars at low temperatures. A wide range of catalysts have been evaluated in thermal-catalytic reforming of tars. These include calcined rocks, clay minerals, ferrous metal oxides, activated alumina and supported-metal catalysts (e.g. nickel, cobalt and other noble metals). However, it is not clear how a catalyst present in the plasma process affects the reforming of tars or a tar model compound at low temperatures. Furthermore, most of previous studies investigated the effect of different operating parameters on the performance of the plasma tar removal process [19, 20], whereas few analyzed the by-products and intermediates in the plasma reforming of tar to better understand the underlying reaction pathways and mechanisms in the plasma process.

Largely, studies in plasma-catalytic processes focused on the conversion efficiency and energy consumption, by comparing the input and output concentration of target compounds using different operating parameters [21]. However, a detailed understanding of the underlying reaction pathways and mechanisms in the plasma processing of tars is still missing. It is of primary important 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 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/γ-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.

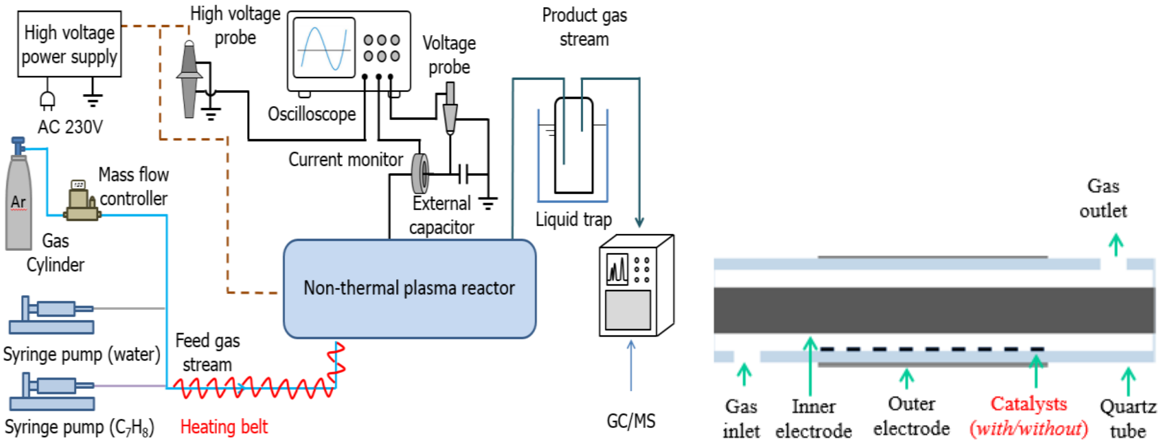
2. Experimental

2.1. Catalyst preparation

The Ni/γ-Al_2O_3 catalysts with different Ni loadings (5, 10 and 20 wt. %) were prepared by the wetness impregnation method using Ni $(NO_3)_2$·$6H_2O$ as the metal precursor. The appropriate weight of γ-Al_2O_3 (1 mm diameter beads) was added to the metal precursor solution and impregnated for 12 hours. 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 experiment was carried out in a coaxial DBD reactor, as shown in Fig.1. A 100 mm-long stainless steel mesh was wrapped over a quartz tube with an inner diameter of 18 mm and outer diameter of 21 mm. A stainless steel 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 [22].



(a) (b)

Fig.1 Schematic diagram of the (a) experimental setup; (b) DBD reactor

A total of 0.5 g of Ni/γ-Al_2O_3 catalyst was packed into the discharge region along the bottom of the quartz tube, partially filling the discharge gap and held by quartz wood. This partial packing method has been 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 [23]. Prior to the plasma-catalytic reaction, the catalysts were in situ reduced in a pure hydrogen discharge 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 fed into the reactor as a carrier gas at 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 then heated to 160 ℃ in a copper pipe with an inner diameter of 4 mm (40 cm in length) equipped with a temperature controller system, to generate a steady-state vapour before flowing into the DBD 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 thermal conductivity detector (TCD) for the detection of H_2, CO, CO_2 and CH_4 and a flame ionization detector (FID) for the measurement of C_2-C_4 hydrocarbons. During the reaction, an ice trap was placed at the exit of the plasma reactor in order to condense any 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) [24]. Measurements were carried out after running the plasma reaction for about 30 min when a steady-state was reached.

For the plasma-catalytic steam reforming of toluene, the toluene conversion X_{C7H8}, was calculated as the ratio of the 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:

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

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

$$Y_{C_xH_y}(\%)=\frac{x\times C_xH_y\ \text{produced}\ (\text{mol/s})}{7\times C_7H_8\ \text{input}\ (\text{mol/s})}\times 100 \qquad (5)$$

The energy efficiency E of the plasma process for toluene conversion was defined as the mass of converted toluene per unit of discharge power.

$$E(\text{g/kWh})=\frac{\text{mass of converted } C_7H_8\ (\text{g/h})}{\text{Discharg power (kW)}} \qquad (6)$$

3. Results and discussion

3.1. Plasma-catalytic steam reforming of toluene

Steam reforming of toluene was carried out in the DBD reactor with and without the Ni catalysts, as shown in Fig 2. Compared with the plasma reaction without a catalyst, the presence of the 10 wt.% Ni/γ-Al_2O_3 catalyst in the plasma significantly enhanced the carbon conversion by around 20% (from 39.5 % to 47.1%), whilst the energy efficiency of the process was increased by 18.0 %. Tao et al reported similar findings in a plasma-catalytic steam reforming of high content toluene (~200 g/Nm^3) over a 5 wt.% Ni/SiO_2 catalyst in a DC plasma reactor [25]. However, extra thermal heating (at 773 K) was used to heat the plasma-catalytic process in their experiments. It was extremely difficult to identify whether the effect of the Ni/SiO_2

catalyst on the enhanced toluene conversion was driven by the plasma or thermal heating or both.

In this study, the Ni catalysts were placed along the bottom of the discharge region in the DBD reactor, while the plasma-catalytic steam reforming reaction was carried out at low temperatures (<200 °C) without any external heating. Therefore, heating effect from the plasma on the catalyst activation and plasma-catalytic reaction was negligible. In addition, this partial packing method could still generate a strong filamentary discharge in the DBD reactor due to the presence of large void fraction in the discharge gap, resulted in strong physical and chemical interactions between the discharge and Ni catalysts [23]. Moreover, when a catalyst is placed in the discharge, polarisation of the catalyst leads to the charge accumulation on the catalyst surface, increasing the local or average electrical field and therefore the number of energetic electrons and reactive species, characterized by the formation of intensified microdischarges around the contact points between the catalyst pellets and those between the catalyst pellet and quartz wall [26, 27]. Previous studies demonstrated that placing a 10 wt.% Ni/γ-Al_2O_3 along the bottom of a DBD reactor enhanced the intensity of current pulses in the plasma-catalytic dry reforming of CH_4 [23], while the mean electric field and mean electron energy of the DBD were enhanced by 9-11% when $BaTiO_3$ and TiO_2 photocatalysts were partially packed in the DBD reactor in the plasma-catalytic conversion of CO_2 [17]. These physical effects have been shown to enhance the conversion of reactants in plasma-catalytic chemical reactions. Clearly, in this study, the enhanced toluene conversion and energy efficiency in the plasma-catalytic steam reforming of toluene can be partly attributed to the physical effects induced by the presence of the Ni catalyst pellets in the plasma.

In addition, increasing the Ni loading from 5% to 20% increased the conversion of toluene and energy efficiency of the plasma-catalytic process, as shown in Fig. 2. For example, the combination of the DBD with the 20 wt.% Ni/γ-Al_2O_3 catalyst showed the highest toluene conversion of ~51.9 % and energy efficiency of 2.6 g/kWh. In the plasma-catalytic reforming reaction at low temperatures, increasing the Ni loading over γ-Al_2O_3 could effectively enhance the catalyst activity owing to the formation of more active Ni sites on the catalyst surface. Aziznia et al also showed that higher conversions of CO_2 and CH_4 were obtained in the low temperature plasma-catalytic dry reforming of CH_4 when a 20 wt.% Ni/γ-Al_2O_3 catalyst was placed in a corona discharge compared with Ni/γ-Al_2O_3 catalysts with a lower Ni loading (5 wt.% and 10 wt.%) [28]. Similar phenomenon was also observed in thermal catalytic chemical reactions. Wang reported that the removal efficiency of tar and hydrogen production increased with increasing Ni loading from 5 wt.% to 20 wt.% [29]. Aziz et al investigated the effect of Ni loading (1-10 wt. %) on CO_2 methanation over Ni/mesoporous silica nanoparticles (MSN) catalysts at different reaction temperatures [30]. They found that increasing the Ni loading enhanced the catalytic activity for CO_2 methanation at low temperatures (<623 K). However, the 10 wt. % Ni/MSN catalyst showed a similar activity as the 5 wt. % Ni/MSN catalyst in CO_2 methanation at high temperatures (>673 K). Similarly, Liu et at reported that there was an optimum Ni loading of 10 wt.% of activated carbon (AC) supported Ni catalysts in thermal catalytic steam reforming of toluene at 200 ^{o}C. They found that further increasing the Ni loading to 15 wt.% increased the nickel particle size and lowered the nickel particle dispersion on the catalyst surface, resulted in the aggregation of Ni particles and increased carbon deposition, and consequently decreased the conversion of toluene. Compared to relatively high temperature thermal catalytic reactions, placing supported metal catalysts in low temperature plasma process can effectively reduce the metal particle size and enhance the metal dispersion on the catalyst surface due to low temperature effect [31]. In this experiment, low temperature plasma reaction is believed to avoid the aggregation of Ni particles on the catalyst surface but increase the catalytic activity for toluene conversion when increasing the Ni loading from 5 wt. % to 20 wt. %. In addition, the presence of conductive Ni active sites on the catalyst also contribute to the spread and expansion of the discharge over the catalyst surface, which may be favourable to the expansion of discharge volume and intensity in the DBD-catalytic process [32].

These results clearly demonstrated that the catalytic effect (e.g. catalyst activity) also plays an important role in enhancing the conversion of toluene and energy efficiency of the plasma-catalytic process besides the physical effects. In the hybrid plasma-catalytic process, the adsorption of reactants on the catalyst surface could be enhanced[26],which would prolong the retention time of toluene and its intermediates in the plasma and therefore improve the collision probability between these pollutants and chemically reactive species, leading to a higher toluene conversion in the plasma-catalytic process.

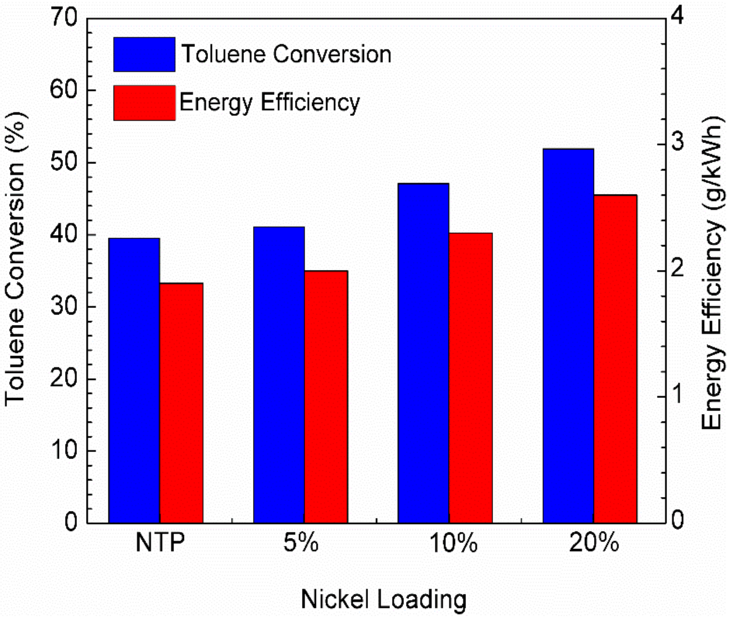


Fig. 2. Toluene conversion and energy efficiency of the plasma process with and without catalysts (toluene concentrate: 17.7 g/Nm^3, discharge power: 35 W, S/C ratio: 2.5, catalyst: 10 wt.% Ni/γ-Al_2O_3)

3.2. Gaseous products

H_2, CO_2 and CH_4 were found as the main gas products in the plasma steam reforming of toluene with and without the Ni catalyst. A small amount of hydrocarbons (C_2H_2, C_2H_4, C_2H_6, C_3H_8 and C_4H_{10}) were also detected. Clearly, the presence of the Ni catalysts in the DBD reactor enhanced the production of H_2 and CO_2, as shown in Fig. 3. Increasing the Ni loading from 5 to 20 wt.% steadily increased the yield of H_2 and CO_2 by 15% and 16%, respectively. It is worth to note that no CO was detected in the gas products. The occurrence of water gas shift reaction (R1) might be the major reason to inhibit the generation of CO in the steam reforming of toluene in the DBD. Moreover, the presence of reactive oxide species (e.g. OH, O radicals) through the dissociation of water by energetic electrons and metastable argon might be able to further oxidize CO (R4 and R5), toluene and its intermediates into CO_2. This plasma reaction might be considered as an attractive hydrogen production process without CO formation suitable for fuel cell applications.

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad \text{(R1)}$$

$$H_2O + e \rightarrow H^- + OH \qquad \text{(R2)}$$

$$H_2O + e \rightarrow 2H + O^- \qquad \text{(R3)}$$

$$OH + CO \rightarrow CO_2 + H \qquad \text{(R4)}$$

$$O + CO \rightarrow CO_2 \qquad \text{(R5)}$$

As shown in Fig. 3, the yield of CH_4 was nearly constant (~10%) when changing the Ni loading, whereas the yield of C_3-C_4 hydrocarbons (less than 1.6 %) increased by increasing the Ni content. Compared to the plasma reforming without a catalyst, placing the 5 wt. % Ni/γ-Al_2O_3 catalyst in the DBD reactor almost did not change the production of C_2H_2 and C_2H_6. However, increasing the Ni loading from 5 to 20 wt. % enhanced the yield of C_2H_2 and C_2H_6. The highest C_2H_2 yield of 5.2% was achieved when the 20 wt.% Ni/γ-Al_2O_3 catalyst was placed in the plasma steam reforming of toluene.

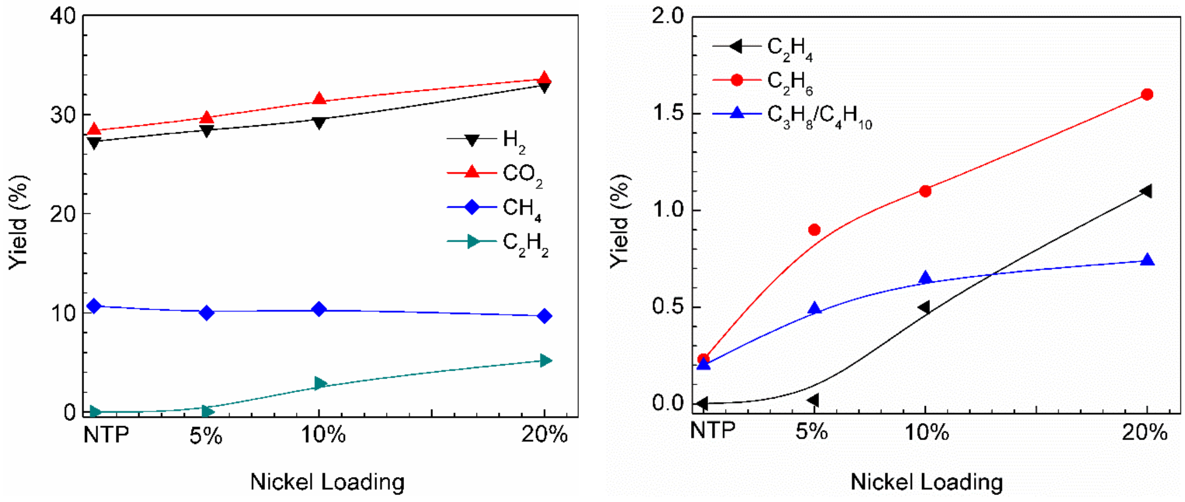


Fig. 3. The effect of Ni loading on the yield of gaseous products (toluene concentrate: 17.7 g/Nm^3, discharge power: 35 W, S/C: 2.5)

3.3. Formation of condensed by-products

Fig. 4 shows the GC-MS chromatogram of condensed by-products collected in the plasma steam reforming of toluene with and without the catalyst. In the plasma reaction without a catalyst, 11 types of organic by-products were detected, including major compounds such as benzene, phenol and (butoxymethyl)-benzene. Additionally, aliphatic compounds such as methyl ester, diol, octadecadienoic acid and the linear compounds 5, 7-Dodecadiyn-1, 12-diol were also detected, which could be generated from the cleavage of toluene ring, and the recombination and hydrogenation of the resulting fragments of intermediates. The presence of the 5 wt.% $Ni/\gamma\text{-}Al_2O_3$ catalyst in the plasma process significantly inhibited the formation of organic by-products. As shown in Fig. 4(b), only six types of condensed compounds were detected, among which phenol, 2,4-Hexadien-1-ol and (butoxymethyl)-benzene were identified as the major organic by-products. It is worth noting that the amount of phenol and (butoxymethyl)-benzene formed in the plasma-catalytic reforming reaction was several orders of magnitude lower than those generated in the plasma reaction without the Ni catalyst. These results clearly demonstrated that the coupling of the DBD and the Ni/γ-Al_2O_3 catalyst promoted the conversion of toluene into gas products (e.g. H_2), whilst significantly minimized the formation of undesirable organic by-products (Fig. 4).

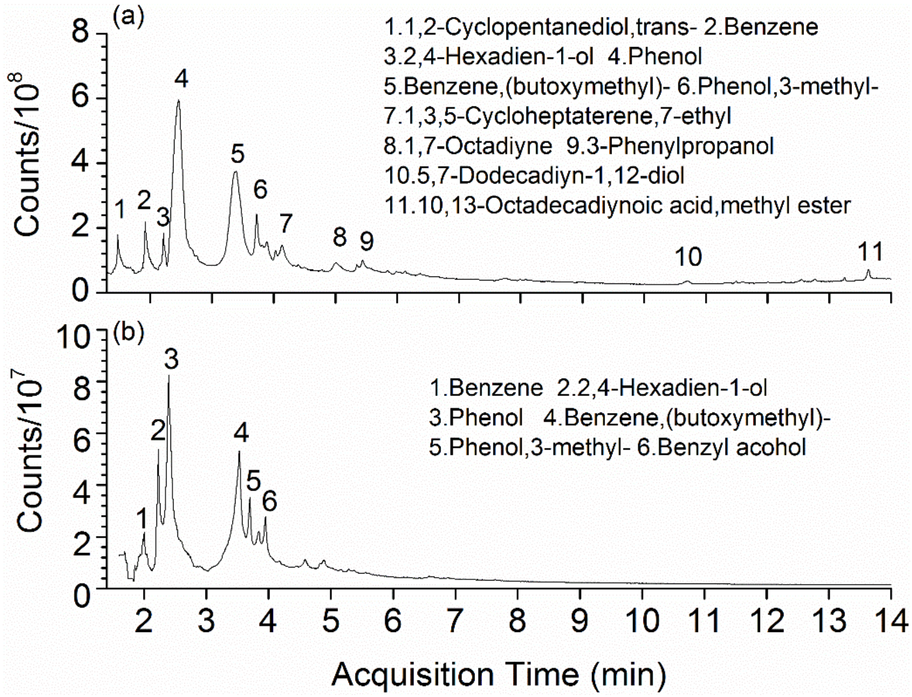


Fig. 4. GC-MS chromatogram of condensed by-products collected in the plasma steam reforming of toluene (a) without a catalyst, and (b) with the 5 wt. % Ni/γ-Al_2O_3 catalyst (toluene concentration: 17.7 g/Nm^3, discharge power: 35 W, S/C: 2.5, catalyst: 0.5g)

3.4. Reaction mechanisms and pathways of toluene destruction

The reaction mechanisms involved in the destruction of low concentration toluene (50 -500 ppm) as a model VOC in air or nitrogen plasmas without a catalyst have been investigated and proposed in previous studies [21, 33]. However, very limited work has been focused on the investigation of the reaction mechanisms and pathways in the plasma steam reforming of toluene as a model tar compound, especially in the presence of a catalyst. Compared to the removal of toluene as a model VOC, the reaction pathways present in the plasma steam reforming of toluene could be different due to the presence of high content toluene and steam. To get new insights into the possible reaction routes in this plasma process, the analysis of both gaseous and condensed liquid by-products were carried out in the plasma reaction with and without the Ni catalyst. It is well known that only gas-phase reactions are involved in the plasma steam reforming of toluene in the absence of a catalyst. However, the presence of the Ni catalyst in the plasma makes the reaction more complicated as plasma driven surface reactions occur besides the gas-phase reactions.

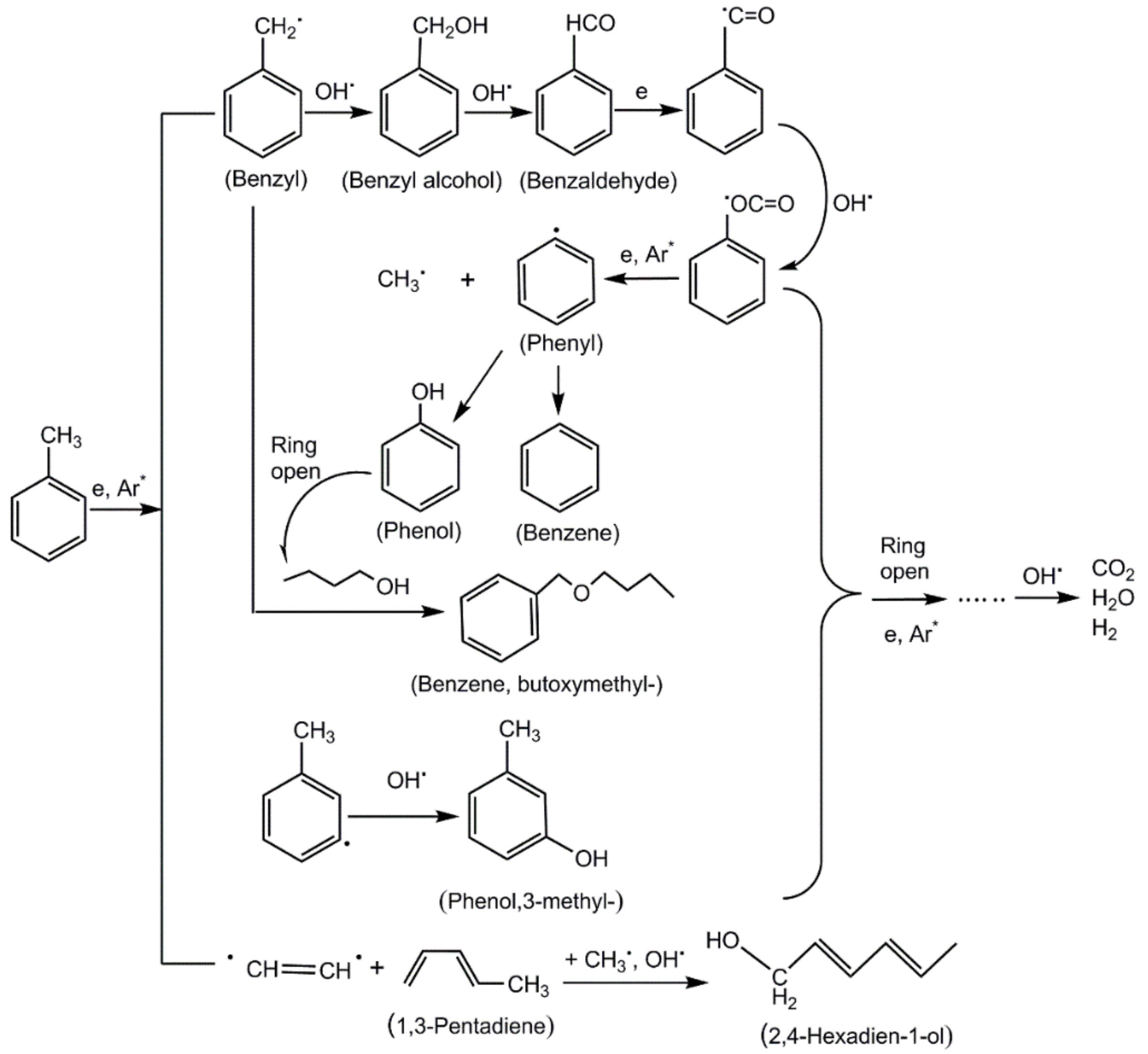
The destruction of toluene as a model tar compound in the argon DBD can be initiated through two major reaction routes: (i) direct electron impact dissociation of toluene and (ii) reaction with chemically reactive species including OH and Ar metastable species. The ionization of Ar requires a much higher electron energy (15.76 eV) compared to the excitation of Ar to its metastable states Ar^* (e.g. 11.55 eV). Therefore, in the Ar DBD, Ar is more likely to be excited to its metstable states rather than being ionized [34]. Previous studies have shown that metastable Ar species play an important role in initiating chemical reactions [35]. In the presence of steam in the plasma reaction, OH radicals can be produced from the dissociation of water by electrons and Ar*. The generated OH radicals can oxidize toluene and its intermediates, opening a new reaction route for the conversion of toluene, resulting in the enhanced conversion and energy efficiency of the plasma process [36].

Different bond energies of chemical bonds in toluene determine the reaction pathways involved in the plasma conversion of toluene. The dissociation energy of C-H bond in methyl is 3.7 eV, which is smaller than that of C-H bond in aromatic ring (4.3 eV), C-C bond between methyl group and aromatic ring (4.4 eV), C-C bond (5.0-5.3 eV) and C=C bond in aromatic ring (5.5 eV). Therefore, the primary reaction pathway of toluene decomposition could be the H-abstraction from methyl group by energetic electrons or reactive species such as Ar* and OH

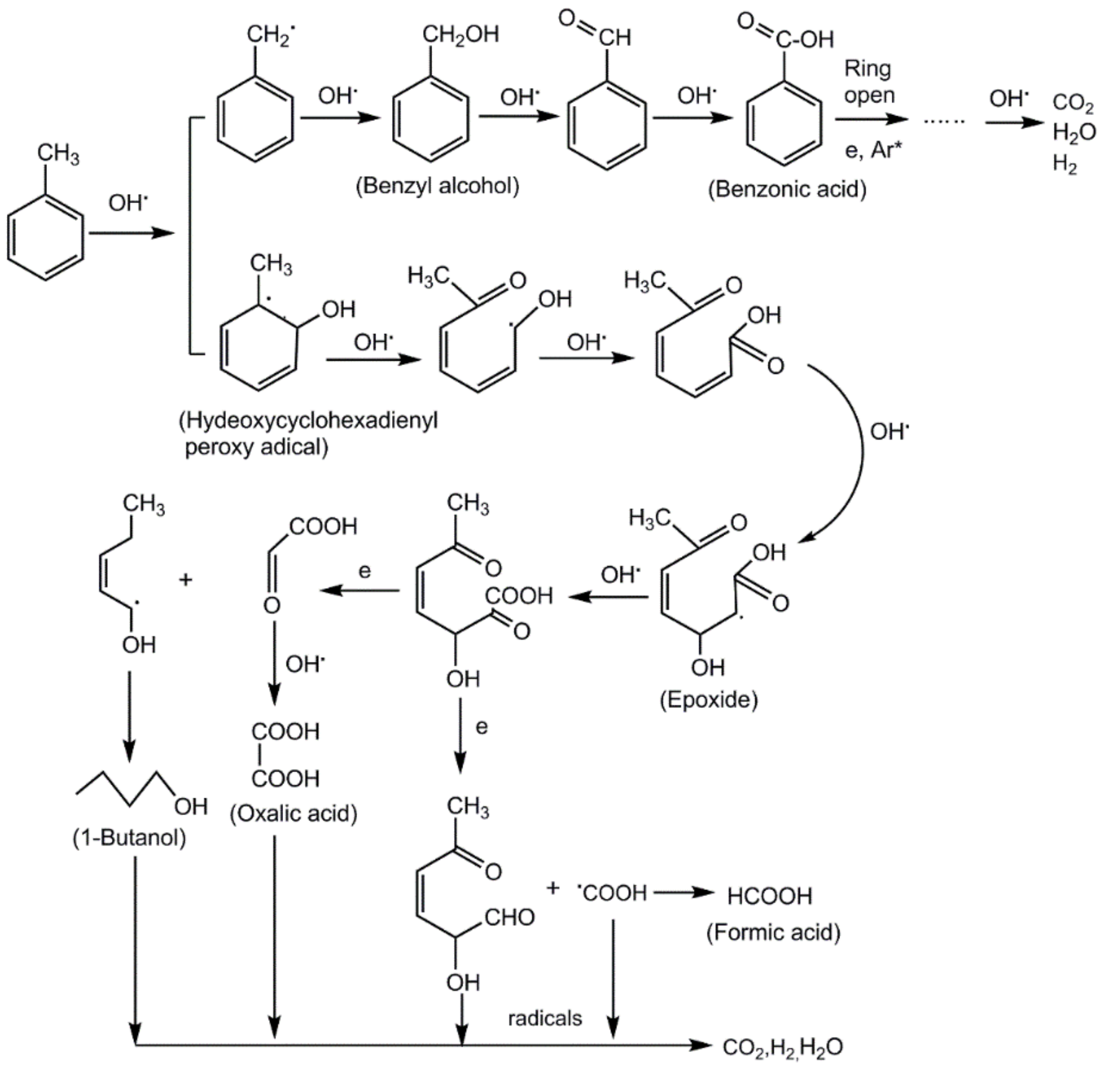
[37]. The H-abstraction from the methyl group forms a benzyl radical, which could further react with OH to generate benzyl alcohol. The formed benzyl alcohol can be converted to benzaldehyde, followed by further reactions with electrons and reactive species to form a phenyl radical [38]. In addition, the C-C bond between methyl and aromatic ring and C-H bond in the aromatic ring can be broken through the reactions with energetic electrons and metastable Ar species, generating phenyl, methyl, and toluene radicals [21]. As shown in Fig 5 (a), the recombination of phenyl with H and OH radicals could produce benzene and phenol, respectively, while adding OH to the aromatic ring of toluene radicals produces 3-methyl phenol, as identified by GC-MS. Moreover, ring opening and cracking of phenol via electron impact dissociation forms butyl alcohol, which then reacts with benzyl to generate benzene, (butoxymethyl). These aromatic intermediates can be further ruptured by electrons and Ar^* species to form ring-opening by-products and then oxidized by OH to end-products such as CO_2 and H_2O.

Toluene can also be decomposed by the cleavage of benzene ring through collisions with reactive species, e.g. OH radicals, producing hydroxycyclohexadienyl type peroxy radicals (Fig 5(b)), which has been confirmed in the previous modeling and experimental studies [38-40]. This unstable reactive compound can form a peroxide bridge radical, a precursor for the formation carbonyl and epoxide [40]. The carbonyl reaction route opens the benzene ring of toluene via a series of oxidation by OH radicals to form a relatively stable epoxide, which can be further decomposed by electrons or reactive species, forming substances with small molecular mass, such as oxalic acid and acetic acid.

The presence of the Ni catalysts in the plasma steam reforming of toluene enhanced the production of most gas products, whilst significantly reduced the formation of condensed organic by-products. These findings suggest that the combination of the plasma with the Ni catalysts shifted the primary reaction pathways of toluene destruction from the dehydrogenation or oxygenation of methyl group to direct cleavage of toluene ring, which can be evidenced by the enhanced yield of hydrogen and C_2H_2. Previous experimental and theoretical studies showed that acetylene was most likely formed by rupturing the toluene ring through the collisions with electrons and Ar^* species [41]. Recently, Zhu et al. also reported that high energetic electrons could breakdown toluene ring, forming acetylene and methyl-cyclobutadiene in the plasma decomposition of toluene as a tar surrogate using a rotating gliding arc discharge [42]. In this work, the detected C_5H_6 might be 1, 3-pentadiene, which sequentially reacted with methyl and OH radicals to form linear hydrocarbons such as 2, 4-hexadien-1-ol. In the hybrid plasma-catalytic reforming of toluene, plasma-assisted surface reactions also contributed to the enhanced reaction performance. In our experiment, the Ni catalyst pellets were placed along the button of the quartz tube in the discharge region and can directly interact with the plasma. Partial packing of the Ni catalyst pellets in the DBD still formed predominant micro-discharges across the electrode gap and induced strong interactions between the plasma and Ni catalyst, which is favourable for the plasma induced surface reactions on the surface of the Ni catalyst [23]. In this plasma-catalysis configuration, both toluene and intermediates from the gas phase reactions can be adsorbed onto the surface of the Ni catalyst. Short-lived reactive species (e.g. O, OH) initially generated close to or on the catalyst surface can also be involved in the surface reactions. The excited species generated in the plasma might promote the adsorption of toluene and intermediates onto the catalyst surface [43]. The residence time of toluene and intermediates in the plasma reaction region could be prolonged due to the catalyst effect. The enhanced adsorption process increases the collisions of toluene molecules with energetic species, leading to an acceleration of the plasma chemical reactions, both in gas phase and on the catalyst surface. The adsorbed species could also react with oxidative radicals, forming intermediates such as benzoic acid, before finally being oxidized to end-products such as CO_2 and H_2O.



(a)



(b)

Fig. 5. Possible reaction pathways for toluene destruction initiated by (a) energetic electrons and Ar^*, and (b) OH radicals

4. Conclusion

In this work, a coaxial DBD plasma reactor was developed for the hybrid plasma-catalytic steam reforming of toluene as a model tar compound from biomass gasification. Ni catalyst was placed in the plasma reaction region to induce strong interactions between the plasma and catalyst. Compared to the plasma reaction without a catalyst, the coupling of the plasma with the Ni/Al_2O_3 catalysts enhanced the conversion of toluene and H_2 yield, whilst significantly suppressed the formation of undesirable aromatic organic by-products. Nickel loading was found as a critical parameter affecting the performance of the plasma-catalytic reaction. Increasing the Ni content of the Ni/γ-Al_2O_3 catalyst from 5 wt. % to 20 wt. % considerably enhanced the toluene conversion, the yield of H_2, C_2H_2 and C_2H_6 and the energy efficiency of the hybrid process. The enhanced performance of the hybrid process can be attributed to both the gas phase reactions and plasma-assisted surface reactions. Based on the analysis of the gas products and liquid organic by-products, the possible reaction mechanisms and pathways involved in the plasma-catalysis reforming of toluene were proposed and discussed.

Acknowledgement

The support of this work by the EPSRC SUPERGEN Bioenergy Challenge II Programme (EP/M013162/1) and EPSRC Impact Acceleration Account are gratefully acknowledged.

Reference

1. Chen, G., et al., Biomass gasification integrated with pyrolysis in a circulating fluidised bed. Solar Energy, 2004. **76**(1-3): p. 345-349.
2. Hanne, R., et al., Thermal plasma-sprayed nickel catalysts in the clean-up of biomass gasification gas. Fuel, 2011. **90**(3): p. 1076-1089.
3. Anis, S. and Z.A. Zainal, Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review. Renewable and Sustainable Energy Reviews, 2011. **15**(5): p. 2355-2377.
4. Ni, M., et al., An overview of hydrogen production from biomass. Fuel Processing Technology, 2006. **87**(5): p. 461-472.
5. Fagbemi, L., L. Khezami, and R. Capart, Pyrolysis products from different biomasses: application to the thermal cracking of tar. Appl Energy, 2001. **69**(4): p. 293-306.
6. Pathak, B.S., et al., Design and development of sand bed filter for upgrading producer gas to IC engine quality fuel. Internaltional Energy Journal 2007. **8**: p. 15-20.
7. Devi, L., et al., Olivine as tar removal catalyst for biomass gasifiers: Catalyst characterization. Applied Catalysis a-General, 2005. **294**(1): p. 68-79.
8. Kong, M., et al., Influence of supports on catalytic behavior of nickel catalysts in carbon dioxide reforming of toluene as a model compound of tar from biomass gasification. Bioresource Technology, 2011. **102**(2): p. 2004-2008.
9. Noichi, H., A. Uddin, and E. Sasaoka, Steam reforming of naphthalene as model biomass tar over iron–aluminum and iron–zirconium oxide catalyst catalysts. Fuel Processing Technology, 2010. **91**(11): p. 1609-1616.
10. Świerczyński, D., et al., Steam reforming of tar from a biomass gasification process over Ni/olivine catalyst using toluene as a model compound. Applied Catalysis B: Environmental, 2007. **74**(3-4): p. 211-222.

11. Li, D., et al., Metal catalysts for steam reforming of tar derived from the gasification of lignocellulosic biomass. Bioresour Technol, 2015. **178**: p. 53-64.

12. Josuinkas, F.M., et al., Steam reforming of model gasification tar compounds over nickel catalysts prepared from hydrotalcite precursors. Fuel Processing Technology, 2014. **121**: p. 76-82.

13. Ashok, J. and S. Kawi, Nickel-Iron Alloy Supported over Iron-Alumina Catalysts for Steam Reforming of Biomass Tar Model Compound. Acs Catalysis, 2014. **4**(1): p. 289-301.

14. Zhu, X., et al., Plasma-catalytic removal of formaldehyde over Cu–Ce catalysts in a dielectric barrier discharge reactor. Applied Catalysis B: Environmental, 2015. **170-171**: p. 293-300.

15. Liu, S.Y., et al., Nonoxidative Conversion of Methane in a Dielectric Barrier Discharge Reactor: Prediction of Reaction Performance Based on Neural Network Model. The Journal of Physical Chemistry C, 2014. **118**(20): p. 10686-10693.

16. Zhu, X., et al., Plasma-catalytic removal of a low concentration of acetone in humid conditions. Rsc Advances, 2014. **4**(71): p. 37796-37805.

17. Mei, D., et al., Plasma-photocatalytic conversion of CO2 at low temperatures: Understanding the synergistic effect of plasma-catalysis. Applied Catalysis B: Environmental, 2016. **182**: p. 525-532.

18. Whitehead, J.C., Plasma catalysis: A solution for environmental problems. Pure and Applied Chemistry, 2010. **82**(6).

19. Nair, S.A., et al., Tar removal from biomass-derived fuel gas by pulsed corona discharges. Fuel Processing Technology, 2003. **84**(1-3): p. 161-173.

20. Eliott, R.M., et al., Tar Reforming under a Microwave Plasma Torch. Energy & Fuels, 2013. **27**(2): p. 1174-1181.

21. Huang, H.B., et al., Byproducts and pathways of toluene destruction via plasma-catalysis. Journal of Molecular Catalysis a-Chemical, 2011. **336**(1-2): p. 87-93.

22. Mei, D., et al., Plasma-assisted conversion of CO2in a dielectric barrier discharge reactor: understanding the effect of packing materials. Plasma Sources Science and Technology, 2015. **24**(1): p. 015011.

23. Tu, X. and J.C. Whitehead, Plasma-catalytic dry reforming of methane in an atmospheric dielectric barrier discharge: Understanding the synergistic effect at low temperature. Applied Catalysis B: Environmental, 2012. **125**: p. 439-448.

24. Manion, J.A., et al., NIST Chemical Kinetics Database, NIST Standard Reference Database 17. 2015: Gaithersburg, Maryland.

25. Tao, K., et al., Plasma enhanced catalytic reforming of biomass tar model compound to syngas. Fuel, 2013. **104**: p. 53-57.

26. Neyts, E.C. and B. A, Understanding plasma catalysis through modelling and simulation-a review. Journal of Physics D: Applied Physics, 2014. **47**(22): p. 224010.

27. Istadi and N. Amin, Co-generation of synthesis gas and C2+ hydrocarbons from methane and carbon dioxide in a hybrid catalytic-plasma reactor: A review. Fuel, 2006. **85**(5-6): p. 577-592.

28. Aziznia, A., et al., Comparison of dry reforming of methane in low temperature hybrid plasma-catalytic corona with thermal catalytic reactor over Ni/γ-Al2O3. Journal of Natural Gas Chemistry, 2012. **21**(4): p. 466-475.

29. Wang, D., Study of Ni/Char Catalyst for Biomass Gasification in an Updraft Gasifier: Influence of Catalyst Granular Size on Catalytic Performance. BIORESOURCES, 2013. **8**(3): p. 3479-3489.

30. Aziz, M.A.A., et al., CO2 methanation over Ni-promoted mesostructured silica nanoparticles: Influence of Ni loading and water vapor on activity and response surface methodology studies. Chemical Engineering Journal, 2015. **260**: p. 757-764.

31. Liu, X., et al., Low-temperature catalytic steam reforming of toluene over activated carbon supported nickel catalysts. Journal of the Taiwan Institute of Chemical Engineers, 2016.

32. Srivastava, N. and C.J. Wang, Effects of water addition on OH radical generation and plasma properties in an atmospheric argon microwave plasma jet. Journal of Applied Physics, 2011. **110**(5).

33. Guo, Y.-f., et al., Toluene removal by a DBD-type plasma combined with metal oxides catalysts supported by nickel foam. Catalysis Today, 2007. **126**(3-4): p. 328-337.

34. Morgan. LXCat database. 2016; Available from: www.lxcat.net.

35. Taghvaei, H., et al., Hydrogen production through plasma cracking of hydrocarbons: Effect of carrier gas and hydrocarbon type. Chemical Engineering Journal, 2013. **226**: p. 384-392.

36. Liu, S., et al., Steam reforming of toluene as biomass tar model compound in a gliding arc discharge reactor. Chemical Engineering Journal, 2017. **307**: p. 793-802.

37. Kohno, H., et al., Destruction of volatile organic compounds used in a semiconductor industry by a capillary tube discharge reactor. IEEE Trans. Ind. Appl, 1998. **34**(5): p. 953-966.

38. Du, C.M., J.H. Yan, and B. Cheron, Decomposition of toluene in a gliding arc discharge plasma reactor. Plasma Sources Science & Technology, 2007. **16**(4): p. 791-797.

39. Van Durme, J., et al., Abatement and degradation pathways of toluene in indoor air by positive corona discharge. Chemosphere, 2007. **68**(10): p. 1821-9.

40. Bartolotti, L.J. and E.O. Edney, Density functional theory derived intermediates from the OH initiated atmospheric oxidation of toluene. Chem. Phys. Lett., 1995. **245**(1): p. 119-122.

41. Blin-Simiand, N., et al., Plasma reactivity and plasma-surface interactions during treatment of toluene by a dielectric barrier discharge. Plasma Chemistry and Plasma Processing, 2008. **28**(4): p. 429-466.

42. Zhu, F.S., et al., Destruction of toluene by rotating gliding arc discharge. Fuel, 2016. **176**: p. 78-85.

43. Nozaki, T., et al., Kinetic analysis of the catalyst and nonthermal plasma hybrid reaction for methane steam reforming. Energy & Fuels, 2007. **21**(5): p. 2525-2530.