Removal of Benzene as a Tar model compound from a Gas Mixture using Non-thermal plasma Dielectric barrier Discharge reactor

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Abstract

In the present work, the decomposition of benzene as a tar model compound was studied in a gas mixture (CO₂, H₂, CO, and CH₄) using a dielectric barrier discharge (DBD) non-thermal plasma reactor. The combined effect of temperature and power was studied to investigate the performance of the DBD reactor. The decomposition of tar compound increased from 49.9 to

96 % with increasing specific input energy (SIE) from 2.05– 16.4 kWh/m³. The major products were lower hydrocarbons (C₂-C₅) and solid residues. The higher temperature (400 °C) in the presence of plasma (40 W), decreased the conversion of tar compound from 96 to 78 %. However, the selectivity of lower hydrocarbons increases substantially to 52 %, and the formation of solid residues is significantly reduced. Hence, the problematic solid residues formation can be controlled at a higher temperature during the treatment of gasifier product gas using non-thermal plasma.

Keywords: Non-thermal plasma; biomass gasification tar; dielectric barrier discharge; Benzene.

1. Introduction

In the past few decades, the climate of the earth is changing drastically and the emission of greenhouse gases (GHGs) is playing a vital role in affecting the climate. This ongoing growing concern of climate change due to global warming has emerged as one of the vital reasons to explore renewable energy resources [1-3]. The gasification of biomass is an alternative technique to produce eco-friendly fuels for transport and power generation. In this technique, the indirect combustion of solid biomass produces gaseous fuel or synthesis gas (CO+H₂) fuel by partial oxidation [4]. The medium for partial oxidation of biomass gasification can be oxygen, air, or steam. Air gasification produces low-quality gas which has a heating value from 4 to 7 MJm⁻³, so is not good for pipeline transportation due to its lower energy density. However, it is better for boiler, engine, and turbine operations. Higher quality gas is achieved when the gasifying medium is oxygen (10–18 MJm⁻³). Therefore, it is suitable for limited pipeline distribution and the production of valuable chemicals (methanol and gasoline) from synthesis gas. Steam gasification also produces higher quality gas and lower amounts of tar and char than air gasification due to more reactions of water gas [5]. However, the air is mostly

used as a gasifying medium because of the hazards and costs associated with the oxygen medium gasification; and the cost and complexity of multiple reactors are the drawbacks of steam medium gasification [6]. The biomass-based-gaseous fuels have high heat content and can be an excellent source of energy, replacing fossil fuels, in transportation sectors and power production [7]. H_2 can be used as a fuel it can be produced from the gasification of biomass along with other useful products [8-10]. The gasification of biomass can produce a variety of product gases depending upon the nature of feedstock, operating conditions (temperature and pressure), gasifying medium (oxygen/steam/air), and gasification methods [1, 4]. The gasification of biomass produces various lower hydrocarbon products along with N_2 , CO, H_2 , CH_4 , and CO_2 when air is used as a gasifying medium [1]. Apart from these valuable gaseous products, the impurities like tars and particulates are also produced [1, 11, 12]. Tars are complex mixtures of aromatic hydrocarbons and the one ring aromatic hydrocarbons (benzene, toluene, xylene, etc.) are found in maximum concentration, and upon condensation in mechanical parts such as the engine, filters, pipes, and heat exchangers cause serious operational problems [13]. The tar formation can cause blockages in the mechanical equipment, hence, causes a considerable effect on the heat transfer process. This causes a decrease in the efficiency of the process as a result increase in the maintenance and operational cost of the unit operation [14, 15]. Therefore, the decomposition of tar compounds from the product during biomass gasification is of utmost importance [7].

Non-Thermal Plasma (NTP) is an efficient technique to clean product gas from the gasifier. In this technique, the produced electrons are accelerated using the electric fields. The gaseous atoms and molecules are ionized by the high-speed electrons upon impact with them [16]. The energy-value of 5 – 25 eV is needed to ionize or dissociate the gases. [17, 18]. It was reported that the gaseous molecules are dissociated due to the presence of a sufficient quantity of energetic electrons in the Maxwellian distribution [19]. The electrons have a very high

temperature than heavy particles (atoms, molecules, and ions) because these electrons absorb more energy than heavy particles [20]. However, the transfer of energy from electrons to heavy particles is relatively small due to the smaller mass of electrons as compared to the heavy particles [21].

Considerable work has been reported in the literature for the removal of tar compounds using different types of NTPs [22-28]. To investigate the decomposition of tar, researchers studied the performance of the microwave plasmas [29, 30]. They reported that the decomposition of tar decreases at a higher flow rate and concentration. The primary products were acetylene, soot, and benzene derivatives in the N₂ carrier gas. However, the steam addition enhanced the tar conversion into CO₂, H₂, and CO products [30]. Chun et al. [31] reported the decomposition of a tar compound in an externally oscillated plasma reformer. The tar model compound was converted to gaseous products such as CH₄, CO, CO₂, H₂, C₂H₄, and C₂H₆. They observed that the decomposition of benzene also caused the formation of carbon black [31]. Liu et al. [32] reported that the addition of steam not only improved the energy of the process but also increased the tar removal efficiency. Nunnally et al. [22] studied the oxidative steam reforming of tar compounds in a gas mixture using gliding arc discharge (GAD) plasma and found that a higher concentration of tar has an adverse effect on the conversion of the tar model compounds. However, the conversion of tar model compounds increases in the presence of high moisture contents [22]. Hence, the addition of steam enhances the conversion of tar and reduces unwanted by-products.

Non-thermal plasma Dielectric barrier discharge reactor is being used to remove toxic and troublesome compounds from gases and liquid [33-37]. Most recently, Saleem et al. used the dielectric barrier discharge (DBD) reactor to decompose benzene in H₂ and CO₂ carrier gases [38]. The production of solids was observed to completely vanish at an elevated temperature in the presence of H₂ carrier gas. C₁-C₂ were the only major products. It was also observed that

at high-temperature methane had maximum selectivity in H₂ carrier gas [38, 39]. The effect of temperature (20-400 °C) and specific input energy (SIE) (2.05-16.4 kWh/m³) on the performance of the process was also studied. Benzene was considered as a tar analogues due to its thermal stability and it has also been used as tar representative in various literature work [31, 40-44].

In the current study, the decomposition of biomass gasification tar was studied in a gas mixture (CO₂, H₂, CO, and CH₄) using a DBD non-thermal plasma reactor. The process parameters such as temperature and input power correspond to SIE have been investigated to check the performance of the DBD reactor. Furthermore, the combined effect of the temperature and power is elucidated for maximum removal efficiency.

2. Experimental setup and procedure

Fig. 1 shows the schematic diagram of the experimental setup. The NTP coaxial DBD reactor was used to investigate the decomposition of tar representative (benzene). Stainless steel (SS) external electrode (30 mm) was wrapped outside the external quartz tube with 15 mm inner diameter and 18 mm outer diameter. The inner SS electrode was placed inside the inner quartz tube having an outer diameter of 12 mm. The plasma was produced between the annular spaces of the coaxial quartz tubes. A variac AC transformer (purchased from RS online) was connected to the plasma generator (frequency about 20kHz, voltage pk-pk 20 kV, 0-150 W from Newcastle University) to control the discharge power to the DBD reactor. In this study, the input power was varied from 5 to 40 W. The length of the discharge zone depends upon the outer electrode (shortest electrode) [16].

The flow rate of the synthetic product gas mixture (H₂: 41 %, CO: 23.5 %, CO₂: 23 %, and CH₄: 12.5 %) was controlled by using computer-controlled mass flow controllers, connected to gas cylinders (BOC, UK). The gas mixture was passed through a bubbler filled

with benzene (99.8% anhydrous, sigma-Aldrich) to add the vapours. An electric furnace was used to investigate the performance of a DBD plasma reactor under high-temperature conditions. The furnace temperature was controlled, over the range ambient to 400 °C.

The compositions of the reaction product were measured using a Varian 450-GC equipped with a TCD (Thermal conductivity detector) to measure CH₄ and H₂, CO₂, CO, and an FID (flame ionization detector) to measure lighter hydrocarbons (LHC) including C₂ (C₂H₄, C₂H₆), C₃ (C₃H₆, C₃H₈), C₄ (C₄H₈, C₄H₁₀), C₅ (C₅H₁₀, C₅H₁₂), and C₆H₆). There were 5 columns and 3 detectors (2 FID and 1 TCD) along with 2 ovens were equipped on GC. To detect permanent gases (N₂, CH₄, CO, CO₂, O₂, H₂), one of the oven is housed with three columns with TCD: i) HAYESEP T 0.5m×1/8"×2.0mm Ultimetel (#CP81072) ii) HAYESEP Q 0.5m×1/8"×2.0mm Ultimetel (#CP81073) iii) Molsieve 13X 1.5m×1/8"×2.0mm Ultimetel (#CP81071). Whereas, the second oven is housed with 2 columns: i) CP-SIL 5CB column (25 m, 0.25mm, 0.4 µm, #CP7709) to detect hydrocarbons with FID, ii) CP-WAX 52CB column (25 m, 0.32mm, 1.2 µm, #CP7763) to detect alcohols with FID [45].

Fig.1. Experimental setup

2.1 Definitions

The removal efficiency of benzene was defined as follows [46]:

$$d_B = \frac{(C_6H_6)_{in} - (C_6H_6)_{out}}{(C_6H_6)_{in}} \times 100$$

The following formulas were used [23, 47, 48] :

$$\text{Decomposition of CO}_2(\%) = \frac{(CO_2)_{in} - (CO_2)_{out}}{(CO_2)_{in}} \times 100$$

$$\text{Decomposition of CH}_4(\%) = \frac{(CH_4)_{in} - (CH_4)_{out}}{(CH_4)_{in}} \times 100$$

$$\text{LHC selectivity (\%)} = \frac{\sum (m \times \text{moles of } C_mH_n)}{6 \times (\text{Moles of } C_6H_6 \text{ converted}) + \text{Moles of } CH_4 \text{ decomposed}} \times 100$$

Where $m > 1$

$$\text{Specific input energy (SIE) (kWh/m}^3\text{)} = \frac{\text{Power (kW)}}{\text{Total flow rate of gas (m}^3\text{/hr)}}$$

The energy efficiency was calculated using the following formula [45, 49]:

$$\text{Energy efficiency (EE) (}\frac{\text{g}}{\text{kWh}}\text{)} = \frac{\text{benzene decomposed (g/min)} \times 60000}{P \text{ (W)}}$$

3. Results and discussion

3.1 Effect of Specific input energy

Fig. 2 clearly illustrates that the decomposition of benzene increases with an increase in the SIE. The SIE could be controlled through flow rate and input power. However, in this study, the flow rate was not varied, and SIE increased due to an increase in input power. It was reported that increasing the input power produces a higher number of energetic electrons, consequently, the collision between energetic electron and gas molecules enhanced and produce more reactive species [50-53]. Hence, more energetic electrons and reactive species contribute to higher conversion of benzene at higher SIE [54, 55]. Equations 1-3 show that higher-energy electrons can create potential reactive species (O, H, and CH₃) from background gas, which contribute to produce different products. It has been reported that O played a dominant role in the decomposition of tar compounds, whereas H radicals can be terminated by the background gas [56].

These reactive species decompose the benzene

Radical termination reaction can also take place

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175 Fig. 2. Conversion and energy efficiency of benzene as a function of SIE. Operating
 176 conditions: RT, 2.82 s ; Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

177 Darwent et al. [57] reported that C-H has minimum bond dissociation energy in benzene
 178 molecules. This shows that the removal of benzene, via the abstraction of H from the C-H, can
 179 initiate at less SIE. However, at higher SIE, the number of electrons having higher energy
 180 increases which can decompose the C-C bonds as well. The following general reactions (Eq.11-
 181 14) are involved during the cracking of benzene molecules:

182 The energy efficiency reduces with an increase in SIE as shown in Fig. 2. Saleem et al. studied
 183 the decomposition of toluene using H₂ carrier gas and reported similar trends for the
 184 decomposition of tar compounds [39].

Fig. 3 Effect of SIE on (a) the decomposition of CO₂ (b) the decomposition of CH₄, and (c) the vol. % of CO and H₂. Operating conditions: RT, 2.82 s ; Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

Fig. 3 explains the decomposition of CH₄ and CO₂ increases with an increase in SIE. This may be possible due to the increase in the dissociation of CO₂ to CO and O at higher power [58], while methane decomposition endorses the combination of, CH₃, CH₂, and CH radicals [59]. Previously, this has been demonstrated that the reforming of CO₂ and methane (Eq. 15) can cause higher decomposition of CO₂ and methane [48, 60].

Fig.4 Selectivity to individual LHC as a function of SIE. Operating conditions: RT, 2.82 s ;
Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

Fig. 4 illustrates the effect of SIE on the selectivity to C₂-C₅. Previously, it was reported that the selectivity of LHC was 18% at 40 W and the residence time of 2.82 s [61]. In the present work, the selectivity to LHC reaches 24.5 % under the same operating conditions. The increase in selectivity is possible due to the addition of methane in the carrier gas: some of the LHC will be formed due to decomposition of the ring, whereas decomposition of methane can also contribute to the formation of LHC. It has been observed that the impact of electrons generates CH₃, CH₂, and CH, which can agglomerate to produce the lower hydrocarbons [59, 62].

Fig. 5. ln of the remaining fraction of benzene as a function of SIE. Operating conditions: RT, 2.82 s ; Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

It was noted that the NTP processes majorly depend on energy because of very fast plasma reactions [58]. From Fig. 5, the $\ln$ of the remaining fraction of benzene with respect to SIE follows a linear trend. Hence, the removal of benzene in this plasma reactor shows first-order behaviour with respect to SIE.

The removal of benzene formed light yellowish solid residues. These residues would create operational problems, via fouling and eventual blockage of pipework. Hence, it is important to solve this problem. It has been reported that high temperatures in the presence of H radicals could eradicate the production of solids [61].

3.2 Effect of temperature

The effect of temperature at constant input power was investigated on the decomposition of benzene and product distribution. Fig. 6 illustrates the decomposition of benzene as a function of temperature at 40 W power. It can be seen that the decomposition of benzene decreases with an increase in temperature and the drop-in conversion is more prominent after 200 °C. The possible reason is the recombination reactions of hydrogen and phenyl radicals. Previously, it was found that during toluene decomposition, higher temperature promoted the benzene formation under constant input plasma power [39]. Therefore, the decomposition of benzene may be decreased at higher temperatures due to the production of benzene. Moreover, heating the gas could accelerate ionization and lead to the formation of different species that can consume radicals and other reactive species from the plasma. Hence, the benzene conversion was reduced.

Fig.6. Decomposition of benzene and energy efficiency as a function of temperature.

Reaction conditions: SIE, 16.42 kWh/m³ ; RT, 2.82 s ; Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

Fig. 7 shows that the decomposition of CO₂ and CH₄ decreases with increasing temperature. The decomposition of CO₂ and CH₄ decreased from 8.8-2.2 % and 21.2 to 4.3 % respectively, with increasing temperature from ambient to 400 °C. For CO₂, This may be possible due to the recombination reactions of oxygen and carbon mono oxide radicals [63]. However, for CH₄, this may be happened due to the production of methane from the cracking of tar compound because of the combined effect of plasma and temperature [64]. Previously, It has been observed that selectivity to CH₄ increases (60%) during the plasma-assisted cracking of toluene at high temperatures [61].

Fig. 7 Product distribution as a function of temperature. Reaction conditions: SIE, 16.42 kWh/m³ ; RT, 2.82 s ; Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

From Fig. 7, it can be seen that temperature increases the selectivity to C₂-C₅ increases to 52 %. On the contrary, in our previous work, it was reported that increasing the temperature reduced the selectivity to C₂-C₆ because of methane formation [61]. Methane was not included in the carrier gas and it was reported that the cracking of C₂-C₆ to CH₄ occurred at 400 °C and 40 W [65]. In the present work, CH₄ was present in the carrier gas mixture, and it has been observed that CH₄ decomposition can contribute to producing lower hydrocarbons (C₂-C₅)[59]. Therefore, the selectivity to C₂-C₅ depends on the cracking of benzene and the decomposition of methane.

Fig. 8 Selectivity to individual LHC as a function of temperature. Reaction conditions: SIE, 16.42 kWh/m³; RT, 2.82 s; Concentration, 39 g/Nm³; and flow rate, 40.6 ml/min.

Fig. 8 explains that temperature has a positive effect on the selectivity to C₂. However, in our previous study, it was seen that at higher temperature (> 300 °C) selectivity of C₂ started to decrease [61]. This again, perhaps suggests that the addition of CH₄ is acting as a source of C₂. On the other hand, the selectivity of C₃-C₅ started to decline after 300 °C because of the cracking of them. It was found that the production of solid residue was substantially reduced and converted into LHC (52 %). Hence, the combined effect of plasma and temperature could control the formation of problematic solid residues.

4. Conclusions

In summary, higher temperature stimulates the rapture of the aromatic ring due to the presence of hydrogen. Therefore, a solid formation that occurred at ambient temperature decreased at elevated temperature of 400 °C. The decomposition of methane also decreases from 21.2 to 4.3 % at higher temperatures due to the formation reaction of methane from benzene cracking. CH₄ presence in the carrier gas significantly enhances the selectivity to lower hydrocarbons (24.5 %) due to recombination reaction of CH₃, CH₂, and CH radicals, which produced from dissociation of methane in the plasma discharge. At elevated temperature, selectivity to LHC further increased from 24.5 to 52 % due to cracking of the benzene ring. Hence, the higher temperature in the presence of methane promotes the selectivity to lower hydrocarbons during the decomposition of tar compounds.

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