Removal of toluene as a tar analogue in a N$_2$ carrier gas using a non-thermal plasma dielectric barrier discharge (DBD) reactor

Faisal Saleem$^{1,2,*}$, Kui Zhang$^1$, Adam Harvey$^1$

$^1$School of Chemical Engineering and Advanced Materials, Newcastle University Newcastle upon Tyne NE1 7RU

$^2$Department of Chemical and Polymer Engineering, University of Engineering and Technology Lahore, Faisalabad Campus, Pakistan

Keywords: gasification, tar, non-thermal plasma, dielectric barrier discharge

Abstract

The role of N$_2$ carrier gas towards the conversion of tar analogue (toluene) was studied in a non-thermal plasma dielectric barrier discharge (DBD) reactor. The parameters investigated were power (5-40 W), residence time (1.43-4.23 s), toluene concentration (20-82 g/Nm$^3$) and wall temperature (ambient-400 °C). Almost complete removal (99 %) of toluene was observed at 40 W and 4.23s. The main gaseous product was H$_2$ with a maximum selectivity of 40 %. The other gaseous products were lighter hydrocarbons (C$_1$-C$_6$) (5.5%). The selectivity to these lighter hydrocarbons (LHCs) could be increased to 10 % by increasing the temperature to 400 °C. Introducing H$_2$ to the N$_2$ carrier gas at elevated temperatures opened up new reaction routes to enhance the selectivity to LHCs. The selectivity to methane reached 44 % at 35 % H$_2$ at 400 °C, and the total selectivity to LHCs reached 57%.

1. Introduction

Biomass is potentially a source of renewable energy that can help to reduce global warming and replace ever-decreasing of fossil fuel reserves$^1$. Gasification is a promising technology in
which partial oxidation of biomass converts it to a combustible mixture of gases at high temperatures (800-900 °C) \(^2\). The product gas mix is rich in H\(_2\) and CO, which have various applications, including in engines, gas turbines, methanol and hydrocarbon production, hydrogen and natural gas production, and fuel cells \(^3\). In addition, gasification also generates various organic and inorganic by-products. The organic impurities are largely aromatic and polyaromatic compounds, collectively known as “tars”. These compounds can condense in heat exchangers, exit pipes or on particulate filters, and increase the maintenance cost and operational problems \(^4\).

Many studies have been conducted into tar removal by using thermal cracking \(^5\), \(^6\) catalytic cracking \(^7\), \(^8\) and mechanical separation \(^9\), \(^10\). The energy cost significantly increases in thermal cracking due to the requirement for high temperatures (>800°C). Tar can also be decomposed over a catalyst at relatively low temperatures (~600°C) \(^11\). However, the activity of the catalyst reduces with time due to poisoning, sintering and deposition of carbon under reaction conditions, and the operational cost and the catalyst cost is also high. Mechanical separation processes can produce secondary pollution \(^12\) and reduce overall process efficiency.

The non-thermal plasma (NTP) technology is highlighted due to relatively low temperature operations \(^13\). In a non-thermal plasma, the overall temperature of the gas remains as low as ambient temperature, while the average energy of the electrons is high (1-10 eV), which is enough to overcome the dissociation energy of chemical bonds. So, the NTP overcomes the drawback of high temperature requirements in catalytic and thermal conversion, and enables those chemical reactions that are thermodynamically unfavourable at ambient conditions.

NTP Dielectric barrier discharge (DBD) reactors can be considered as an alternative route for the efficient removal of tar compounds. N\(_2\)/O\(_2\) gas mixtures have been used as carrier gases for atmospheric pressure DBD reactors. The decomposition of toluene increased with increasing the oxygen concentration and specific energy density \(^14\). In another study it was reported that
the removal efficiency of toluene increased with increasing plasma power and retention time in discharge zone \(^{15}\).

Here, the role of \(\text{N}_2\) as a carrier gas was studied on the conversion of toluene (as a tar analogue) in a DBD reactor. \(\text{N}_2\) was selected as it is the most significant component of typical biomass gasifier product gas (around 50\%) \(^{16}\). In addition, \(\text{H}_2\) was added into \(\text{N}_2\) carrier gas to reduce the solid residue formation, as it is also an essential component of the product gas from the actual gasifiers \(^{17}\). However, in a previous study, steam was added to eliminate the solid residue and aromatic compounds \(^{18}\), which could also increase the operational cost. Toluene was selected as a tar analogue due to its high thermal stability, low boiling point and simple structure. Its simple structure aids understanding of the mechanism involved in the cracking of tar under non-thermal plasma conditions at low temperatures and ambient pressure. Therefore many studies used toluene as a tar analogue to investigate the performance of the system \(^{19-23}\).

2. Materials and methods

2.1 Experimental setup

The experimental setup is shown in Fig.1. A coaxial cylindrical DBD reactor was used to produce the non-thermal plasma. It consists of two metal electrodes, one inside the inner quartz glass tube (12 mm outer diameter) and the other outside the exterior quartz tube (330 mm length, 15 mm inner diameter, 18 mm outer diameter). The material of construction for both electrodes was 316 stainless steel. The length of the external mesh was 45 mm. The plasma is generated between the annular spaces of coaxial quartz tubes. A variac AC transformer was used to control the input voltage of plasma source unit which delivers power to the DBD reactor, and changed from 5-40 W at a frequency of about 20 kHz. A safety interlock system is used and the power to the DBD reactor will only be supplied if the interlocks are in place.
The length of discharge zone depends upon the overlapping of two electrodes, therefore the length of the shortest electrode (outer electrode) is used to calculate the residence time.

**Fig.1. Experimental setup**

The flow rate of carrier gases (40.6 - 120 ml/min) was regulated by computer-controlled mass flow controllers, which were connected to gas cylinders (BOC, UK, 99.7%). The N₂ and H₂ gas was bubbled through the bubbler and the mixture of toluene vapours and carrier gas passed to the DBD reactor. An electric furnace was used to study the performance of plasma reactor at elevated temperatures. The furnace temperature was controlled from ambient to 400°C, after placing the reactor inside the furnace.

The composition of the product gas is measured by an on-line gas chromatography Varian 450-GC. It is equipped with a thermal conductivity detector and flame ionization detector to measure permanent gases and lower hydrocarbons respectively.

### 2.2 Definitions

The decomposition efficiency of toluene is defined as:
\[ d_I = \frac{\text{moles of toluene in input stream} - \text{moles of toluene in outlet stream}}{\text{moles of toluene in input stream}} \times 100 \]

The selectivity of different products was calculated using the following formulae:

\[ \text{H}_2 \text{ selectivity (\%)} = \frac{\text{moles of H}_2 \text{ produced}}{4 \times \text{Moles of C}_7\text{H}_8 \text{ converted}} \times 100 \]

\[ \text{Lighter hydrocarbons (C}_1\text{-C}_6\text{) selectivity (\%)} = \frac{\sum (m \times \text{moles of C}_m\text{H}_n)}{7 \times \text{Moles of C}_7\text{H}_8 \text{ converted}} \times 100 \]

The energy efficiency is calculated by using following formula:

\[ \text{Energy efficiency (g kWh)} = \frac{\text{toluene converted (g/min)}}{P \text{ (W)} \times 60/3600000} \]

\[ \text{Specific input energy (SIE) (kJ L)} = \frac{P \text{ (W)} \times 60/1000}{\text{Flow rate total (L/min)}} \]

3. **Results and discussion**

3.1 **Effect of power and residence time**

Plasma power plays a key role in the reactions in non-thermal plasmas. A range of products are produced when toluene is cracked, including H\(_2\), lighter hydrocarbons (C\(_1\)-C\(_6\)), and heavier hydrocarbons (>C\(_7\)). The effect of input power on the conversion of toluene is shown in Fig.2 (a), below. Initially, the concentration of toluene was maintained at 33 g/Nm\(^3\). The results show
that high input power favours the cracking of toluene, and nearly complete removal of toluene is obtained at 40 W and residence time of 4.23 s. The conversion of toluene increased because at high power electron density, the electric field is stronger, producing more reactive species, such as radicals, ions, and excited molecules. In a non-thermal plasma, the mean electron energy is in the range of 1-10 eV \(^{24}\). The Maxwellian electron energy distribution function (EEDF) shows the higher the average electron energy is, the more electrons with higher energy will be produced \(^{25}\). These energetic electrons are the hottest species and play a key role for the decomposition of tar compounds.

![Fig.2 (a) Effect of plasma power on the conversion of toluene. Reaction conditions: Ambient temperature; Concentration= 33 g/Nm\(^3\); flow rate=40.6 ml/min; residence time=4.23 s; carrier gas= N\(_2\); and SIE=7.39-59.11 kJ/L.](image-url)
Fig. 2 (b) Effect of plasma power on selectivity of gaseous products. Reaction conditions:

Ambient temperature; toluene concentration= 33 g/Nm$^3$; flow rate=40.6ml/min; residence time=4.23 s; carrier gas= N$_2$; and SIE=7.39-59.11 kJ/L.

Fig. 2 (b) presents the effect of power on the selectivity to gaseous products and the energy efficiency. The selectivity of H$_2$ gradually increases from 5 % to 39% with increasing power from 5 W to 40 W. At lower power the average energy of an electron is not high enough to abstract the hydrogen from the aromatic ring, so the hydrogen originates in the methyl group$^{26}$. However, at higher powers, H$_2$ increases due to the breakage of the aromatic ring. This also increases the selectivity to lower hydrocarbons, which reach 5.5% at 40 W. However, the energy efficiency decreases with increasing the power, and decreases from 15 g/kWh to 2 g/kWh as the power increases from 5 W to 40 W. A similar trend was reported for the removal of tar analogue$^{27,28}$. 
Fig. 3 Effect of residence time on the conversion and towards the selectivity of gaseous products. Reaction conditions: input power=20 W; Ambient temperature; Concentration=33 g/Nm$^3$; carrier gas= N$_2$; and flow rate=40.6-120 ml/min

The effect of residence time on the product selectivity is shown in Fig. 3. With an increase in residence time, the removal efficiency of toluene increased from 93% to 99% at 20 W. This was simply because the toluene molecules spent more time in the plasma discharge zone, so the number of collisions with reactive species (ions, radicals and electrons) and toluene molecules increased. The energy efficiency of the system decreases with increasing residence time. This is possible because at high residence time flow rate decreases, which also reduces the molar flow rate of toluene into the system. Therefore, the amounts of decomposed toluene decrease. Moreover, the toluene conversion for residence times of more than 2 s was almost 100%. Therefore, in this area, additional energy input reduced the apparent energy efficiency.
The selectivity of H₂ increased from 4 % to 18% as the residence time increased from 1.43 s to 4.23 s. The decomposition of aromatic rings increased with increasing residence time due to the increase in the collision frequency of reactive species. However, the selectivity to lower hydrocarbons remained below 1 % at different residence times. Figures 2(b) and 3 show that without any hydrogen in the initial carrier gas, the H₂ selectivity increases with increasing power and residence time. However the content of LHC remains very low. Hence, under these conditions the formation of oligomer/polymer compounds seems to be the main process. From a stoichiometric point of view, the formation of lower hydrocarbons from toluene is probably due to hydrogen consumption. However the formation of simple alkanes such as methane, ethane, propane, butane etc. is a hydrogen consuming process. Therefore, the formation of larger amounts of hydrogen is only possible by the deposition of solid residues.

The reaction scheme below shows the steps involved during the formation of various products. It shows that the decomposition of toluene can take place via high energy electrons or excited species (Step 1). It is probably initiated through hydrogen abstraction from the methyl group (as it has the minimum bond dissociation energy), producing benzyl and hydrogen radicals. The aromatic intermediates can react with each other to produce oligomer/polymer compounds. Step 2 shows that benzene can be produced through radical substitution reactions. Meanwhile high energy electrons and excited species can also attack the aromatic ring (Step 3) to produce ring- opening products (C₁-C₆). H₂ and methane are produced by the combination of radicals (Step 4 and 5).
3.2 Effect of toluene concentration

The concentration of toluene affects the conversion as well as the selectivity (see Figure 4, below). Clearly, cracking decreases with increasing toluene concentration. The maximum toluene conversion (97%) was obtained at the minimum toluene concentration: 20 g/Nm$^3$. Conversion then decreased monotonically up to 82 g/Nm$^3$, where it was 91%. All conditions except toluene concentration were fixed, meaning that a constant number of reactive species were produced.$^3$ Therefore, with increasing the concentration of toluene, the relative amount of reactive species decreased. The energy efficiency of the process, however, increased with
concentration, from 4.7 g/kWh to 18 g/kWh. This was because the production rate of decomposed toluene increased with concentration, whereas the input power and other parameters were kept constant. Similar behaviour was reported before in which toluene decomposition studied using N₂ and steam.

![Graph showing the effect of concentration on toluene conversion and energy efficiency.](image)

**Fig.4 (a)** Effect of concentration on the conversion and energy efficiency. Reaction conditions: input power=10 W; Ambient temperature; flow rate=40.6 ml/min; residence time=4.23 s; carrier gas= N₂; and SIE=14.77 kJ/L.

Fig.4 (b), below, shows the changes in selectivity to gaseous products with respect to concentration. It can be observed that the selectivity of hydrogen decreases from 10.5 % to 6.3% with increasing concentration. Note that the selectivity to lower hydrocarbons remains below 1% at all tested concentrations. This is due to low input power (10W).
In current study, the significant amount of solid residue (67-78 wt. % of the input toluene) was formed inside the discharge zone during the plasma cracking of toluene. In fact, some solid residue was swept into the downstream pipes, the yield of solid residue should be high, and implying the yield of hydrocarbons should be very low. These solids were referred to as polymeric substances, or carbonaceous deposits\textsuperscript{32}. The CHN analysis of the solid residue showed that it contains nearly 80 % carbon. In previous study, it was reported that solid carbon formation occurred and constituted 85 to 90 % of the toluene input\textsuperscript{19}.

In another study, formation of solid particles was reported during the removal of the tar analogue in air that deposited on the catalyst, reducing its efficiency\textsuperscript{33}. In addition, the production of these residues can block the reactor. Therefore, it is very important to avoid the formation of unwanted solid residue. They can often be controlled by improving operating
procedures. For instance, it was reported that production of solid residue could be minimized by increasing the plasma discharge volume and using additional dielectric tubes 34.

3.3 Effect of temperature

Fig.5 (a) presents the effect of temperature on the conversion of toluene and energy efficiency. It can be seen from fig. 5 (a) that the conversion and efficiency are not affected when increasing the temperature from 20 °C to 300 °C. This was partially because nearly complete removal of tar took place at 40 W. However, the decomposition of toluene started to decrease after 300 °C and reduced to 87 % at 400 °C. It has been reported that the decomposition of toluene decreases due to decrease in quartz electric insulativity which affected the plasma characteristics and formation, and reduced the intensity of the discharge 35. Similarly, the decrease in conversion of toluene was observed in CO2 carrier gas at elevated temperatures 36. On the contrary, the decomposition of toluene did not decrease at elevated temperatures in H2 carrier gas and solid formation completely disappeared due to conversion into lower hydrocarbons. Therefore, the decrease in the conversion of toluene in other carrier gases may be possible due to presence of solid residue/soot which influences the plasma properties.

The elevated temperature had a significant influence on the chemistry of the products. Fig.5 (b) presents the effect of temperature towards the selectivity of lower hydrocarbons at different H2 concentrations and it shows that selectivity to lower hydrocarbons increased from 5.5 % to 10 % in the pure N2.
Fig. 5 Effect of temperature on: (a) the conversion of toluene; (b) Total selectivity to LHCs formation (C₁-C₆); (c) Selectivity to individual LHCs, 15% H₂ (d) Selectivity to individual
LHCs, 25% H₂ (e) Selectivity to individual LHCs, 35% H₂. Reaction conditions: input power=40 W; and concentration =33g/Nm³; and residence time=4.23 s; and SIE=59.11 kJ/L

The different concentrations (15-35 %) of hydrogen were added to eliminate the problematic solid formation. It can be seen that selectivity of LHC increases from 20 % to 45 % using 15 % hydrogen at 400 °C, and it reaches 57 % by increasing the hydrogen concentration to 35 %. At high temperatures, hydrocracking of aromatics is responsible for the increase in selectivity of lower hydrocarbons. In the presence of hydrogen, hydrogenation and isomerization reactions occur at lower temperatures at the lower activation energies, whereas cracking requires high temperatures. The following reactions take place at elevated temperature in the presence of hydrogen.

Fig. 6. Reaction mechanism at high temperature

Fig. 5 (c) presents the selectivity of individual lower hydrocarbons. It can be seen that the selectivity of methane gradually increases from 10 % to 20% with increasing the temperature
from ambient to 400°C. The selectivity to C₂-C₃ decreased at higher temperatures due to cracking to CH₄. The production of methane increased due to cleavage of aromatic and aliphatic compounds in the presence of plasma at elevated temperatures 3⁹. However, the formation of benzene occurred at high temperature and its selectivity reached 14 % at 400°C. This was because radical exchange reactions took place at high temperature in the presence of hydrogen 3⁸. Fig. 5 (e) shows that selectivity to methane increased to 44 % by raising the H₂ concentration to 35% at elevated temperature (400°C). This occurred due to plasma assisted hydrocracking conversion of hydrocarbons in the presence of excess H₂ at elevated temperatures ⁴⁰.

4. Conclusions

In this study a DBD reactor was used to decompose a biomass gasification tar analogue (toluene). The performance of the reactor was studied as a function of process conditions: power (5-40 W), residence time (1.43-4.23 s), concentration (20-82 g/Nm³), and temperature (ambient-400 °C). The key findings from the experimental results can be summarized as follows:

1. Almost complete removal of tar was achieved, at 20 W and 4.23 s. The main products were hydrogen, lower hydrocarbons and solid residue.
2. The decomposition efficiency of toluene depends upon power, residence time and concentration. It increases with power and residence time. The maximum conversion here was obtained at 40 W and 4.23 s (the highest level used). The conversion decreased slightly with increasing toluene concentration.
3. At ambient conditions, the selectivity to lower hydrocarbons remained below 6%. However, it increased to 10 % by increasing the temperature to 400°C.
4. Solid deposition took place inside the reactor. This is generally an undesirable effect, but it can be substantially reduced by introducing H₂.

5. At elevated temperatures in the presence of H₂, the selectivity to lower hydrocarbons increased with increasing hydrogen concentration. It reached 57% at a concentration of 35% of H₂ at 400 °C. The main product in these conditions was CH₄, formed from decomposition of the aromatic ring. Its proportion increased with increasing temperature and power to as high as 44%.

Acknowledgements

The financial support is provided to first author by University of Engineering and Technology Lahore, Pakistan to conduct PhD research, and the EPSRC Supergen Bioenergy Hub.

References


