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1 **Hybrid plasma-catalytic steam reforming of toluene as biomass**
2 **tar model compound over Ni/Al₂O₃ catalyst**

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1 **Abstract**

2 In this study, plasma-catalytic steam reforming of toluene as a biomass tar model compound
3 was carried out in a coaxial dielectric barrier discharge (DBD) reactor. The effect of Ni/Al₂O₃
4 catalysts with different nickel loadings (5-20 wt. %) on the performance of the plasma-catalytic
5 gas cleaning process was evaluated in terms of toluene conversion, yield of gas products, by-
6 products formation and energy efficiency of the plasma-catalytic process. Compared to the
7 plasma reaction without a catalyst, the combination of DBD with the Ni catalysts significantly
8 enhanced the toluene conversion, hydrogen yield and energy efficiency of the plasma process,
9 whilst significantly reduced the formation of organic by-products. Increasing the Ni loading of
10 the catalyst improved the performance of the plasma-catalytic processing of toluene, with the
11 highest toluene conversion of 52 % and energy efficiency of 2.6 g/kWh when placing the 20
12 wt.% Ni/Al₂O₃ catalyst in the plasma. The possible reaction pathways in the plasma-catalytic
13 process were proposed through the combined analysis of both gas and liquid products.

14

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

1 **1. Introduction**

2 Biomass has great potential to make a major contribution to low carbon pathways in the UK
3 and globally, contributing to the UK's goal of reducing its greenhouse gas emissions by 80%
4 by 2050 and the international mitigation target of a maximum 2 degrees Celsius temperature
5 rise. The gasification of biomass represents a major thermochemical route to produce a high
6 energy value syngas from a source which is renewable and CO₂-neutral [1]. The product gas
7 or synthesis gas (a mixture of H₂ and CO) produced from gasification can be used for the
8 generation of electricity and heat by direct combustion in internal combustion engines, while
9 high quality synthesis gas can also be used as an important chemical feedstock for the synthesis
10 of a wide range of valuable fuels and chemicals. Clearly, biomass can make a significant
11 contribution to all three key energy sectors: electricity, heat and transport [2].

12 However, one of the major challenges in the biomass gasification process is contamination of
13 the product syngas with tar. Tar is a complex mixture of condensable hydrocarbons with
14 molecular weight higher than benzene, some of which are carcinogenic. The concentration of
15 tar in the produced syngas from biomass gasification varies from 1 g/m³ up to 100 g/m³,
16 depending on the operating conditions of the gasification process [3] . The formation of tar
17 causes major process and syngas end-use problems, including tar blockages, plugging and
18 corrosion in downstream fuel lines, filters, engine nozzles and turbines, and had been a major
19 barrier for the development and deployment of biomass gasification process [1-3]

20 Considerable efforts have been devoted to the removal of tars in product gas from biomass
21 gasification using different processes, including thermal cracking [4, 5], physical separation [6]
22 and catalytic reforming [7-10]. Thermal cracking of tars requires very high reaction
23 temperature (>800 °C) and thus cause a high energy input. Physical separation of tars could
24 reduce the efficiency of the overall process and has great potential to cause secondary pollution.

1 Along with the requirement for high temperature in thermal catalytic steam reforming process,
2 rapid deactivation of catalysts due to coke deposition is another major challenge in thermal-
3 catalytic process.

4 So far many types of catalysts have been reported for tar conversion, such as calcined rocks,
5 clay minerals, ferrous metal oxides, activated alumina and supported-metal catalysts (e.g.
6 nickel, cobalt and other noble metals) [11]. Nickel catalysts mainly supported on alumina, have
7 been extensively investigated for steam reforming of biomass tar because of its low cost,
8 abundance and high initial activity [12, 13]. However, the metal catalysts may suffer from
9 deactivation due to sintering, coke deposition and poisoning with sulphur and chlorine. Coke
10 deposition is one of the most serious issues in catalytic reforming of hydrocarbons, especially
11 for aromatic hydrocarbons [3].

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

1 A more effective use of plasma is possible by exploiting its inherent synergetic potential
2 through the combination of plasma with heterogeneous catalysts, which can activate the
3 catalysts at low temperatures and improve their activity and stability, resulting in the
4 remarkable enhancement of reactant conversion, selectivity, and yield of target products, as
5 well as the energy efficiency of the plasma-catalytic process [14, 17]. This novel hybrid process
6 has attracted tremendous interest for environmental clean-up, methane activation, CO₂
7 conversion, synthesis of carbon nanomaterials and catalysts [18]. However, very limited work
8 has been focused on the use of non-thermal plasma for the removal of tars from the gasification
9 of biomass or waste. To the best of our knowledge, no work has been dedicated to the
10 investigation of hybrid plasma-catalytic process for the cleaning of tars at low temperatures. A
11 wide range of catalysts have been evaluated in thermal-catalytic reforming of tars. These
12 include calcined rocks, clay minerals, ferrous metal oxides, activated alumina and supported-
13 metal catalysts (e.g. nickel, cobalt and other noble metals). However, it is not clear how a
14 catalyst present in the plasma process affects the reforming of tars or a tar model compound at
15 low temperatures. Furthermore, most of previous studies investigated the effect of different
16 operating parameters on the performance of the plasma tar removal process [19, 20], whereas
17 few analyzed the by-products and intermediates in the plasma reforming of tar to better
18 understand the underlying reaction pathways and mechanisms in the plasma process.

19 Largely, studies in plasma-catalytic processes focused on the conversion efficiency and energy
20 consumption, by comparing the input and output concentration of target compounds using
21 different operating parameters [21]. However, a detailed understanding of the underlying
22 reaction pathways and mechanisms in the plasma processing of tars is still missing. It is of
23 primary important to analyze both the gas and condensed liquid products in the plasma-
24 catalytic steam reforming process to get new insights into the reaction pathways, which would
25 provide valuable information for the further optimization of the plasma-catalytic process.

1 The present study aimed to demonstrate the effectiveness of the hybrid plasma-catalytic
2 process for the removal of a tar model compound and provide an insight of toluene destruction
3 pathways in the plasma-catalytic process. In this work, an in-plasma catalysis (IPC) system
4 based on a coaxial dielectric barrier discharge (DBD) reactor was developed for the steam
5 reforming of toluene, a typical model tar compound representing a major stable aromatic
6 product in the tars formed in high temperature biomass gasification processes. The effect of
7 Ni/ γ -Al₂O₃ catalysts with different Ni loadings (5 to 20 wt.%) on the plasma-catalytic removal
8 of toluene was investigated in terms of toluene conversion, energy efficiency of the plasma-
9 catalytic process and the distribution of gas products. The plasma steam reforming process
10 without a catalyst was also carried out for comparison. Moreover, the possible reaction
11 pathways involved in the plasma reactions were proposed and discussed through combined
12 quantitative and qualitative analysis of gas and liquid products.

13 **2. Experimental**

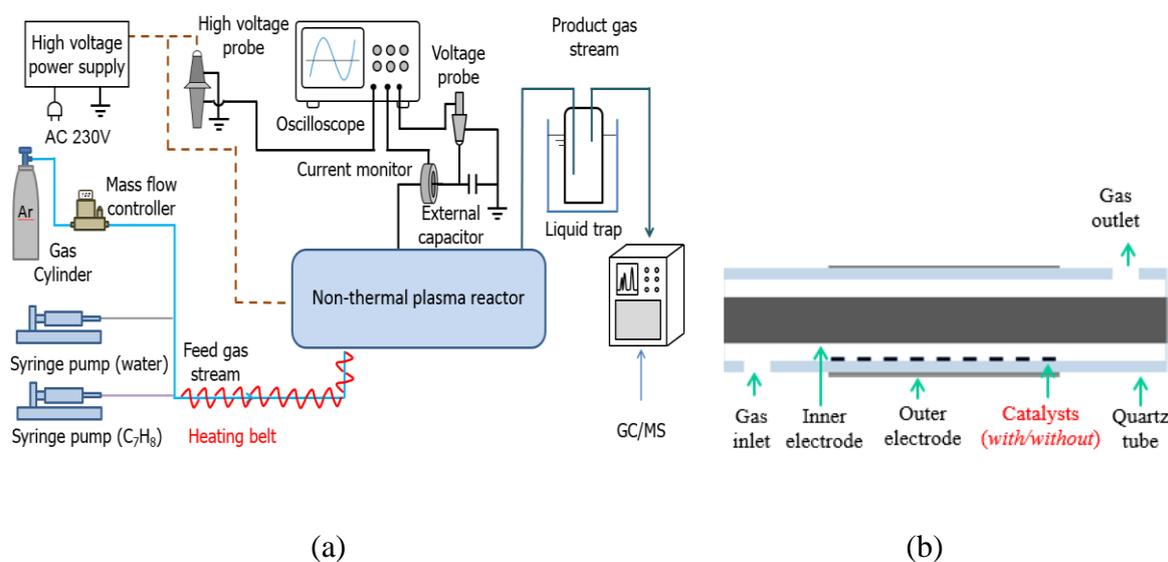
14 **2.1. Catalyst preparation**

15 The Ni/ γ -Al₂O₃ catalysts with different Ni loadings (5, 10 and 20 wt. %) were prepared by the
16 wetness impregnation method using Ni (NO₃)₂·6H₂O as the metal precursor. The appropriate
17 weight of γ -Al₂O₃ (1 mm diameter beads) was added to the metal precursor solution and
18 impregnated for 12 hours. The above solution was dried at 100 °C until most of water was
19 evaporated. The obtained samples were heated at 100 °C for 24 h, followed by the calcination
20 at 750 °C for 3 h.

21 **2.2. Experimental setup**

22 The experiment was carried out in a coaxial DBD reactor, as shown in Fig.1. A 100 mm-long
23 stainless steel mesh was wrapped over a quartz tube with an inner diameter of 18 mm and outer
24 diameter of 21 mm. A stainless steel rod with a diameter of 14 mm was used as an inner

1 electrode and placed in the axis of the quartz tube. As a result, the length of the discharge region
 2 was 100 mm with a discharge gap of 2 mm. The inner electrode was connected to a high voltage
 3 output and the outer electrode was grounded via an external capacitor C_{ext} (0.47 μ F). The DBD
 4 reactor was connected to an AC high voltage power supply with a maximum peak voltage of
 5 30 kV and a frequency of 5-20 kHz. In this work, the frequency was fixed at 9 kHz. The applied
 6 voltage was measured by a high voltage probe (Testec, TT-HVP 15 HF), while the voltage on
 7 the external capacitor was recorded by a voltage probe (Tektronix P5100) to obtain the charge
 8 generated in the discharge. All the electrical signals were recorded by a 4-channel digital
 9 oscilloscope (Tektronix MDO 3024). The Q-U Lissajous method was used to determine the
 10 discharge power (P) of the DBD reactor. A homemade online power measurement system was
 11 used to monitor and control the discharge power in real time [22].



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

17 A total of 0.5 g of Ni/ γ -Al₂O₃ catalyst was packed into the discharge region along the bottom
 18 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

1 and catalyst in a DBD reactor and consequently promoted the plasma-catalytic chemical
2 reactions in our previous studies [23]. Prior to the plasma-catalytic reaction, the catalysts were
3 in situ reduced in a pure hydrogen discharge at a discharge power of 60 W and a flow rate of
4 50 ml/min for 1 h in the same DBD reactor. Then, argon was fed into the reactor as a carrier
5 gas at a flow rate of 150 ml/min. Toluene (C_7H_8 , purity $\geq 99\%$, Aldrich) solution and
6 deionized water were injected into the preheated pipe by high-resolution syringe pumps (KDS
7 Legato, 100) at a flow rate of 0.2 ml/h and 0.6 ml/h, respectively. The steam-to-carbon molar
8 ratio (S/C ratio) was fixed at 2.5 throughout the experiment. The mixed stream was then heated
9 to 160 °C in a copper pipe with an inner diameter of 4 mm (40 cm in length) equipped with a
10 temperature controller system, to generate a steady-state vapour before flowing into the DBD
11 reactor.

12 **2.3. Methods of analysis and the definition of parameters**

13 The gas products were analyzed by a two-channel gas chromatography (Shimadzu, GC-2014)
14 equipped with a thermal conductivity detector (TCD) for the detection of H_2 , CO, CO_2 and CH_4
15 and a flame ionization detector (FID) for the measurement of C_2 - C_4 hydrocarbons. During the
16 reaction, an ice trap was placed at the exit of the plasma reactor in order to condense any liquid
17 products. The collected liquid samples were analyzed by a gas chromatography – mass
18 spectrometry (GC-MS, Agilent GC 7820 A, MSD) and qualitatively identified using the mass
19 spectral library from National Institutes for Standards and Technology (NIST) [24].
20 Measurements were carried out after running the plasma reaction for about 30 min when a
21 steady-state was reached.

22 For the plasma-catalytic steam reforming of toluene, the toluene conversion $X_{C_7H_8}$, was
23 calculated as the ratio of the carbon in the carbon-containing gas products (CO_2 , C_2H_2 , C_2H_4 ,
24 C_2H_6 and C_3H_8) to the carbon in the input toluene:

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

The yield of the products was defined as follows:

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

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

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

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

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

9

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 -Al₂O₃ 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/Nm³) over a 5 wt.% Ni/SiO₂ 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/SiO₂

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

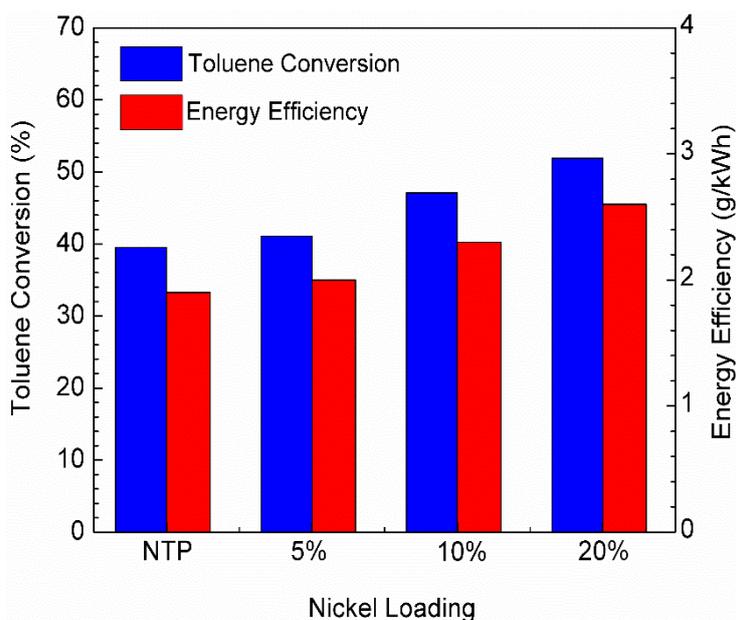
3 In this study, the Ni catalysts were placed along the bottom of the discharge region in the
4 DBD reactor, while the plasma-catalytic steam reforming reaction was carried out at low
5 temperatures ($<200^{\circ}\text{C}$) without any external heating. Therefore, heating effect from the plasma
6 on the catalyst activation and plasma-catalytic reaction was negligible. In addition, this partial
7 packing method could still generate a strong filamentary discharge in the DBD reactor due to
8 the presence of large void fraction in the discharge gap, resulted in strong physical and chemical
9 interactions between the discharge and Ni catalysts [23]. Moreover, when a catalyst is placed
10 in the discharge, polarisation of the catalyst leads to the charge accumulation on the catalyst
11 surface, increasing the local or average electrical field and therefore the number of energetic
12 electrons and reactive species, characterized by the formation of intensified microdischarges
13 around the contact points between the catalyst pellets and those between the catalyst pellet and
14 quartz wall [26, 27]. Previous studies demonstrated that placing a 10 wt.% Ni/ $\gamma\text{-Al}_2\text{O}_3$ along
15 the bottom of a DBD reactor enhanced the intensity of current pulses in the plasma-catalytic
16 dry reforming of CH_4 [23], while the mean electric field and mean electron energy of the DBD
17 were enhanced by 9-11% when BaTiO_3 and TiO_2 photocatalysts were partially packed in the
18 DBD reactor in the plasma-catalytic conversion of CO_2 [17]. These physical effects have been
19 shown to enhance the conversion of reactants in plasma-catalytic chemical reactions. Clearly,
20 in this study, the enhanced toluene conversion and energy efficiency in the plasma-catalytic
21 steam reforming of toluene can be partly attributed to the physical effects induced by the
22 presence of the Ni catalyst pellets in the plasma.

23 In addition, increasing the Ni loading from 5% to 20% increased the conversion of toluene
24 and energy efficiency of the plasma-catalytic process, as shown in Fig. 2. For example, the
25 combination of the DBD with the 20 wt.% Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst showed the highest toluene

1 conversion of ~51.9 % and energy efficiency of 2.6 g/kWh. In the plasma-catalytic reforming
2 reaction at low temperatures, increasing the Ni loading over γ -Al₂O₃ could effectively enhance
3 the catalyst activity owing to the formation of more active Ni sites on the catalyst surface.
4 Aziznia et al also showed that higher conversions of CO₂ and CH₄ were obtained in the low
5 temperature plasma-catalytic dry reforming of CH₄ when a 20 wt.% Ni/ γ -Al₂O₃ catalyst was
6 placed in a corona discharge compared with Ni/ γ -Al₂O₃ catalysts with a lower Ni loading (5
7 wt.% and 10 wt.%) [28]. Similar phenomenon was also observed in thermal catalytic chemical
8 reactions. Wang reported that the removal efficiency of tar and hydrogen production increased
9 with increasing Ni loading from 5 wt.% to 20 wt.% [29]. Aziz et al investigated the effect of
10 Ni loading (1-10 wt. %) on CO₂ methanation over Ni/mesoporous silica nanoparticles (MSN)
11 catalysts at different reaction temperatures [30]. They found that increasing the Ni loading
12 enhanced the catalytic activity for CO₂ methanation at low temperatures (<623 K). However,
13 the 10 wt. % Ni/MSN catalyst showed a similar activity as the 5 wt. % Ni/MSN catalyst in CO₂
14 methanation at high temperatures (>673 K). Similarly, Liu et al reported that there was an
15 optimum Ni loading of 10 wt.% of activated carbon (AC) supported Ni catalysts in thermal
16 catalytic steam reforming of toluene at 200 °C. They found that further increasing the Ni
17 loading to 15 wt.% increased the nickel particle size and lowered the nickel particle dispersion
18 on the catalyst surface, resulted in the aggregation of Ni particles and increased carbon
19 deposition, and consequently decreased the conversion of toluene. Compared to relatively high
20 temperature thermal catalytic reactions, placing supported metal catalysts in low temperature
21 plasma process can effectively reduce the metal particle size and enhance the metal dispersion
22 on the catalyst surface due to low temperature effect [31]. In this experiment, low temperature
23 plasma reaction is believed to avoid the aggregation of Ni particles on the catalyst surface but
24 increase the catalytic activity for toluene conversion when increasing the Ni loading from 5
25 wt. % to 20 wt. %. In addition, the presence of conductive Ni active sites on the catalyst also

1 contribute to the spread and expansion of the discharge over the catalyst surface, which may
2 be favourable to the expansion of discharge volume and intensity in the DBD-catalytic process
3 [32].

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



11
12 Fig. 2. Toluene conversion and energy efficiency of the plasma process with and without
13 catalysts (toluene concentrate: 17.7 g/Nm³, discharge power: 35 W, S/C ratio: 2.5, catalyst:
14 10 wt.% Ni/ γ -Al₂O₃)

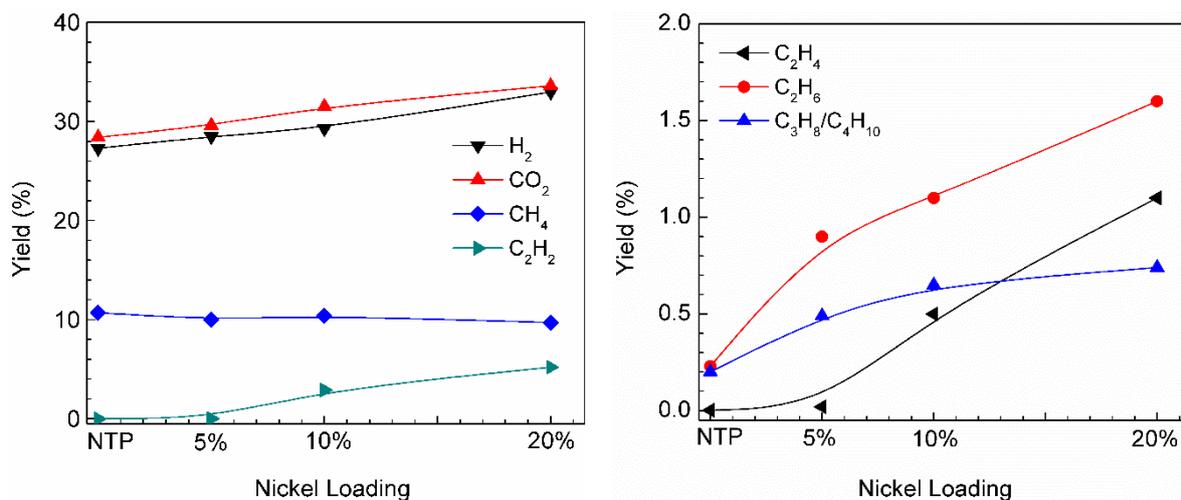
15

16 3.2. Gaseous products

1 H₂, CO₂ and CH₄ were found as the main gas products in the plasma steam reforming of toluene
2 with and without the Ni catalyst. A small amount of hydrocarbons (C₂H₂, C₂H₄, C₂H₆, C₃H₈
3 and C₄H₁₀) were also detected. Clearly, the presence of the Ni catalysts in the DBD reactor
4 enhanced the production of H₂ and CO₂, as shown in Fig. 3. Increasing the Ni loading from 5
5 to 20 wt.% steadily increased the yield of H₂ and CO₂ by 15% and 16%, respectively. It is
6 worth to note that no CO was detected in the gas products. The occurrence of water gas shift
7 reaction (R1) might be the major reason to inhibit the generation of CO in the steam reforming
8 of toluene in the DBD. Moreover, the presence of reactive oxide species (e.g. OH, O radicals)
9 through the dissociation of water by energetic electrons and metastable argon might be able to
10 further oxidize CO (R4 and R5), toluene and its intermediates into CO₂. This plasma reaction
11 might be considered as an attractive hydrogen production process without CO formation
12 suitable for fuel cell applications.



18 As shown in Fig. 3, the yield of CH₄ was nearly constant (~10%) when changing the Ni loading,
19 whereas the yield of C₃-C₄ hydrocarbons (less than 1.6 %) increased by increasing the Ni
20 content. Compared to the plasma reforming without a catalyst, placing the 5 wt. % Ni/ γ -Al₂O₃
21 catalyst in the DBD reactor almost did not change the production of C₂H₂ and C₂H₆. However,
22 increasing the Ni loading from 5 to 20 wt. % enhanced the yield of C₂H₂ and C₂H₆. The highest
23 C₂H₂ yield of 5.2% was achieved when the 20 wt.% Ni/ γ -Al₂O₃ catalyst was placed in the
24 plasma steam reforming of toluene.



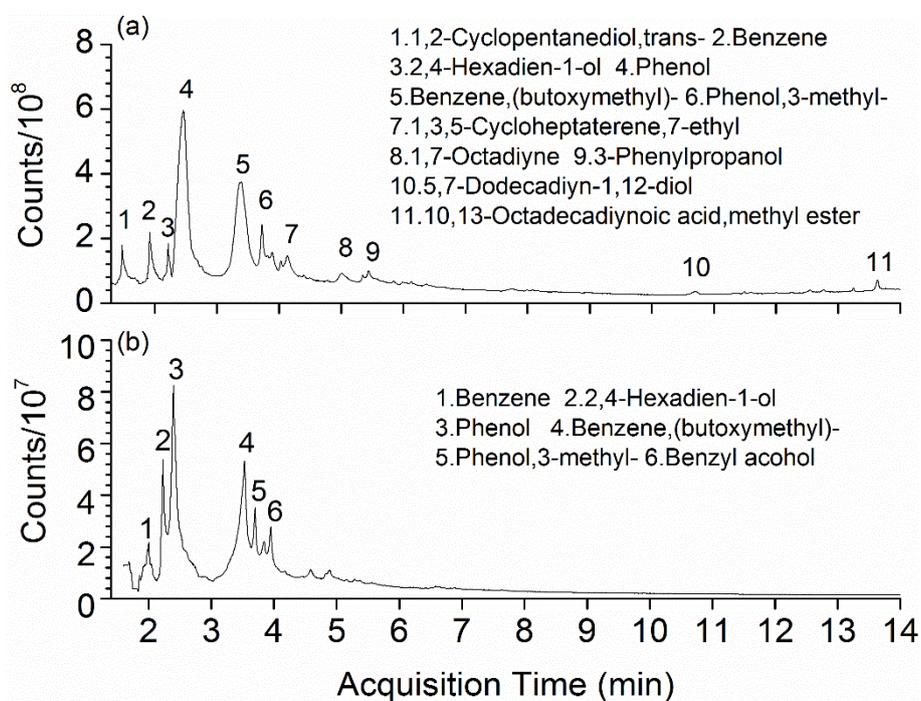
1 Fig. 3. The effect of Ni loading on the yield of gaseous products (toluene concentrate: 17.7
 2 g/Nm³, discharge power: 35 W, S/C: 2.5)

3

4 3.3. Formation of condensed by-products

5 Fig. 4 shows the GC-MS chromatogram of condensed by-products collected in the plasma
 6 steam reforming of toluene with and without the catalyst. In the plasma reaction without a
 7 catalyst, 11 types of organic by-products were detected, including major compounds such as
 8 benzene, phenol and (butoxymethyl)-benzene. Additionally, aliphatic compounds such as
 9 methyl ester, diol, octadecadienoic acid and the linear compounds 5, 7-Dodecadiyn-1, 12-diol
 10 were also detected, which could be generated from the cleavage of toluene ring, and the
 11 recombination and hydrogenation of the resulting fragments of intermediates. The presence of
 12 the 5 wt.% Ni/ γ -Al₂O₃ catalyst in the plasma process significantly inhibited the formation of
 13 organic by-products. As shown in Fig. 4(b), only six types of condensed compounds were
 14 detected, among which phenol, 2,4-Hexadien-1-ol and (butoxymethyl)-benzene were
 15 identified as the major organic by-products. It is worth noting that the amount of phenol and
 16 (butoxymethyl)-benzene formed in the plasma-catalytic reforming reaction was several orders
 17 of magnitude lower than those generated in the plasma reaction without the Ni catalyst. These

1 results clearly demonstrated that the coupling of the DBD and the Ni/ γ -Al₂O₃ catalyst promoted
2 the conversion of toluene into gas products (e.g. H₂), whilst significantly minimized the
3 formation of undesirable organic by-products (Fig. 4).



4
5 Fig. 4. GC-MS chromatogram of condensed by-products collected in the plasma steam
6 reforming of toluene (a) without a catalyst, and (b) with the 5 wt. % Ni/ γ -Al₂O₃ catalyst
7 (toluene concentration: 17.7 g/Nm³, discharge power: 35 W, S/C: 2.5, catalyst: 0.5g)

8

9 3.4. Reaction mechanisms and pathways of toluene destruction

10 The reaction mechanisms involved in the destruction of low concentration toluene (50 -500
11 ppm) as a model VOC in air or nitrogen plasmas without a catalyst have been investigated and
12 proposed in previous studies [21, 33]. However, very limited work has been focused on the
13 investigation of the reaction mechanisms and pathways in the plasma steam reforming of
14 toluene as a model tar compound, especially in the presence of a catalyst. Compared to the
15 removal of toluene as a model VOC, the reaction pathways present in the plasma steam

1 reforming of toluene could be different due to the presence of high content toluene and steam.
2 To get new insights into the possible reaction routes in this plasma process, the analysis of both
3 gaseous and condensed liquid by-products were carried out in the plasma reaction with and
4 without the Ni catalyst. It is well known that only gas-phase reactions are involved in the
5 plasma steam reforming of toluene in the absence of a catalyst. However, the presence of the
6 Ni catalyst in the plasma makes the reaction more complicated as plasma driven surface
7 reactions occur besides the gas-phase reactions.

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

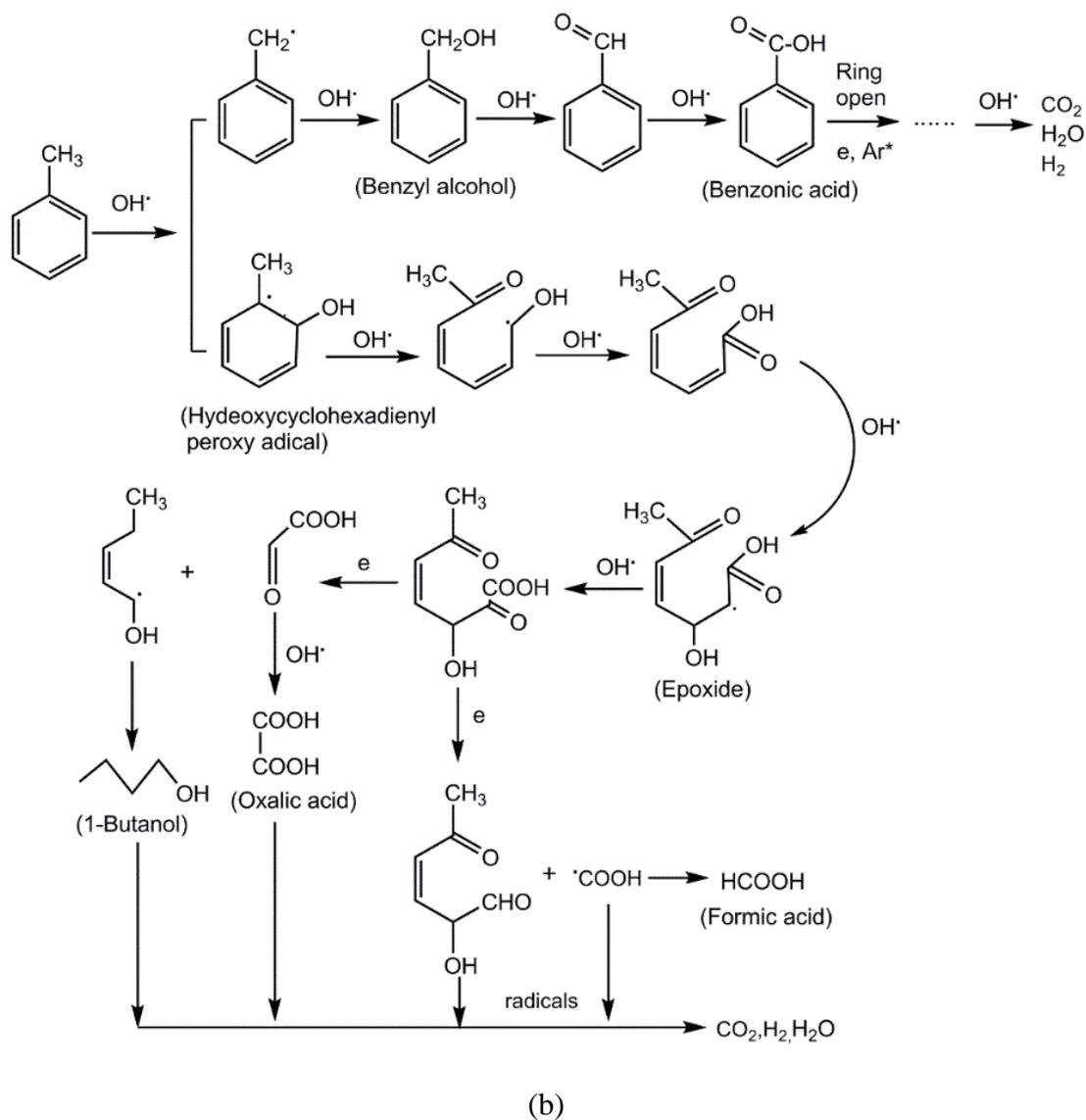
19 Different bond energies of chemical bonds in toluene determine the reaction pathways involved
20 in the plasma conversion of toluene. The dissociation energy of C-H bond in methyl is 3.7 eV,
21 which is smaller than that of C-H bond in aromatic ring (4.3 eV), C-C bond between methyl
22 group and aromatic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

1 [37]. The H-abstraction from the methyl group forms a benzyl radical, which could further
2 react with OH to generate benzyl alcohol. The formed benzyl alcohol can be converted to
3 benzaldehyde, followed by further reactions with electrons and reactive species to form a
4 phenyl radical [38]. In addition, the C-C bond between methyl and aromatic ring and C-H bond
5 in the aromatic ring can be broken through the reactions with energetic electrons and metastable
6 Ar species, generating phenyl, methyl, and toluene radicals [21]. As shown in Fig 5 (a), the
7 recombination of phenyl with H and OH radicals could produce benzene and phenol,
8 respectively, while adding OH to the aromatic ring of toluene radicals produces 3-methyl
9 phenol, as identified by GC-MS. Moreover, ring opening and cracking of phenol via electron
10 impact dissociation forms butyl alcohol, which then reacts with benzyl to generate benzene,
11 (butoxymethyl). These aromatic intermediates can be further ruptured by electrons and Ar*
12 species to form ring-opening by-products and then oxidized by OH to end-products such as
13 CO₂ and H₂O.

14 Toluene can also be decomposed by the cleavage of benzene ring through collisions with
15 reactive species, e.g. OH radicals, producing hydroxycyclohexadienyl type peroxy radicals
16 (Fig 5(b)), which has been confirmed in the previous modeling and experimental studies [38-
17 40]. This unstable reactive compound can form a peroxide bridge radical, a precursor for the
18 formation carbonyl and epoxide [40]. The carbonyl reaction route opens the benzene ring of
19 toluene via a series of oxidation by OH radicals to form a relatively stable epoxide, which can
20 be further decomposed by electrons or reactive species, forming substances with small
21 molecular mass, such as oxalic acid and acetic acid.

22 The presence of the Ni catalysts in the plasma steam reforming of toluene enhanced the
23 production of most gas products, whilst significantly reduced the formation of condensed
24 organic by-products. These findings suggest that the combination of the plasma with the Ni

1 catalysts shifted the primary reaction pathways of toluene destruction from the
2 dehydrogenation or oxygenation of methyl group to direct cleavage of toluene ring, which can
3 be evidenced by the enhanced yield of hydrogen and C_2H_2 . Previous experimental and
4 theoretical studies showed that acetylene was most likely formed by rupturing the toluene ring
5 through the collisions with electrons and Ar^* species [41]. Recently, Zhu et al. also reported
6 that high energetic electrons could breakdown toluene ring, forming acetylene and methyl-
7 cyclobutadiene in the plasma decomposition of toluene as a tar surrogate using a rotating
8 gliding arc discharge [42]. In this work, the detected C_5H_6 might be 1, 3-pentadiene, which
9 sequentially reacted with methyl and OH radicals to form linear hydrocarbons such as 2, 4-
10 hexadien-1-ol. In the hybrid plasma-catalytic reforming of toluene, plasma-assisted surface
11 reactions also contributed to the enhanced reaction performance. In our experiment, the Ni
12 catalyst pellets were placed along the bottom of the quartz tube in the discharge region and can
13 directly interact with the plasma. Partial packing of the Ni catalyst pellets in the DBD still
14 formed predominant micro-discharges across the electrode gap and induced strong interactions
15 between the plasma and Ni catalyst, which is favourable for the plasma induced surface
16 reactions on the surface of the Ni catalyst [23]. In this plasma-catalysis configuration, both
17 toluene and intermediates from the gas phase reactions can be adsorbed onto the surface of the
18 Ni catalyst. Short-lived reactive species (e.g. O, OH) initially generated close to or on the
19 catalyst surface can also be involved in the surface reactions. The excited species generated in
20 the plasma might promote the adsorption of toluene and intermediates onto the catalyst surface
21 [43]. The residence time of toluene and intermediates in the plasma reaction region could be
22 prolonged due to the catalyst effect. The enhanced adsorption process increases the collisions
23 of toluene molecules with energetic species, leading to an acceleration of the plasma chemical
24 reactions, both in gas phase and on the catalyst surface. The adsorbed species could also react



1

2

3 Fig. 5. Possible reaction pathways for toluene destruction initiated by (a) energetic electrons

4 and Ar^* , and (b) OH radicals

5

6 4. Conclusion

7 In this work, a coaxial DBD plasma reactor was developed for the hybrid plasma-catalytic
 8 steam reforming of toluene as a model tar compound from biomass gasification. Ni catalyst
 9 was placed in the plasma reaction region to induce strong interactions between the plasma and
 10 catalyst. Compared to the plasma reaction without a catalyst, the coupling of the plasma with
 11 the Ni/ Al_2O_3 catalysts enhanced the conversion of toluene and H_2 yield, whilst significantly

1 suppressed the formation of undesirable aromatic organic by-products. Nickel loading was
2 found as a critical parameter affecting the performance of the plasma-catalytic reaction.
3 Increasing the Ni content of the Ni/ γ -Al₂O₃ catalyst from 5 wt. % to 20 wt. % considerably
4 enhanced the toluene conversion, the yield of H₂, C₂H₂ and C₂H₆ and the energy efficiency of
5 the hybrid process. The enhanced performance of the hybrid process can be attributed to both
6 the gas phase reactions and plasma-assisted surface reactions. Based on the analysis of the gas
7 products and liquid organic by-products, the possible reaction mechanisms and pathways
8 involved in the plasma-catalysis reforming of toluene were proposed and discussed.

9

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