

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

3 S. Y. Liu^a, D. H. Mei^a, M. A Nahil^b, S. Gadkari^c, S. Gu^c, P. T. Williams^b and X. Tu^{a*}

4 *^a Department of Electrical Engineering and Electronics, University of Liverpool,*

5 *Liverpool L69 3GJ, UK*

6 *^b School of Chemical & Process Engineering, University of Leeds, Leeds LS2 9JT, UK*

7 *^c School of Chemical and Process Engineering, University of Surrey, Surrey GU2 7XH, UK*

8
9 *** Corresponding Author**

10 Dr. Xin Tu

11 Department of Electrical Engineering and Electronics,

12 University of Liverpool,

13 Liverpool, L69 3GJ,

14 UK

15 Tel: +44-1517944513

16 E-mail: xin.tu@liverpool.ac.uk

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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) plasma reactor. The effect of
4 Ni/Al₂O₃ catalysts with different nickel loadings (5-20 wt. %) on the plasma-catalytic gas
5 cleaning process was evaluated in terms of toluene conversion, gas yield, by-products
6 formation and energy efficiency of the plasma-catalytic process. Compared to the plasma
7 reaction without a catalyst, the combination of DBD with the Ni/Al₂O₃ catalysts significantly
8 enhanced the toluene conversion, hydrogen yield and energy efficiency of the plasma process,
9 whilst significantly reduced the production of organic by-products. Increasing 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:** plasma-catalysis; non-thermal plasma; dielectric barrier discharge; biomass
16 gasification; tar removal

1 **1. Introduction**

2 Biomass has great potential to make a major contribution to the low carbon economy and
3 reaching COP21 targets. Biomass gasification has been regarded as a key thermochemical
4 route for the production of a higher value syngas from a renewable and CO₂-neutral source
5 [1]. The product gas or synthesis gas (a mixture of H₂ and CO) produced from biomass
6 gasification can be used for generating electricity and heat by direct combustion in internal
7 engines, while high quality synthesis gas can also be used as an important chemical feedstock
8 for the synthesis of a variety of valuable fuels and chemicals. Clearly, biomass can make a
9 significant contribution to all three key energy sectors: transport, heat and electricity [2, 3].

10 However, one of the major challenges in the biomass gasification process is contamination
11 of the product syngas with tar, which is a complex mixture of condensable hydrocarbons with
12 molecular weight higher than benzene, some of which are carcinogenic. The content of tar in
13 the produced syngas from biomass gasification varies from 1 g/m³ up to 100 g/m³, depending
14 on the operating conditions of the gasification process [4]. The production of tars in biomass
15 gasification process leads to major process and syngas end-use problems, including tar
16 blockages, plugging and corrosion in downstream fuel lines, filters, engine nozzles and
17 turbines, and has been a major barrier for the development and deployment of biomass
18 gasification process [3, 4]. Considerable efforts have been focused on the removal of tars in
19 product gas from biomass gasification using different processes, including thermal cracking
20 [5, 6], physical separation [7] and catalytic reforming [3, 8-10]. Thermal cracking of tars
21 requires very high reaction temperature (>800 °C) and thus cause a high energy input.
22 Physical separation of tars could reduce the efficiency of the overall process and has great
23 potential to cause secondary pollution. Along with the requirement for high temperature in
24 thermal catalytic reforming process, rapid deactivation of catalysts due to coke deposition is
25 the major challenge in thermal-catalytic reforming process.

1 The least researched, yet predicted to be the most attractive and effective, is the plasma gas
2 cleaning process. Non-thermal plasma has been demonstrated as an effective solution for the
3 removal of organic gas pollutants (e.g. volatile organic compounds VOCs) and synthesis of
4 chemicals and fuels [11]. In non-thermal plasmas, the produced electrons are highly energetic
5 (1-10 eV) and can break most chemical bounds of inert molecules, producing reactive species
6 including free radicals, excited atoms, ions and molecules for a variety of chemical reactions.
7 In addition, high reaction and fast reaching of a steady state in a plasma process allows rapid
8 switch on and off the plasma process compared to other thermal processes, which
9 significantly enhance the overall energy efficiency and provides a promising route for plasma
10 process supplied by renewable energy (e.g. wind power or solar power) to act as an efficient
11 chemical energy storage localized or distributed system at peak grid times [12, 13].

12 A more effective use of plasma is to integrate plasma process with heterogeneous catalysis,
13 combining the advantages of fast and low temperature reaction by non-thermal plasmas and
14 selective synthesis from catalysis. The combined plasma-catalytic process has great potential
15 to produce a synergy, which can low the activation energy of catalysts and enhance the
16 conversion of reactants, the selectivity and yield of desirable products, and the efficiency of
17 the plasma process [11, 14]. This novel hybrid process has attracted significant interest for
18 gas clean-up, methane activation, CO₂ conversion, synthesis of carbon nanomaterials and
19 catalysts [15]. However, very limited work has been focused on the use of non-thermal
20 plasma for the removal of tars from the gasification of biomass or waste. To the best of our
21 knowledge, no work has been dedicated to the investigation of hybrid plasma-catalytic
22 process for the removal of tars from biomass gasification. So far, a range of catalysts have
23 been evaluated in thermal-catalytic reforming of tars at high temperatures, such as calcined
24 rocks, clay minerals, ferrous metal oxides, activated alumina and supported-metal catalysts
25 (e.g. nickel, cobalt and other noble metals) [16]. Nickel catalysts mainly supported on

1 alumina, have been extensively investigated for thermal catalytic tar reforming because of its
2 high initial activity, abundance and low cost. However, catalyst deactivation due to coke
3 deposition remains a major challenge in catalytic reforming of tars. Our previous works
4 showed that the coupling of plasma with Ni/Al₂O₃ catalysts can significantly reduce carbon
5 deposition in plasma-catalytic reforming of biogas compared to thermal catalytic reactions
6 [17]. However, it is not clear how a catalyst (e.g. Ni/Al₂O₃) present in the plasma process
7 affects the reforming of tars or a tar model compound at low temperatures. Furthermore,
8 previous studies mainly investigated the effect of different operating parameters on the
9 performance of the plasma tar removal process [18, 19], whereas few analyzed the by-
10 products and intermediates in the plasma reforming of tar to better understand the underlying
11 reaction pathways and mechanisms in the plasma process. In addition, a detailed
12 understanding of the underlying reaction pathways and mechanisms in the plasma processing
13 of tars is still missing. It is of primary importance to analyze both the gas and condensed
14 liquid products in the plasma-catalytic steam reforming process to get new insights into the
15 reaction pathways, which would provide valuable information for the further optimization of
16 the plasma-catalytic process.

17 The present study aimed to demonstrate the effectiveness of the hybrid plasma-catalytic
18 process for the removal of a tar model compound and provide an insight of toluene
19 destruction pathways in the plasma-catalytic process. In this work, an in-plasma catalysis
20 (IPC) system based on a coaxial dielectric barrier discharge (DBD) reactor was developed for
21 the steam reforming of toluene, a typical model tar compound representing a major stable
22 aromatic product in the tars formed in high temperature biomass gasification processes. The
23 effect of Ni/γ-Al₂O₃ catalysts with different Ni loadings (5 to 20 wt.%) on the plasma-
24 catalytic removal of toluene was investigated in terms of toluene conversion, energy
25 efficiency of the plasma-catalytic process and the distribution of gas products. The plasma

1 steam reforming process without a catalyst was also carried out for comparison. Moreover,
2 the possible reaction pathways involved in the plasma reactions were proposed and discussed
3 through combined quantitative and qualitative analysis of gas and liquid products.

4

5 **2. Experimental**

6 **2.1. Catalyst preparation**

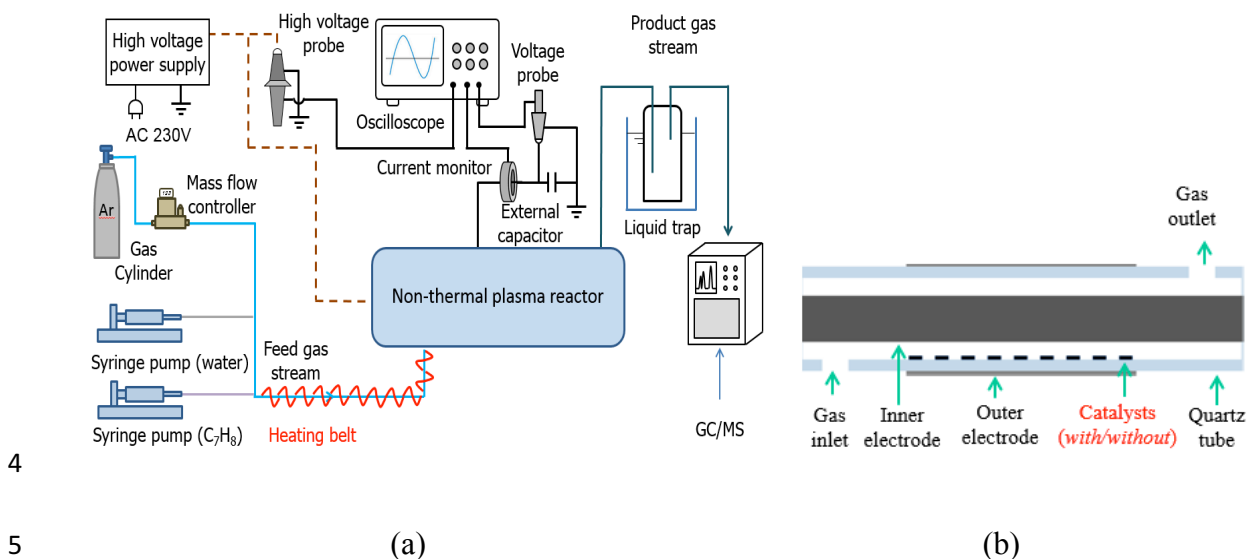
7 The Ni/ γ -Al₂O₃ catalysts with different Ni loadings (5, 10 and 20 wt. %) were prepared by
8 the wetness impregnation method. The appropriate weight of γ -Al₂O₃ (1 mm diameter beads)
9 was added to the metal precursor solution and impregnated for 12 hours. The above solution
10 was dried at 100 °C until most of water was evaporated. The obtained samples were heated at
11 100 °C for 24 h, followed by the calcination at 750 °C for 3 h.

12

13 **2.2. Experimental setup**

14 The experiments were carried out in a coaxial DBD reactor (Fig.1). A 100 mm-long
15 stainless steel (SS) mesh was wrapped over a quartz tube with an inner diameter of 18 mm
16 and outer diameter of 21 mm. A SS rod with a diameter of 14 mm was used as an inner
17 electrode and placed in the axis of the quartz tube. As a result, the length of the discharge
18 region was 100 mm with a discharge gap of 2 mm. The inner electrode was connected to a
19 high voltage output and the outer electrode was grounded via an external capacitor C_{ext} (0.47
20 μ F). The DBD reactor was connected to an AC high voltage power supply with a maximum
21 peak voltage of 30 kV and a frequency of 5-20 kHz. In this work, the frequency was fixed at
22 9 kHz. The applied voltage was measured by a high voltage probe (Testec, TT-HVP 15 HF),
23 while the voltage on the external capacitor was recorded by a voltage probe (Tektronix P5100)
24 to obtain the charge generated in the discharge. All the electrical signals were recorded by a

1 4-channel digital oscilloscope (Tektronix MDO 3024). The Q-U Lissajous method was used
2 to determine the discharge power (P) of the DBD reactor. A homemade online power
3 measurement system was used to monitor and control the discharge power in real time [20].



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

7 A total of 0.5 g of Ni/ γ -Al₂O₃ catalyst was packed into the plasma region along the bottom
8 of the quartz tube, partially filling the discharge gap and held by quartz wood. This partial
9 packing method has been shown to effectively enhance the interactions between the plasma
10 and catalyst in a DBD reactor and consequently promoted the plasma-catalytic chemical
11 reactions in our previous studies [21]. Before the reaction, the catalysts were reduced in a H₂
12 plasma at a discharge power of 60 W and a flow rate of 50 mL/min for 1 h in the same DBD
13 reactor. Then, argon was used as a carrier gas with a flow rate of 150 mL/min. Toluene (C₇H₈,
14 purity \geq 99%, Aldrich) solution and deionized water were injected into the preheated pipe
15 by high-resolution syringe pumps (KDS Legato, 100) at a flow rate of 0.2 ml/h and 0.6 mL/h,
16 respectively. The steam-to-carbon molar ratio (S/C ratio) was fixed at 2.5 throughout the
17 experiment. The mixed stream was heated to 160 °C in a copper pipe with an inner diameter

1 of 4 mm (40 cm in length) controlled a temperature controller system, to produce a steady-
2 state vapour before flowing into the plasma reactor.

3

4 **2.3. Methods of analysis and the definition of parameters**

5 The gas products were analyzed by a two-channel gas chromatography (Shimadzu, GC-
6 2014) equipped with a flame ionization detector (FID) for the measurement of C₁-C₄
7 hydrocarbons and a thermal conductivity detector (TCD) for the analysis of H₂, CO, CO₂ and
8 CH₄. During the reaction, an ice trap was placed at the exit of the DBD reactor to condense
9 liquid products. The collected liquid samples were analyzed by a gas chromatography – mass
10 spectrometry (GC-MS, Agilent GC 7820 A, MSD) and qualitatively identified using the mass
11 spectral library from National Institutes for Standards and Technology (NIST) [22]. All the
12 measurements were performed after running the plasma reaction for around 30 mins when the
13 plasma reaction reached a steady-state.

14 In the plasma reforming reaction, the conversion of toluene $X_{C_7H_8}$, was calculated as the moles
15 of carbon in the carbon-containing gas products (CO₂, C₂H₂, C₂H₄, C₂H₆ and C₃H₈) to the
16 carbon in the input toluene:

$$17 \quad X_{C_7H_8} (\%) = \frac{\text{Moles of carbon in the produced gas}}{\text{Moles of carbon in the feed}} \times 100 \quad (2)$$

18 The yield of the products was defined as follows:

$$19 \quad Y_{H_2} (\%) = \frac{H_2 \text{ produced (mol/s)}}{4 \times C_7H_8 \text{ input (mol/s)} + H_2O \text{ input (mol/s)}} \times 100 \quad (3)$$

$$20 \quad Y_{CO_2} (\%) = \frac{CO_2 \text{ produced (mol/s)}}{7 \times C_7H_8 \text{ input (mol/s)}} \times 100 \quad (4)$$

1
$$Y_{C_xH_y} (\%) = \frac{x \times C_xH_y \text{ produced (mol/s)}}{7 \times C_7H_8 \text{ input (mol/s)}} \times 100 \quad (5)$$

2 The energy efficiency (E) of the plasma reforming toluene conversion was defined as the
3 mass of converted toluene per unit of discharge power.

4
$$E (\text{g/kWh}) = \frac{\text{mass of converted } C_7H_8 \text{ (g/h)}}{\text{discharge power (kW)}} \quad (6)$$

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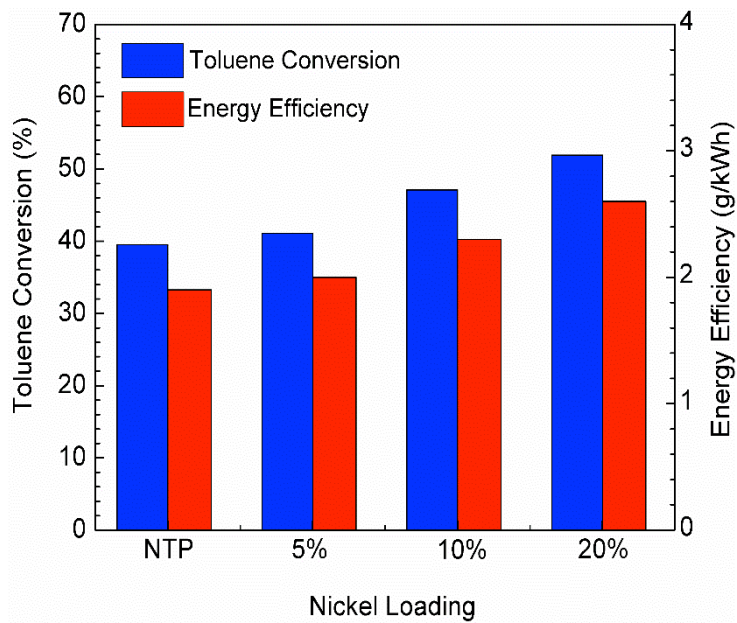
6 **3. Results and discussion**

7 **3.1. Plasma-catalytic steam reforming of toluene**

8 Plasma steam reforming of toluene was carried out in the DBD reactor with and without the
9 Ni catalysts, as shown in Fig. 2. Compared with the plasma reaction without a catalyst, the
10 presence of the 10 wt.% Ni/ γ -Al₂O₃ catalyst in the plasma significantly enhanced the carbon
11 conversion by around 20% (from 39.5 % to 47.1%), whilst the energy efficiency of the
12 process was increased by 18.0 %. Tao et al reported similar findings in a plasma-catalytic
13 steam reforming of high content toluene (~200 g/Nm³) over a 5 wt.% Ni/SiO₂ catalyst in a
14 DC plasma reactor [23]. However, extra thermal heating (at 773 K) was used to heat the
15 plasma-catalytic process in their experiments. Therefore, it was extremely difficult to identify
16 whether the effect of the Ni/SiO₂ catalyst on the enhanced toluene conversion was driven by
17 the plasma or thermal heating or both [23].

18 In this study, the Ni catalysts were placed along the bottom of the discharge region in the
19 DBD reactor, while the plasma-catalytic steam reforming reaction was carried out at low
20 temperatures (<200 °C) without any external heating. Therefore, heating effect from the
21 plasma on the catalyst activation and plasma-catalytic reaction was negligible. As shown in
22 Fig. 3, this partial packing method could still generate a strong filamentary discharge in the

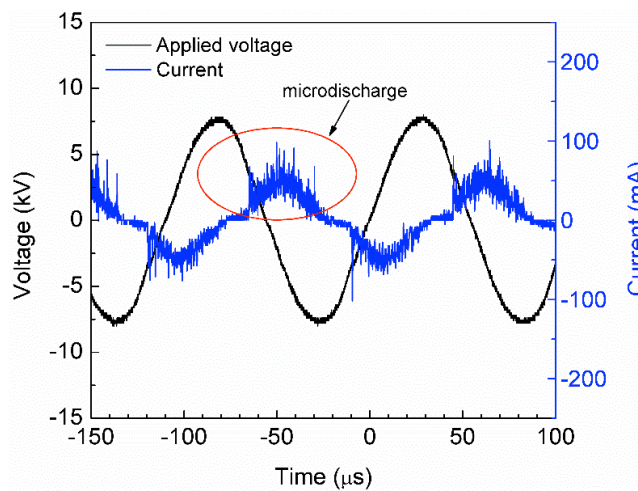
1 DBD reactor due to the presence of large void fraction in the discharge gap, resulted in strong
2 physical and chemical interactions between the discharge and Ni catalysts [21]. Compared to
3 the plasma reaction without packing, the shape of the Lissajous figure was almost same when
4 the catalysts were partially packed into the discharge region (Fig. 4). Moreover, when a
5 catalyst is placed in the discharge, polarisation of the catalyst leads to the charge
6 accumulation on the catalyst surface, increasing the local or average electrical field and
7 therefore the number of energetic electrons and reactive species, characterized by the
8 formation of intensified microdischarges around the contact points between the catalyst
9 pellets and those between the catalyst pellet and quartz wall [24, 25]. Previous studies
10 demonstrated that placing a 10 wt.% Ni/ γ -Al₂O₃ along the bottom of a DBD reactor enhanced
11 the intensity of current pulses in the plasma-catalytic dry reforming of CH₄ [21], while the
12 mean electric field and mean electron energy of the DBD were enhanced by 9-11% when
13 BaTiO₃ and TiO₂ photocatalysts were partially packed in the DBD reactor in the plasma-
14 catalytic conversion of CO₂ [14]. These physical effects have been shown to enhance the
15 conversion of reactants in plasma-catalytic chemical reactions. Similar phenomenon was also
16 observed in Fig. 2. Clearly, in this study, the enhanced toluene conversion and energy
17 efficiency in the plasma-catalytic steam reforming of toluene can be partly attributed to the
18 physical effects induced by the presence of the Ni catalyst pellets in the plasma.



1

2 Fig. 2. Toluene conversion and energy efficiency of the plasma process with and without
 3 catalysts (toluene concentrate: 17.7 g/Nm³, discharge power: 35 W, S/C ratio: 2.5, catalyst:
 4 10 wt.% Ni/ γ -Al₂O₃)

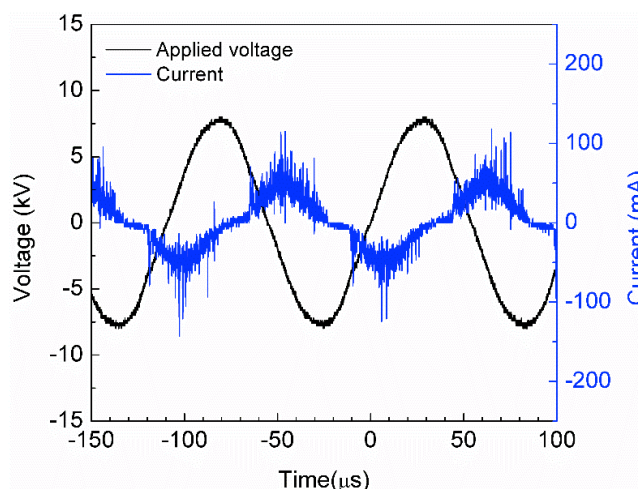
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(a)



(b)

Fig. 3. Electrical signals of the DBD (a) without packing; (b) with 10 wt.% Ni/ γ -Al₂O₃

catalyst

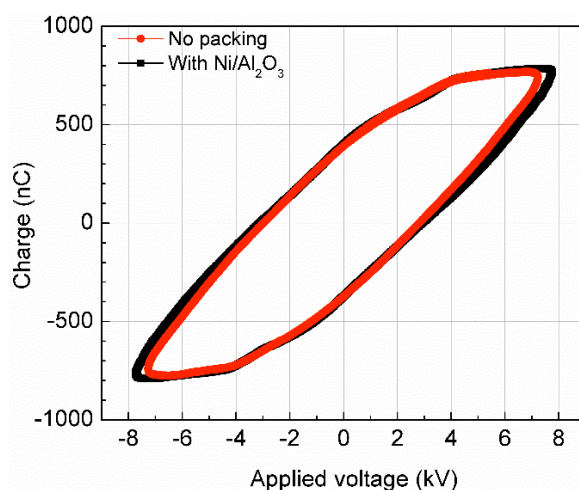


Fig. 4. Lissajous figures of DBD plasma with and without 10 wt.% Ni/ γ -Al₂O₃ catalyst at a constant discharge power of 35 W.

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 -Al₂O₃ catalyst showed the highest toluene conversion of ~51.9 % and energy efficiency of 2.6 g/kWh. In the plasma-catalytic reforming

1 reaction at low temperatures, increasing the Ni loading over γ -Al₂O₃ could effectively
2 enhance the catalyst activity owing to the formation of more active Ni sites on the catalyst
3 surface. Aziznia et al also showed that higher conversions of CO₂ and CH₄ were obtained in
4 the low temperature plasma-catalytic dry reforming of CH₄ when a 20 wt.% Ni/ γ -Al₂O₃
5 catalyst was placed in a corona discharge compared with Ni/ γ -Al₂O₃ catalysts with a lower Ni
6 loading (5 wt.% and 10 wt.%) [26]. Similar phenomenon was also observed in thermal
7 catalytic chemical reactions. Wang reported that the removal efficiency of tar and hydrogen
8 production increased with increasing Ni loading from 5 wt.% to 20 wt.% [27]. Aziz et al
9 investigated the effect of Ni loading (1-10 wt. %) on CO₂ methanation over Ni/mesoporous
10 silica nanoparticles (MSN) catalysts at different reaction temperatures [28]. They found that
11 increasing the Ni loading enhanced the catalytic activity for CO₂ methanation at low
12 temperatures (< 623 K). However, the 10 wt. % Ni/MSN catalyst showed a similar activity as
13 the 5 wt. % Ni/MSN catalyst in CO₂ methanation at high temperatures (>673 K). Similarly,
14 Liu et al reported that there was an optimum Ni loading of 10 wt.% of activated carbon (AC)
15 supported Ni catalysts in thermal catalytic steam reforming of toluene at 200 °C. They found
16 that further increasing the Ni loading to 15 wt.% increased the nickel particle size and
17 lowered the nickel particle dispersion on the catalyst surface, resulted in the aggregation of
18 Ni particles and increased carbon deposition, and consequently decreased the conversion of
19 toluene. Compared to relatively high temperature thermal catalytic reactions, placing
20 supported metal catalysts in low temperature plasma process can effectively reduce the metal
21 particle size and enhance the metal dispersion on the catalyst surface due to low temperature
22 effect [29]. In this experiment, low temperature plasma reaction is believed to avoid the
23 aggregation of Ni particles on the catalyst surface but increase the catalytic activity for
24 toluene conversion when increasing the Ni loading from 5 wt. % to 20 wt.%. In addition, the
25 presence of conductive Ni species on the catalyst also contribute to the expansion of the

1 plasma over the catalyst surface, which may be favourable to the expansion of discharge
2 volume and intensity in the DBD-catalytic process [30].

3 These results clearly demonstrated that the catalytic effect (e.g. catalyst activity) also plays
4 an important role in enhancing the conversion of toluene and efficiency of the plasma-
5 catalytic process besides the physical effects. In the hybrid plasma-catalytic process, the
6 adsorption of reactants on the catalyst surface could be enhanced [24], which would increase
7 the retention time of toluene and its intermediates in the plasma and therefore improve the
8 collision probability between these pollutants and chemically reactive species, leading to a
9 higher toluene conversion in the plasma-catalytic process.

10

11 **3.2. Gaseous products**

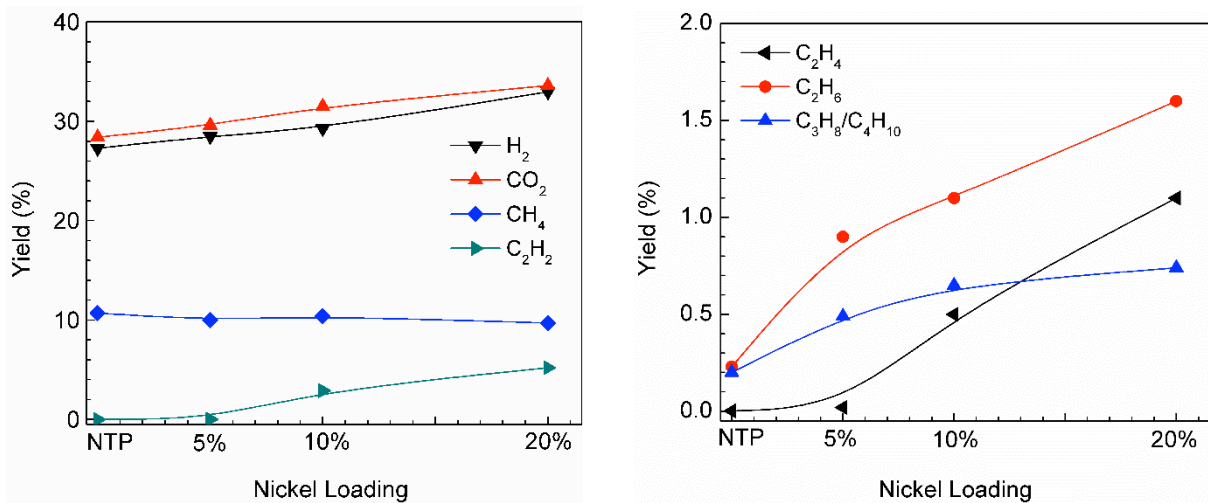
12 H₂, CO₂ and CH₄ were found as the main gas products in the plasma steam reforming of
13 toluene with and without the Ni catalyst. A small amount of hydrocarbons (C₂H₂, C₂H₄, C₂H₆,
14 C₃H₈ and C₄H₁₀) were also detected. Clearly, the presence of the Ni catalysts in the DBD
15 reactor enhanced the production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





5 As shown in Fig. 5, the yield of CH_4 was nearly constant (~10%) when changing the Ni
 6 loading, whereas the yield of $\text{C}_3\text{-C}_4$ hydrocarbons (less than 1.6 %) increased by increasing
 7 the Ni content. Compared to the plasma reaction with no catalyst, placing the 5 wt.% Ni/ γ -
 8 Al_2O_3 catalyst in the DBD reactor almost did not change the production of C_2H_2 and C_2H_6 .
 9 However, increasing Ni content from 5 to 20 wt. % enhanced the yield of C_2H_2 and C_2H_6 .
 10 The highest C_2H_2 yield of 5.2% was achieved when the 20 wt.% Ni/ γ - Al_2O_3 catalyst was
 11 placed in the plasma steam reforming of toluene.

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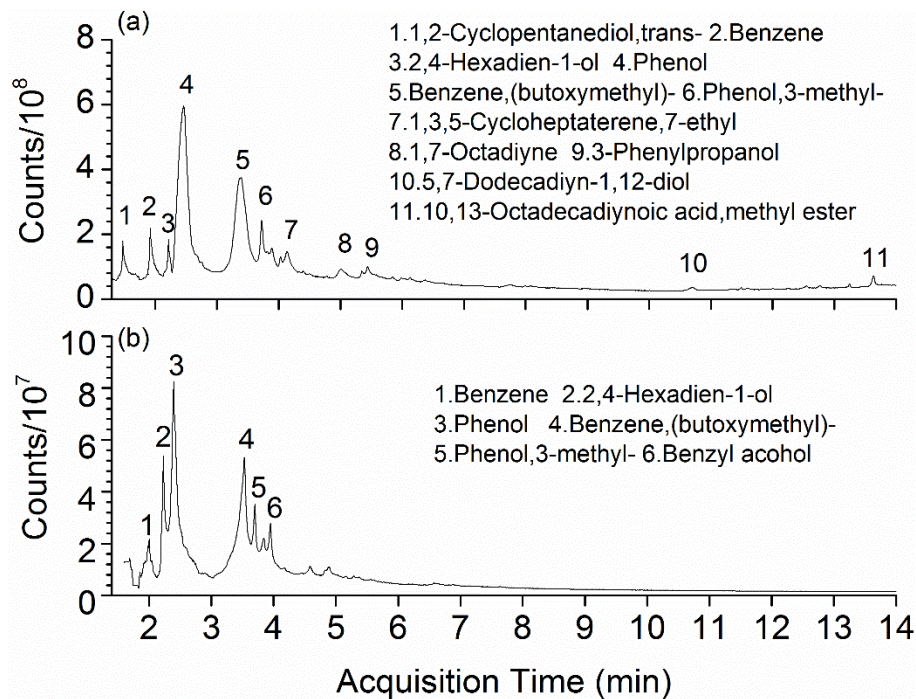


13 Fig. 5. The effect of Ni loading on the yield of gaseous products (toluene concentrate: 17.7
 14 g/Nm³, discharge power: 35 W, S/C: 2.5)

15

16 **3.3. Formation of condensed by-products**

1 Fig. 6 shows the GC-MS chromatogram of condensed by-products collected in the plasma
2 steam reforming of toluene with and without the catalyst. In the plasma reaction without a
3 catalyst, 11 types of organic by-products were detected, including major compounds such as
4 benzene, phenol and (butoxymethyl)-benzene. Additionally, aliphatic compounds such as
5 methyl ester, diol, octadecadienoic acid and the linear compounds 5, 7-Dodecadiyn-1, 12-diol
6 were also detected, which could be generated from the cleavage of toluene ring, and the
7 recombination and hydrogenation of the resulting fragments of intermediates. The presence
8 of the 5 wt.% Ni/ γ -Al₂O₃ catalyst in the plasma process significantly inhibited the formation
9 of organic by-products. As shown in Fig. 6(b), only six types of condensed compounds were
10 detected, among which phenol, 2,4-Hexadien-1-ol and (butoxymethyl)-benzene were
11 identified as the major organic by-products. It is worth noting that the amount of phenol and
12 (butoxymethyl)-benzene formed in the plasma-catalytic reforming reaction was several
13 orders of magnitude lower than those generated in the plasma reaction without the Ni catalyst.
14 These results clearly demonstrated that the coupling of the DBD and the Ni/ γ -Al₂O₃ catalyst
15 promoted the conversion of toluene into gas products (e.g. H₂), whilst significantly
16 minimized the formation of undesirable organic by-products (Fig. 6).



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6 3.4. Reaction mechanisms and pathways of toluene destruction

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Fig. 6. 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-Al₂O₃ catalyst (toluene concentration: 17.7 g/Nm³, discharge power: 35 W, S/C: 2.5, catalyst: 0.5g)

The reaction mechanism in the destruction of toluene (50 -500 ppm) as a model VOC in air or nitrogen plasmas without a catalyst has been investigated and proposed in previous studies [31, 32]. However, very limited work has focused on the understanding of the reaction routes in the plasma 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

1 reactions are involved in the plasma reforming of toluene without the Ni catalyst. However,
2 placing the Ni catalyst in the DBD makes the reaction more complicated as plasma driven
3 surface reactions occur besides the gas-phase reactions.

4 The destruction of toluene as a model tar compound in the argon DBD can be initiated
5 through two major reaction routes: (i) direct electron impact dissociation of toluene and (ii)
6 reaction with chemically reactive species including OH and Ar metastable species. The
7 ionization of Ar requires a much higher electron energy (15.76 eV) compared to the
8 excitation of Ar to its metastable states Ar* (e.g. 11.55 eV). Therefore, in the Ar DBD, Ar is
9 more likely to be excited to its metastable states rather than being ionized [33]. Previous
10 studies have shown that metastable Ar species play an important role in initiating chemical
11 reactions [34]. The presence of steam in the plasma could generate OH radicals from the
12 dissociation of water by electrons and Ar*. The generated OH radicals can oxidize toluene
13 and its intermediates, opening a new reaction route for the conversion of toluene, resulting in
14 the enhanced conversion and energy efficiency of the plasma process [35].

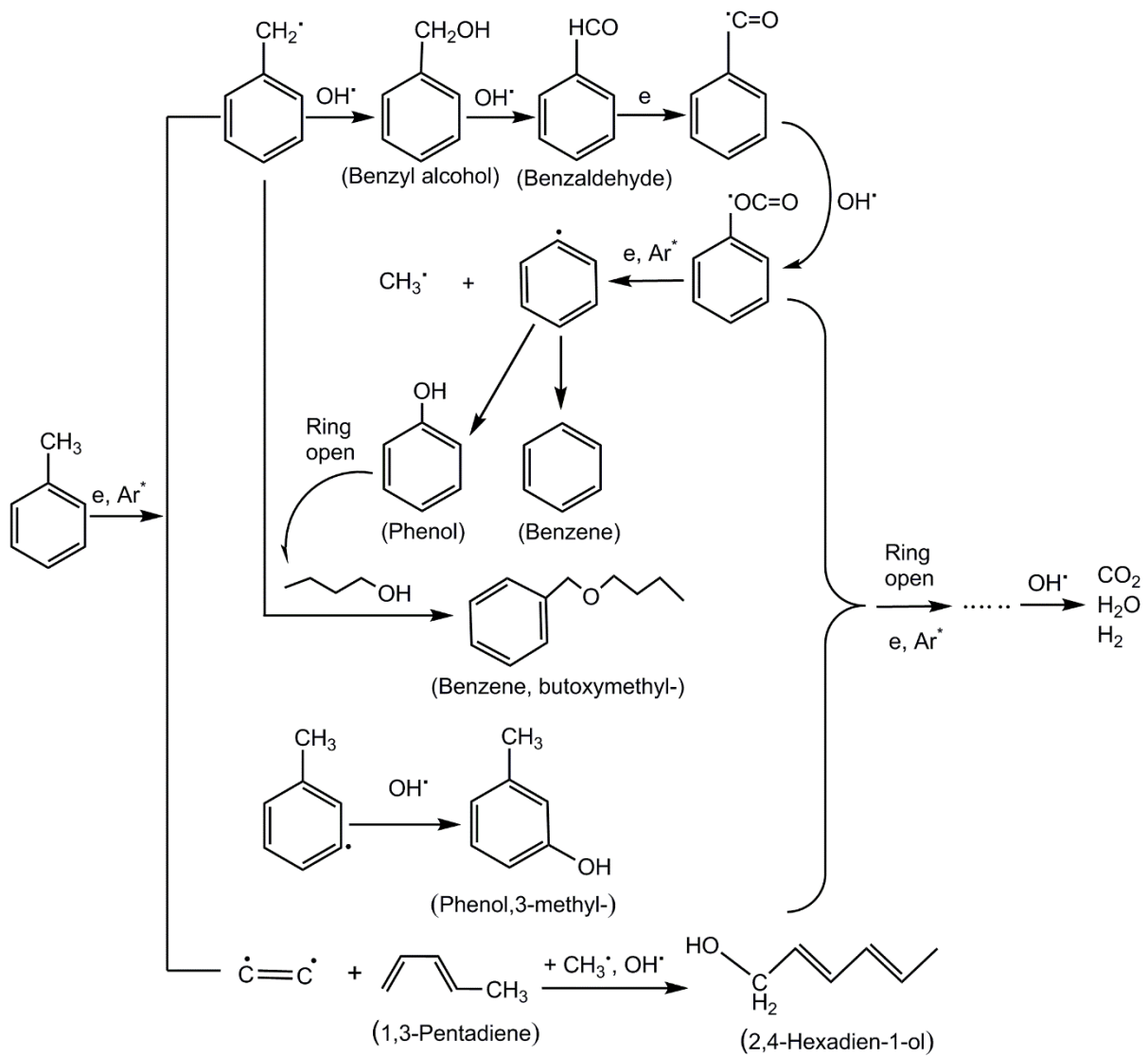
15 Different bond energies of chemical bonds in toluene determine the reaction pathways
16 involved in the plasma conversion of toluene. The dissociation energy of C-H bond in methyl
17 is 3.7 eV, which is smaller than that of C-H bond in aromatic ring (4.3 eV), C-C bond
18 between aromatic ring and methyl group (4.4 eV), C-C bond (5.0-5.3 eV) and C=C bond in
19 aromatic ring (5.5 eV). Therefore, the primary reaction pathway of toluene decomposition
20 could be the H-abstraction from methyl group by energetic electrons or reactive species such
21 as Ar* and OH [36]. The H-abstraction from the methyl group forms a benzyl radical, which
22 could further react with OH to generate benzyl alcohol. The formed benzyl alcohol can be
23 converted to benzaldehyde, followed by further reactions with electrons and reactive species
24 to form a phenyl radical [37]. In addition, the C-C bond between methyl and aromatic ring

1 and C-H bond in the aromatic ring can be broken through the reactions with energetic
2 electrons and metastable Ar species, generating phenyl, methyl, and toluene radicals [32]. As
3 shown in Fig. 7(a), the recombination of phenyl with H and OH radicals could produce
4 benzene and phenol, respectively, while adding OH to the aromatic ring of toluene radicals
5 produces 3-methyl phenol, as identified by GC-MS. Moreover, ring opening and cracking of
6 phenol via electron impact dissociation forms butyl alcohol, which then reacts with benzyl to
7 generate benzene, (butoxymethyl). These aromatic intermediates can be further ruptured by
8 electrons and Ar^{*} species to form ring-opening by-products and then oxidized by OH to end-
9 products such as CO₂ and H₂O.

10 Toluene can also be decomposed by the cleavage of benzene ring through collisions with
11 reactive species, e.g. OH radicals, producing hydroxycyclohexadienyl type peroxy radicals
12 (Fig. 7(b)), which has been confirmed in the previous modeling and experimental studies [37-
13 39]. This reactive compound is unstable and can form a peroxide bridge radical, a precursor
14 for the formation carbonyl and epoxide [39]. The carbonyl reaction route opens the benzene
15 ring of toluene via a stepwise oxidation by OH species to form a relatively stable epoxide,
16 which can be further decomposed by electrons or active species, forming small molecules,
17 such as oxalic acid and acetic acid.

18 The presence of the Ni catalysts in the plasma steam reforming of toluene enhanced the
19 production of most gas products, whilst significantly reduced the formation of condensed
20 organic by-products. These findings suggest that the combination of the plasma with the Ni
21 catalysts shifted the primary reaction pathways of toluene destruction from the
22 dehydrogenation or oxygenation of methyl group to direct cleavage of toluene ring, which
23 can be evidenced by the enhanced yield of hydrogen and C₂H₂. Previous experimental and
24 theoretical studies showed that acetylene was most likely formed by rupturing the toluene

1 ring through the collisions with electrons and Ar* species [40]. Recently, Zhu et al. also
2 reported that high energetic electrons could breakdown toluene ring, forming acetylene and
3 methyl-cyclobutadiene in the plasma decomposition of toluene as a tar surrogate using a
4 rotating gliding arc discharge [41]. In this work, the detected C₅H₆ might be 1, 3-pentadiene,
5 which sequentially reacted with methyl and OH radicals to form linear hydrocarbons such as
6 2, 4-hexadien-1-ol. In the hybrid plasma-catalytic reforming of toluene, plasma-assisted
7 surface reactions also contributed to the enhanced reaction performance. In our experiment,
8 the Ni catalyst pellets were placed along the bottom of the quartz tube in the discharge region
9 and can directly interact with the plasma. Partial packing of the Ni catalyst pellets in the DBD
10 still formed predominant micro-discharges across the electrode gap and induced strong
11 interactions between the plasma and Ni catalyst, which is favourable for the plasma induced
12 surface reactions on the surface of the Ni catalyst [21]. In this plasma-catalysis configuration,
13 both toluene and its intermediates formed in the gas phase reactions can be adsorbed on the
14 surface of the Ni catalyst. Short-lived reactive species (e.g. O, OH) initially generated close
15 to or on the catalyst surface can also be involved in the surface reactions. The excited species
16 generated in the plasma might accelerate the adsorption of toluene and intermediates onto the
17 catalyst surface [42]. The residence time of toluene and intermediates in the plasma reaction
18 region could be prolonged due to the catalyst effect. The enhanced adsorption increases the
19 collisions of toluene with energetic species, consequently accelerates the plasma reactions,
20 both in the gas phase and on the catalyst surface. The adsorbed species could also react with
21 oxidative radicals, forming intermediates such as benzoic acid, before finally oxidized to
22 produce end-products such as CO₂ and H₂O.



(a)

1

2

3

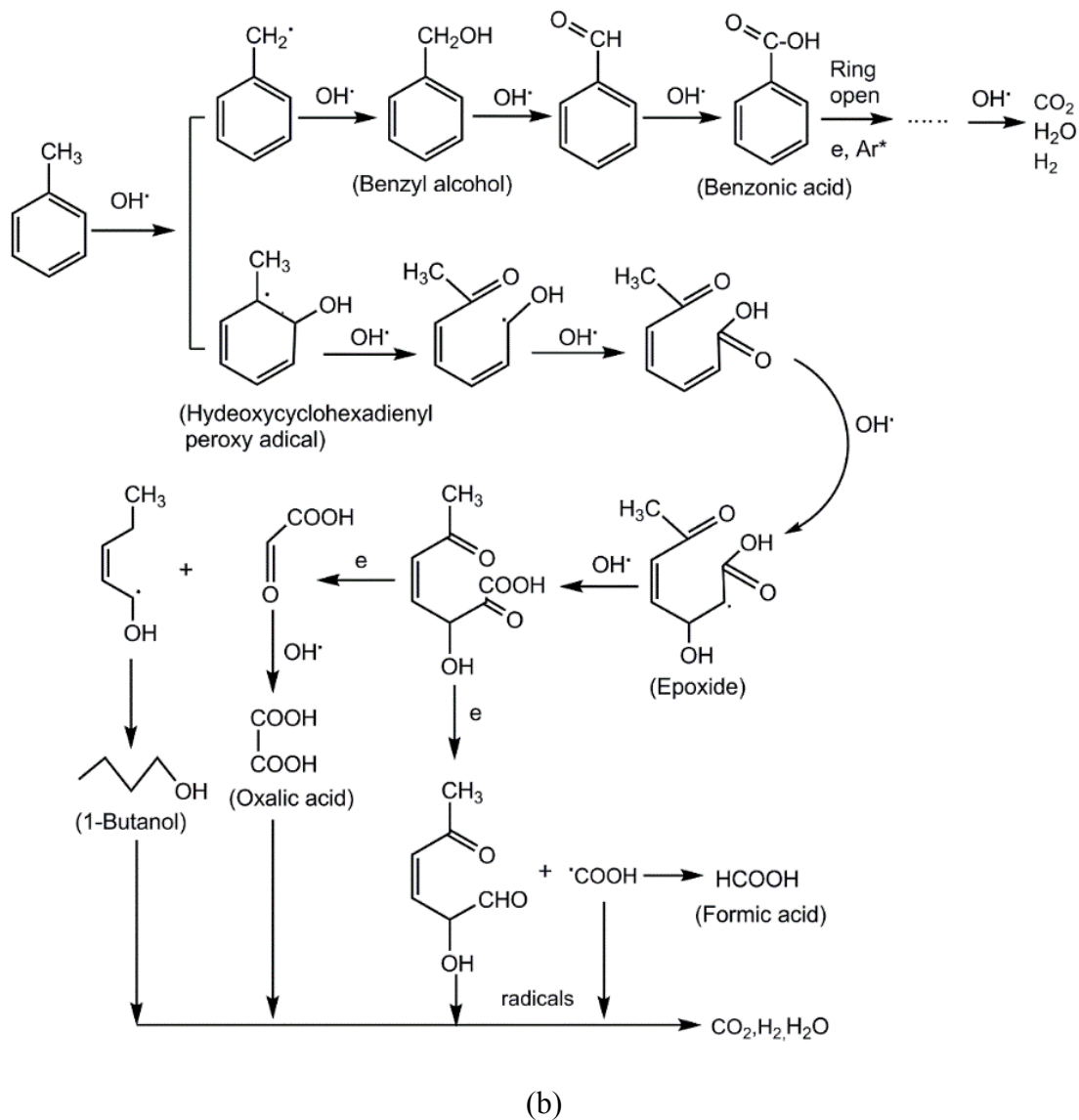


Fig. 7. Possible reaction pathways for toluene destruction initiated by (a) energetic electrons and Ar^* , and (b) OH radicals

4. Conclusion

The effect of $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts on the plasma-catalytic steam reforming of toluene as a model tar compound was carried out in a DBD plasma reactor. The possible reaction mechanisms and pathways involved in the plasma-catalysis reforming of toluene were proposed and discussed. Compared to the plasma process without catalyst, the coupling of plasma with the Ni catalysts enhanced the conversion of toluene and H_2 yield, whilst

1 significantly suppressed the formation of undesirable by-products. Increasing the Ni content
2 from 5 wt. % to 20 wt. % considerably enhanced the performance of the hybrid process,
3 which can be attributed to the enhanced catalytic activity due to enhanced dispersion of Ni
4 species on the catalyst surface. These findings suggest that the combination of the plasma
5 with the Ni catalysts shifted the primary reaction pathways of toluene destruction from the
6 dehydrogenation or oxygenation of methyl group to direct cleavage of toluene ring, which
7 can be evidenced by the enhanced yield of hydrogen and C₂H₂.

8

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12

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