The role of CO₂ in the conversion of toluene as a tar surrogate in a non-thermal plasma dielectric barrier discharge reactor

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Abstract

The decomposition of toluene (a model tar compound) in CO₂ was investigated at ambient and elevated temperatures in a dielectric barrier discharge (DBD). The effects of reaction parameters such as residence time (0.47 s to 4.23 s), plasma power (5 W to 40 W), toluene concentration (20g/Nm³ to 82 g/Nm³) and temperature (20°C to 400°C) were investigated. The DBD was shown to be an effective technique for tar removal. The percentage removal of tar increased with increasing plasma power and residence time (to as high as 99%, at the residence time of 4.23 s). The maximum selectivity to the two major gaseous products, CO and H₂, were 73.5% and 21.9% respectively. Solid residue formation was also observed inside the reactor. The synergetic effect of temperature and plasma power was studied. As temperature increased the decomposition of toluene decreased slightly from 99% to 88% (from ambient to 400°C, at 40 W), and the selectivity of CO and H₂ decreased

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due to the increased rate of recombination of CO and O. The selectivity to lower hydrocarbons (LHC) increased with temperature.

1. Introduction

The use of biomass as a source of renewable energy is gaining attention because of the depletion of fossil fuels and global warming. Biomass gasification is a method for producing alternative, eco-friendly fuels for power generation and transport. It is an indirect combustion process in which solid biomass is converted to synthesis gas or gaseous fuel by partial oxidation at high temperatures ¹. The product gas contains high concentrations of H₂ and CO, which is usually referred to as synthesis gas, or “syngas”. The composition of syngas depends upon several parameters including the gasification method, the nature of the feedstock, operating conditions, etc. It can be used for production of valuable chemicals and, as fuels in gas engines and gas turbines. In addition to syngas, the product gas also contains dust and gas impurities such as nitrogen, chlorine, sulphur and tar compounds ². Among these, tar is the most problematic by-product, as it can condense in engines, filters and heat exchangers upon cooling in the downstream of the gasifier. It increases the maintenance cost and decreases the process efficiency. Therefore, the effective removal of tar compounds is desirable ³.

Generally, decomposition of tar is applied after the gasifier and there are a variety of methods that can be used to eliminate tar compounds, such as mechanical separation, thermal cracking and catalytic cracking. In mechanical separation, tar is removed by: Venturi scrubbers, water scrubbers, ESP, rotational particle separators or cyclones. However, these methods only remove or capture the tar from producer gas, causing secondary pollution. Moreover, the chemical energy associated with tars is also wasted⁴.

Thermal and catalytic cracking can be used to decompose tar compounds, but these technologies also have disadvantages: operating cost, for instance, is significantly increased by maintaining high temperature in thermal cracking ⁵. Catalytic cracking is a good way to decompose tar into valuable products and operates at lower temperatures than thermal decomposition of tar ⁶. However, various catalysts may be poisoned due to their high affinity for sulphur and chlorine. Fouling, which arises due to coking, is another problem, and it is difficult to control unless the feed of the gasifier is well tested. The major contaminants of the product gas are chlorine, sulphur and nitrogen compounds ⁷. Hence it is a significant challenge to decompose the tar completely, due to its complex nature and the unavailability of proven, efficient technology.

Downstream non-thermal plasma (NTP) treatment of tar is a possible solution due to its high efficiency and compact design. The NTP produces high energy electrons (1-10eV) that decompose the carrier gas and generate reactive species at normal temperature ⁸. It consists of many active species, which cause electron impact excitation, light excitation, dissociation excitation, ionization, radiative recombination and atomic photoionization, etc. These phenomena or combinations of them can convert the tar into lighter hydrocarbons.

Various plasma techniques have been used to crack biomass gasification tars, using toluene as a tar surrogate. The results obtained so far were generated by plasma-enhanced catalytic steam reforming, where it has been found that the removal efficiency of toluene can be increased from 37% to 57% using non-thermal plasma. The selectivity towards CO and H₂ has been shown to increase in the presence of Ni/SiO₂ ⁹.

Nair used pulsed corona discharge plasma for the removal of tar from product gas¹⁰. It was demonstrated that the cracking of naphthalene in nitrogen is more economical than cracking in product gas. It had been observed that the energy requirement for this process was very high, as 20% of the output energy of the biomass gasification was consumed to remove the tar from fuel gas¹⁰. The efficiency, at 95%, was higher than thermal or catalytic cracking.

An atmospheric dielectric barrier discharge (DBD) reactor is a more attractive method for conversion of tar compounds. It has been widely studied for the removal of volatile organic compounds to address environmental problems¹¹. It has been demonstrated that the removal efficiency increases with increasing residence time and specific input energy. In another study, a wire plate dielectric barrier discharge was used with alumina/nickel foam/manganese oxide catalyst to investigate the decomposition of toluene at ambient pressure and temperature¹². The complete removal of toluene was shown to be possible. Manganese catalysts and a DBD reactor were used to decompose the toluene in air as carrier gas¹³.

In this study, a DBD was used to decompose the toluene in CO₂ carrier gas. The role of CO₂ in product selectivity and decomposition of tar analogues was investigated as it makes up a significant proportion (15%-25%) of the gasifier effluent¹⁴. It can help to understand the mechanism of tar decomposition in actual product gas from gasifiers, which mainly consists of CO₂, H₂, CO and N₂¹⁴. The effects of power, residence time, concentration and temperature on the removal of toluene and towards the selectivity of various compounds. Toluene was selected, as it has been used for many studies of gasification tars, due to its high thermal stability, simple structure and low boiling point.

2. Materials and Methods

2.1 Experimental setup

Fig.1 presents the experimental setup used in this study. A cylindrical dielectric barrier discharge (DBD) was used, consisting of two metal electrodes, one outside a cylindrical glass quartz tube (330 mm length, 15 mm inner diameter, 18 mm outer diameter) and the other inside the inner tube (outer diameter 12 mm). Both the outer mesh and inner metal sheet were made from 316 stainless steel. The plasma was generated in the annular space between the coaxial cylindrical tubes. The input voltage of the plasma power source unit and the plasma power dissipated in the plasma reactor were controlled using a variac.

The gas cylinders (BOC, UK, 99.8%) were connected to mass flow controllers, which were computer-controlled to regulate the flow of gas streams. The gases were passed through a bubbler to saturate them with toluene (Figure 1). The concentration of toluene was fixed at 82g/Nm³. To study the effect of temperature on the performance of plasma, the reactor was placed inside a tubular furnace that had a maximum temperature of 400°C.

The composition of product gas was measured using a Varian 450-GC. Argon gas (mobile phase) was used to carry the product gas through the column, and zeolite (13x) molecular sieve was used as a packing (stationary phase) material inside the column.

2.2 Definitions

The decomposition efficiency of toluene and CO₂ were defined as:

$$d_T = \frac{\text{moles of toluene in input stream} - \text{moles of toluene in outlet stream}}{\text{moles of toluene in input stream}} \times 100$$

$$\text{CO}_2 \text{ decomposition} = \frac{\text{moles of CO}_2 \text{ converted}}{\text{moles of CO}_2 \text{ input}} \times 100$$

The selectivity of different products were defined as follows:

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

$$\text{CO selectivity (\%)} = \frac{\text{moles of CO produced}}{7 \times \text{Moles of C}_7\text{H}_8 \text{ converted} + \text{moles of CO}_2 \text{ converted}} \times 100$$

$$\text{LHC selectivity (\%)} = \frac{\sum (m \times \text{moles of C}_m\text{H}_n)}{7 \times \text{Moles of C}_7\text{H}_8 \text{ converted}} \times 100$$

The yield of products was defined as:

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{moles of H}_2 \text{ produced}}{4 \times \text{total moles of C}_7\text{H}_8 \text{ inlet stream}} \times 100$$

$$\text{CO yield (\%)} = \frac{\text{moles of CO produced}}{7 \times \text{moles of C}_7\text{H}_8 \text{ input} + \text{moles of CO}_2 \text{ input}} \times 100$$

The energy efficiency was calculated using the following formula:

$$\text{Energy efficiency (}\frac{\text{g}}{\text{kWh}}\text{)} = \frac{\text{grams of toluene converted per min}}{P \text{ (W)} \times 60/3600000}$$

The carbon balance was defined as:

$$\text{Carbon balance} = \frac{\sum C_{\text{measured}}}{\sum C_{\text{feed}}} \times 100$$

3. Results and discussion

3.1 Effect of Power

Plasma power is an important factor affecting the reaction in a NTP. Toluene decomposition products include CO, H₂, lighter hydrocarbons (LHC) including C₁-C₅, and heavier hydrocarbons. Fig.2 (a) shows the effect of input plasma power on decomposition of toluene. The initial concentration of toluene was 82g /Nm³. It was observed that toluene decomposition efficiency increased with increasing plasma power. The maximum removal of toluene was 99%, achieved at 40 W and a residence time of 4.23s. Previous experimental studies showed that increasing plasma power increased the electron density, electric field and gas temperature¹⁵, which could increase the conversion of toluene. Moreover, the formation of active species, such as ions, radicals, and excited molecules can also enhance the cracking of toluene.

Fig.2 (a) also shows that the energy efficiency decreases from 22 g/kWh to 5 g/kWh with increasing plasma power from 5 W to 40 W. The similar results were reported for destruction of toluene in gliding arc discharge¹⁶.

Fig.2 (b) shows the selectivities of various gaseous products as a function of the discharge power at a residence time of 4.23 s. The selectivity to CO slightly increases from 5 to 10 W, after which it rises exponentially up to 30 W. This is because the dissociation of CO₂ also increases at high power, which increases the selectivity of CO exponentially. The selectivity to H₂ increases linearly with power, whereas the selectivity of lower hydrocarbons remains below 4 % at various levels of power.

Fig.2 (c) presents the relationship between yield of valuable gases and discharge power. The yield of both products (CO and H₂) shows a linear relationship with power. The yields of CO and H₂ reach 17 and 21 % respectively, at 40 W and 4.23 s. Clearly, increasing plasma power is beneficial for improving the yield of CO and H₂.

The effect of power on the decomposition of CO₂ is shown in fig.2 (d). The graph shows that decomposition of CO₂ increases with the rise of plasma power, and the maximum decomposition of CO₂ (14 %) is obtained at 40 W and 4.23 s. This is consistent with previous experimental results regarding CO₂ decomposition¹⁷.

In NTP, the cracking of CO₂ may take place through electroionization dissociation channels and electron impact dissociation:

The threshold energy requirement for electron impact dissociation (Reaction (1)) is 5.5 eV¹⁸, whereas the all other three channels (Reaction (2),(3) and (4)) require electron energies from 19 to 40eV¹⁹. Therefore, the main reaction for CO₂ decomposition is likely to be the electron impact dissociation. The dissociated O and CO can combine to produce CO₂ or O₂²⁰, as follows:

3.2 Effect of concentration

The decomposition of toluene was studied at various concentrations (20 g/Nm³, 32 g/Nm³, 60 g/Nm³ and 82g/Nm³), to observe the effect on the conversion of toluene. Fig. 3(a) shows that the removal efficiency of toluene decreased from 94% to 77% when increasing the concentration to 82 g/Nm³. The decomposition efficiency of toluene decreased as the concentration increased. This has also been observed in rotating gliding arc discharges²¹. Fig. 3 (b) presents the selectivity of different gaseous compounds, it can be seen that the selectivity of CO decreases from 78% to 36 % as the concentration increases. The selectivities to hydrogen and LHC also decrease with increasing the concentration of toluene.

Fig.3 (c) represents that, at 20 W, the percentage decomposition of CO₂ increases from 5.4 % to 7.8 % with changing the concentration from 20 g/Nm³ to 82 g/Nm³. This may be due to increasing collisions between O radicals and toluene radicals rather than CO,

which increases the consumption of O, thereby shifting the CO₂ decomposition equilibrium to the product side.

Fig.3 (d) shows the effect of concentration of toluene on the energy efficiency of plasma. The energy efficiency increases from 5 g/kWh to 16 g/kWh by changing the concentration from 20 g/Nm³ to 82 g/Nm³. This is because the quantity of cracked toluene increased, whereas the plasma input energy and flow rate were kept constant. This agrees with previous work in which GAD(Gliding arc plasma) plasma¹⁶ and RGD(Rotating gliding arc discharge) plasma²¹ were used.. However, the efficiencies are higher: GAD plasma (3.6g/kWh)²² and microwave plasma (4.52 g/kWh)²³.

3.3 Effect of residence time

The residence time is an important parameter influencing tar decomposition. Figure 4 (a), below, shows that the decomposition of toluene increases with increasing residence time. At 40 W, decomposition of toluene increases continuously from 71% to 99%, as the residence time increases from 0.47 s to 4.23 s. Similar results were reported for the decomposition of toluene by GAD ¹⁶.

The selectivity towards the various gaseous products are also shown in fig. 4(a). H₂ and CO are two major gaseous products that form during the decomposition of toluene. The selectivity of both products increased with increasing residence time, and the maximum selectivity reached 73.5% for CO and 21.9 % for H₂, at 4.23 s and 40 W of power. This may be due to the increase in the residence time in the plasma discharge, which increases collision frequency between toluene molecules, electrons and reactive radicals (O). It has previously been observed that O radicals are produced from the dissociation of CO₂ in plasma reactor¹⁷. They react with toluene fragments to produce CO and hydrogen ¹². The

hydrogen is probably formed from toluene by H-extraction, because initially, hydrogen atoms come from the methyl group, as the C-H bonds in CH₃ are the weakest bonds in the C₇H₈ molecule²⁴. As for CO and LHC, they are probably formed by the decomposition of C-C bond, as it is suggested that toluene is decomposed in plasma by two types of reaction: (1) abstraction of methyl group (2) cracking of benzene ring²⁵. LHC could be produced by decomposition of C-C bond with reaction energy values less than 8 eV²⁶. The selectivity to lower hydrocarbons, which slightly increases with increasing residence time. However, it remains lower than 4% at all tested conditions, which is consistent with previous experimental results²¹.

Fig. 4(b) shows that the yield of CO and H₂ also increased with residence time, which would ultimately increase the production of valuable syngas. It was reported that decomposition of toluene could be achieved via three routes: (a) dissociation through electron impact, (b) radical reactions, and, (c) ion-molecule reactions²⁶. It was noted that the most important channel for the initial reactions in toluene cracking was electron impact. The 2nd important mechanism for toluene decomposition was radical attack. However, the direct ion process does not have a significant effect on destruction of toluene²⁷. Fig.4 (b) also shows the effect of residence time on the decomposition of CO₂. The trend of the graph shows that the decomposition of CO₂ increased linearly with residence time from 7% to 14 %, with increasing residence time, from 0.47 to 4.23 s, at 40 W. It is similar to Yu et al. (2012), who reported CO₂ decomposition in a DBD reactor. The expected toluene destruction process is represented in fig. 5.

During the treatment of toluene, formation of a solid, black deposit was observed inside the plasma zone. It was noted that the solid residue showed agglomerating tendencies.

The formation of solid deposits decreases with increasing the residence time. The mass of the residue was determined by measuring the weight of the reactor before and after the reaction. It was observed that, at 40 W and 4.23 s, the formation of solid residue increased with decreasing residence time. Guo et al. reported that the formation of solid residue increased in limited supply of oxygen¹². The deposits was dark brown and tarry. Similar deposits have been described as polymeric substances, or carbonaceous deposits²⁸.

These solid residues can clog the reactor if not managed properly. These deposits can be removed from the surfaces of the DBD reactor by converting them into CO, CO₂ and lower hydrocarbons. It was reported that in the presence of excess oxygen, almost all decomposed toluene were transformed to CO₂ and CO¹². Moreover, the presence of other gases like CO₂, CO, N₂ and H₂ in the product gas from gasifier can contribute towards the removal of solid residue¹⁴. It has previously been demonstrated that the solid deposition problem could also be resolved by increasing the plasma volume and placing additional dielectric tubes²⁹.

3.4 Effect of Temperature

Experiments were performed to determine the dependence of decomposition efficiency of toluene and product distribution, on temperature and plasma power, at a specific residence time (4.23 s). Fig. 6(a) shows that conversion of toluene slightly decreases with increasing temperature, from 200°C to 400°C, due to the increasing rate of the recombination reaction of the CO and O radicals, which reduces the amount of reactive species²⁰. Consequently, the conversion decreases from 99 % to 88 %, at 40 W. This contrasts with Song *et al.* (2002), who reported high removal rates of toluene from air at elevated temperature³⁰. Elsewhere, it was shown that elevated temperature increased the

removal efficiency of VOC. This was explained by the increased kinetic reaction of O radicals with tar compounds³¹. However, in those experiments air was used as a carrier gas instead of CO₂ to decompose VOC. It was found that decomposed O and CO radicals could be combined to form CO₂ and O₂ and reduced the concentration of reactive species in the plasma zone²⁰. Elevated temperature favours recombination reactions. Fig. 6 (c) shows that the decomposition of CO₂ decreases with increasing temperature (due to recombination reactions of dissociative radicals).

A possible reason for decreasing the conversion of toluene at elevated temperature in CO₂, is the re-association of O and CO radicals rather than O radicals reacting with toluene. In this way, the overall conversion of toluene is reduced in CO₂ carrier gas at elevated temperature.

Fig. 6 (b) and(c) shows the selectivity and yield of CO H₂ and LHC .The selectivities of CO and H₂ decrease from 73.5% to 49 % for CO, and from 21.9 % to 12.6 % for H₂, by increasing the temperature to 400°C. However, selectivity to LHC increases gradually from 3.5 to 12.8 % with the increase of temperature. A possible reason is the hydrocracking of toluene at elevated temperature , leading to a higher concentration of lower hydrocarbons(C₁-C₅)^{32, 33}.

4. Conclusions

The cracking of toluene in non-thermal plasmas was studied in a CO₂ carrier gas(15%-25% of the gasifier effluent)¹⁴ of the gasifier , to study the effects of this component of gasifier producer gas in isolation. The effects of plasma power and residence time on the selectivities of various gaseous products, at room temperature and elevated temperature, were investigated. The major findings can be summarized as follows:

- i. Toluene conversion increases with power and residence time. The maximum conversion (99%) was obtained at 40 W and 4.23 s of residence time (the highest levels used). The major products are H₂, CO and solid residue.
- ii. Lower hydrocarbons (C₁-C₄) are also produced during the cracking of toluene. They remain below 3.5% at ambient temperature, but increased up to 12.8% as the temperature was increased to 400°C.
- iii. At elevated temperature toluene conversion decreases due to reactions of O and CO radicals, selectivity. The yields of H₂ and CO also decrease.
- iv. Solid deposits were observed inside the reactor. The formation of solid residue is a negative outcome and needs to be resolved. However, other gases in the typical mixture from gasifier may have a role in removing/converting the residues.

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Fig.1. Experimental setup

Fig.2 Effect of plasma power on: (a) the conversion of toluene; (b) selectivity of CO, H₂ and LHC at residence time 4.23 s; (c) Yield of CO and H₂ at 4.23 s; and (d) decomposition of CO₂.

(Reaction conditions: concentration = 82 g/Nm³; Temperature=ambient; and residence time=4.23 s)

Fig.3 Effect of concentration: (a) on the conversion of toluene; (b) selectivity of CO, H₂ and LHC at 10 W; (c) on decomposition of CO₂; and (d) energy efficiency.

(Reaction conditions: residence time= 4.23 s; and Temperature=ambient)

Fig.4 Effect of residence time (a) on the conversion of toluene and towards selectivity of CO H₂ and LHC (C₁-C₅); (b) on the decomposition of CO₂ and towards yield of CO and H₂.

(Reaction conditions: concentration = 82 g/Nm³; Temperature=ambient; and Power=40 W)

Fig.5 Reactions schematic

Fig.6 Effect of temperature on: (a) the conversion of toluene; (b) selectivity of CO, H₂ and LHC (C₁-C₅); (c) on the yield of CO, H₂ and decomposition of CO₂.

(Reaction conditions: input power=40 W; concentration = 82 g/Nm³; and residence time=4.23 s)

Fig.2 Effect of plasma power on: (a) the conversion of toluene; (b) selectivity of CO, H₂ and LHC at residence time 4.23 s; (c) Yield of CO and H₂ at 4.23 s; and (d) decomposition of CO₂. Reaction conditions: concentration = 82 g/Nm³; gas flow rate=40.6ml/min; Temperature=ambient; and residence time=4.23 s

Fig.3 Effect of concentration: (a) on the conversion of toluene; (b) selectivity of CO, H₂ and LHC at 10 W; (c) on decomposition of CO₂; and (d) energy efficiency. Reaction conditions: gas flow rate= 40.6ml/min; residence time= 4.23 s; and Temperature=ambient

(a)

(b)

Fig.4 Effect of residence time (a) on the conversion of toluene and towards selectivity of CO H₂ and LHC (C₁-C₅); (b) on the decomposition of CO₂ and towards yield of CO and H₂. Reaction conditions: concentration = 82 g/Nm³; Temperature=ambient; gas flow rate=40.6-120 ml/min; and Power=40 W

Fig.5 .Reactions schematic

Fig.7 Effect of temperature on: (a) the conversion of toluene; (b) selectivity of CO, H_2 and LHC ($\text{C}_1\text{-C}_5$); (c) on the yield of CO, H_2 and decomposition of CO_2 . Reaction conditions: input power=40 W; gas flow rate=40.6ml/min; concentration = 82 g/Nm^3 ; and residence time=4.23 s