Plasma-assisted decomposition of a biomass gasification tar analogue into lower hydrocarbons in a synthetic product gas using a dielectric barrier discharge reactor

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Abstract

Cleaning product gas from biomass gasification is one of the major challenges for the application of biomass as a renewable energy source for power generation and value-added chemical synthesis. Non-thermal plasmas are a novel alternative technology for decomposing such tar compounds. In this research, the use of a dielectric barrier discharge (DBD) reactor was investigated for the decomposition of toluene (a tar surrogate) in a synthetic product gas containing H₂, CO and CO₂. The effect of residence time (0.95-2.82 s), plasma power (5-40 W), concentration (20-82 g/Nm³), and temperature (ambient -400 °C) were investigated. It was demonstrated that the percentage removal of tar increased with increasing plasma power and residence time. 99%+ removal of toluene was observed at a plasma power of 40 W (the highest power used) and a residence time of 2.82 s (the highest residence time used). At ambient temperature, the toluene decomposition products include CO, lighter hydrocarbons, and solid residue. Unfortunately, at low temperatures, there was substantial solid residue formation. The synergetic effect of temperature and plasma was investigated to determine whether it could decrease residue formation. It was found that the solid residue completely disappeared at 400 °C. Furthermore, the selectivity and the yield of lower hydrocarbons increased with operating temperature. However, the yield of CO decreased due to the termination of radicals through the combination of CO and O at higher temperatures. Overall, this work demonstrates that toluene can be almost completely converted to smaller molecules by a DBD non-thermal

plasma, and that a degree of control can be established by varying power, residence time and temperature, including eliminating the problem of solid residue formation

1. Introduction

Biomass is a source of renewable energy, and can reduce greenhouse gas emission and its use is increasing due to increasing demand for energy and global warming issues associated with fossil fuels. Biomass gasification is a thermochemical method for generating alternative, green fuels for power production and transport [1]. A partial oxidation of solid biomass is carried out at high temperature (700-850°C) to produce gaseous fuel [2]. Due to the high concentration of CO and H₂ in the product gas, which is often referred to as “synthesis gas”, it can be used to produce valuable chemicals via Fischer-Tropsch process and as fuels in gas turbines and engines. When steam is used as gasifying agent the product gas consists of CO₂, CO, H₂, and various lighter hydrocarbons [3]. Moreover, volatile alkali metals, ash and tars are also present as impurities [2]. Several parameters influences the composition of the product gas including: gasification method, operating conditions, nature of feedstock, etc. Tar in the product gas creates significant operational and maintenance problems by condensing in engines, heat exchangers and filters upon cooling downstream of the gasifier, leading to lower process efficiency and higher maintenance costs [4, 5]. Tar is a condensable mixture of aromatic and poly aromatic hydrocarbons [6]. The efficient cracking of tar is necessary for the successful commercialization of gasification of biomass [1].

Employing non-thermal plasma to decompose tar and pollutants is potentially advantageous due to its compact and simple design. Kim et al (2004) evaluated the effectiveness of NTP for cleaning air. The study compared four different NTP methods (pulsed corona discharge reactor, DBD reactor, surface discharge reactor, and ferroelectric pellet packed bed reactor) for their efficacy in decomposing benzene used as model compound. Its decomposition was studied as

a function of the specific input energy in an O_2/N_2 gas mixture. It was reported that the conversion of benzene reached 75% in a DBD reactor at a specific input energy of 600 J/L, and increased with specific input energy [7]. In another study, Nair studied the decomposition of naphthalene as a tar model compound, and it was reported that the removal efficiency of tar compound increased with increasing CO_2 concentration due to the formation of O radicals. It is also reported that the presence of CO in fuel gas negatively affected the tar decomposition efficiency due to the combination of O radicals with CO [8].

In steam gasification, the gasifier product gas is a mixture of CO_2 , H_2 , CO, and various by-products [3]. Hence, the decomposition of tar in a synthetic fuel gas consisting of CO_2 , CO, and H_2 , has been investigated using NTP technology. In this work, the performance of a DBD was investigated for cracking toluene in synthetic fuel gas (CO_2 :30 %; CO:20 %; H_2 :50 %). The variables investigated were power, temperature, residence time and concentration. Toluene was chosen as a tar analogue because of its simple structure, high thermal stability, and low boiling point.

2. Methodology

2.1 Experimental setup

The experimental setup is shown in Fig.1. The cylindrical dielectric barrier discharge (DBD) 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). The material used for the construction of both electrodes was stainless steel grade 316. Both the outer mesh and inner metal sheet were made of the same metal. The plasma was generated between the annular spaces of the coaxial quartz tubes. A variac AC transformer was used to control the input voltage of plasma generator which delivers power to DBD reactor. In this study, the power supplied to the DBD reactor was varied

from 5 to 40 W, at a frequency of 20 kHz. The length of the 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.

The flow rate of the carrier gas and the synthetic product gas mixture (H_2 :50%; CO_2 :30%; CO :20%), was regulated by computer-controlled mass flow controllers, connected to gas cylinders (BOC, UK). The gas mixture was bubbled through an ice-bath bubbler filled with toluene to add the toluene vapour. An electric furnace was used to study the performance of plasma reactor at elevated temperature. The furnace temperature was controllable over a range varying from ambient to 400 °C, after placing the reactor inside the furnace. The composition of the product gas was measured by gas chromatography using a Varian 450-GC.

Fig.1. Experimental setup

2.2 Definitions

The removal efficiency of toluene was defined as follows:

$$d_1 = \frac{\text{moles of toluene in input stream} - \text{moles of toluene in outlet stream}}{\text{moles of toluene in input stream}} \times 100$$

The following formulae were used to calculate the yield and selectivity of different products:

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

$$\text{CH}_4 \text{ yield (\%)} = \frac{\text{moles of CH}_4 \text{ produced}}{7 \times \text{Moles of C}_7\text{H}_8 \text{ in} + \text{moles of CO}_2 \text{ in} + \text{moles of CO in}}$$

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

$$\text{Specific input energy (SIE)} = \frac{\text{Power (kW)}}{\text{Total flow rate of gas (m}^3\text{/hr)}} \times 100$$

The energy efficiency was calculated using following formula:

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

3. Results and discussion

3.1 Effect of Power

Figure 2(a) clearly demonstrates that toluene removal increases with the power input to the DBD. This behaviour was expected: as power increases, the number of higher energy electrons increases, which increases the rate of activation of the reactant molecules by formation of free

Fig.2 Effect of plasma power on (a) the conversion and energy efficiency of toluene, (b) the selectivity and yield of different gaseous products(c) individual lower hydrocarbons (d) mole (%) of CO₂ and H₂. Reaction conditions: Concentration=33g/Nm³; residence time=2.82 s; flow rate=40.6 ml/min; SIE=2.05-16.4 kWh/m³; and Temperature=ambient

radicals and ions. The effect of power on the energy efficiency of the system is also shown in fig. 2(a). The energy efficiency decreases with increasing power, from 13 g/kWh to 1.9 g/kWh as the power is increased from 5 to 40 W. Essentially, this is due to “diminishing returns” as

the conversion approaches 100%. Similar trends have been reported for the removal of tar analogues [9]. It was observed that at 10 W more than 93% of the tar analogue is decomposed. Therefore, to calculate the operational cost, specific energy input (4.10 kWh/m^3) was calculated at 10 W. This specific input energy was used to calculate cost of treatment of gas stream in current plasma system. It should be noted however that the operating costs per unit volume would decrease with increasing scale and optimisation of the design.

Fig.2 (b) shows that the yield of CO gradually increases from 2.6% to 8.8% as the power increases from 5 to 40 W, and the selectivity to $\text{C}_2\text{-C}_5$ increases from 7.3 to 18%. It can be observed from fig. 2(c) that the selectivity and yield of lower hydrocarbons increased with power. At lower powers, the average electron energy is not high enough to crack aromatic C-C bonds, hence a greater proportion of lower hydrocarbons is observed at higher powers. In addition, in this case it is clear that the formation of active species, such as radicals, ions, and excited molecules can also increase selectivity to CO and LHCs. It has previously reported that dissociation by electron impact played a significant role in the decomposition of aromatic compounds [10-12].

It was reported that the bond dissociation energy of different bonds in toluene decreases in the following order: C=C and C-C in aromatic ring > C-H in aromatic ring > C-C between methyl and aromatic ring (4.4 eV) > C-H bond in methyl group (3.7 eV) [10, 11, 13]. For this reason, decomposition of toluene could begin with abstraction of an H-atom from the methyl group, as the bond dissociation energies of these C-H bonds are the lowest [14], via electron impact, excited species or radicals and the reaction scheme is shown below in fig.3. The abstraction of H atom produces H radicals and benzyl radicals. The aromatic ring containing intermediate compounds can self-polymerise. The reactive species can separate the methyl group from toluene to produce benzene and methyl radicals. These radicals can react with H radicals to

produce methane. Meanwhile ring opening products (C₁-C₅) form due to impact of high energy electrons which directly start the cleavage of the aromatic ring.

Fig.3 Reaction mechanism

3.2 EFFECT OF RESIDENCE TIME

The effect of residence time is also clear (Fig. 4(a)) since decomposition increases with the residence time, as would be expected. Understanding the combined effects of these 2 variables (residence time and power) is part of the development of a design protocol for plasma reactors for this application, based on the relative costs of increasing residence time (thereby increasing the size of the reactor and therefore capital cost for a given duty) and increasing power (thereby increasing operating cost). As evident in Fig. 4(a), with increasing residence time, the conversion of toluene increased from 76% to 96% at 20 W, as the number of opportunities for collision between active species, energetic electrons and toluene's molecules increased [9]. However, the energy efficiency decreases with increasing residence time. To increase the residence time the flow rate needs to be reduced, which also decreases the flow rate of toluene. Therefore, the energy efficiency is reduced at high residence time due to a decrease in the total amount of decomposed toluene.

(a)

(b)

(c)

Fig.4 Effect of residence time (a) on the conversion and energy efficiency of toluene, (b) on the selectivity and yield of different gaseous products (c) on individual lower hydrocarbons. Reaction conditions: Concentration=33g/Nm³; Power=20 W; flow rate=40.6-120 ml/min; and Temperature=ambient

These results are consistent with a previous experimental study in which decomposition of toluene was investigated in a DBD reactor [15]. The selectivity and yield of different gaseous products are shown in fig. 4(b) and (c). The yield of CO increases from 1.9 % to 5.7 %, and selectivity of C₂-C₅ increases from 3 to 11 % with the increasing residence time. Similarly, Fig.4 (c) shows that the yield of methane gas and selectivity of C₂-C₅ also increase with residence time. This is possibly due to the cleavage of the aromatic ring due to high number of collisions between tar analogue and reactive species, or second phase reactions.

3.3 Effect of concentration

The concentration of toluene was varied from 20 to 82 g/Nm³. Fig.5 (a) shows the effect of concentration on the conversion and energy efficiency. It can be observed that the conversion of toluene decreased with increasing toluene concentration. The maximum conversion was obtained at 20 g/Nm³ (95.5%), then decreased monotonically when increasing the

concentration up to 82 g/Nm³ (68%). At constant power, the plasma-generated reactive species react with the toluene to decompose it. However, when the concentration is increased whilst keeping the others parameters constant, the relative amount of toluene molecules increases with respect to reactive species and the conversion is reduced. However, the energy efficiency of the process increased with increasing concentration, as the number of molecules of toluene converted increased. Here, the value increased from 4.6 g/kWh to 13.5 g/kWh over the range studied here. The similar effect of concentration has been reported previously in gliding arc discharge [16]. Fig.5 (b) and (c) shows the changes in selectivity and yield of gaseous products with respect to concentration. The yields of CO, LHC (C₂-C₅) and CH₄ decrease with increasing concentration. Again, this is due to a fixed number of electron and active species interacting with higher concentrations of toluene molecules.

(c)

Fig.5 Effect of concentration (a) on the conversion and energy efficiency of toluene, (b) on the selectivity and yield of different gaseous products(c) on individual lower hydrocarbons.

Reaction conditions: Residence time=2.82 s; Power=10 W; flow rate=40.6 ml/min; and Temperature=ambient

This behaviour is consistent with previous experimental results in which the effect of concentration has been studied on the removal of tar analogue [17]. It was also observed that solid residue was produced in the discharge zone during the cracking of tar analogue at ambient temperature. Yellowish deposits have been previously reported when operating in limited oxygen [18]. Here, in an attempt to mitigate this effect, the synergetic effect of temperature and plasma was studied to avoid the formation of hazardous solid residue.

3.4 Effect of temperature

The performance of DBD reactors was studied at elevated temperatures. The effect of temperature and power on the conversion of toluene is shown in fig. 6 (a). It can be noted that the decomposition of toluene does not change when increasing the temperature over the

(a)

(b)

(c)

(d)

(e)

(f)

Fig.6 Effect of temperature on: (a) The conversion of toluene; (b) Total selectivity and yield of LHC and CO at 20 W; Selectivity and yield of different LHC at (c) 10 W (d) 20 W (e) 30 W (f) 40 W

W and (f) 40 W. (Reaction conditions: concentration = 33 g/Nm³; residence time=2.82 s;
flow rate=40.6 ml/min)

power range 20 to 40 W. However, at 10 W, it varied from 82% to 91%. It may be decreased
due to formation of solid deposits in the plasma zone. This is also possible due to the radical
termination reaction of CO and O to form CO₂ [19].

It was reported that the decomposition of toluene in CO₂ carrier gas decreased with increasing
temperature in DBD reactor [15]. However, toluene conversion is not significantly affected by
increasing the temperature at higher powers (20-40 W). This is because the reaction is mainly
a function of the number of energetic electrons and excited species generated by the plasma.
The influence of elevated temperature on the selectivity and yield of products is shown in fig.
6(b) at 20 W. It shows that the selectivity to lower hydrocarbons (C₂-C₆) increased with
increasing temperature up to 400°C at 20 W. This is possibly due to hydrocracking of toluene
into lower hydrocarbons (C₁-C₆) becoming significant at elevated temperatures [20, 21].
However, the yield of CO slightly decreases with increasing temperature, probably because of
the recombination reactions of CO and O radicals. Hydrocracking of toluene could occur
through three different routes: (a) isomerization, (b) hydrogenation-dehydrogenation, and (c)
cracking reactions [22]. The first two types of reactions can occur at lower temperatures
because of their low activation energy, while cracking reactions of aromatics require higher
temperatures [23]. These cracking reaction can take place through primary (ring opening)
secondary and tertiary cracking [22].

Fig.6 (c) shows the effect of temperature on the selectivity to lower hydrocarbons (C₂-C₆) and
the yield of methane at 10 W. It can be observed that the selectivity of each individual lower
hydrocarbons increases with increasing the temperature. The selectivities to C₂ and benzene

reach 9.5 and 21.7 % at 400°C, respectively. However, the selectivity to C₂₊ alkanes and alkenes remains below 10%. The yield and selectivity of lower hydrocarbons increases with temperature because of cracking reactions at high temperatures, while for benzene this occurs via radical substitution reactions [20]. It has previously been reported that the production of methane and aromatics increases with increasing the temperature in the presence of H radicals [20, 23].

The effect of power on yield and selectivity of lower hydrocarbons at elevated temperature can be observed from fig. 6(c to f). Clearly, the yield of methane increases with increasing power, whereas the selectivity to benzene exhibits a clear decrease due to impact of reactive species. The yield of methane increases from 1.04 % to 7.5 % with increasing the temperature at 40 W. This is because the presence of H radicals at elevated temperature promotes the formation of methane [24]. In addition, at high power, the fragmentation of the benzene ring because of energetic electron and excited species increase the yield of methane as well.

Fig.7 Reaction mechanism at elevated temperature

The selectivity to benzene decreases to 8% at 40 W. This occurs because the electrons produced at 40 W are energetic enough to decompose the aromatic carbon-carbon bonds. It was reported that the formation of methane increases to 10% when increasing the temperature up to 450 °C in the presence of a catalyst [23].

The effect of temperature on the production of C₂-C₅ species at 40 W can be observed in fig 6 (f). The selectivity to C₂ hydrocarbons increases with increasing temperature up to 300°C and after that decreases at 400°C, while for >C₃ it started to decrease above 200°C. This was due to hydrocracking of these hydrocarbons into methane. It has previously been reported that cracking of C₂ to C₄ increased with increasing temperature and converted to methane [24]. It has been observed that cracking of ethane increases with increasing temperature from 260 to 322°C producing methane, while cracking of C₃ increased even at lower temperature range (206-240°C) and produced methane[24].

4. Conclusions

In this study, decomposition of toluene as a tar surrogate was evaluated in a dielectric barrier discharge (DBD) reactor using a synthetic fuel gas mixture (H₂:50 %, CO₂:30 % and CO:20 %). Power (5 – 40 W), temperature (20-400 °C), concentration of toluene (20-82 g/Nm³) and residence time (0.95-2.82 s) were varied to investigate the performance of the DBD reactor and its selectivity towards valuable gaseous products.

The main findings were:

- i. The conversion of toluene can be as high as 99% and the latter was converted to CO, lower hydrocarbons (LHC) and solid residue.
- ii. The conversion increases with both power and residence time.
- iii. At ambient temperature, solids appeared inside the reactor, which would create problems due to fouling and blockages over time. However, here we demonstrated that this problem can be eliminated by increasing the wall temperature. A further benefit of increasing the temperature was that it increased both the selectivity and yield of the lower hydrocarbons.

- iv. Formation of methane increased with increasing the temperature and power. The highest yield of methane in this study was 7.5 %, at 400°C and 40 W of power.

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References

- [1] L. Devi, K.J. Ptasinski, F.J.J.G. Janssen, A review of the primary measures for tar elimination in biomass gasification processes, Biomass and bioenergy, 24 (2003) 125-140.

- [2] I. Narvaez, A. Orio, M.P. Aznar, J. Corella, Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas, *Industrial & Engineering Chemistry Research*, 35 (1996) 2110-2120.
- [3] S. Luo, B. Xiao, Z. Hu, S. Liu, X. Guo, M. He, Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: Influence of temperature and steam on gasification performance, *International Journal of hydrogen energy*, 34 (2009) 2191-2194.
- [4] P. McKendry, Energy production from biomass (part 3): gasification technologies, *Bioresource technology*, 83 (2002) 55-63.
- [5] P.A. Simell, J.O. Hepola, A.O.I. Krause, Effects of gasification gas components on tar and ammonia decomposition over hot gas cleanup catalysts, *Fuel*, 76 (1997) 1117-1127.
- [6] A.V. Bridgwater, The technical and economic feasibility of biomass gasification for power generation, *Fuel*, 74 (1995) 631-653.
- [7] H.-H. Kim, H. Kobara, A. Ogata, S. Futamura, Comparative assessment of different nonthermal plasma reactors on energy efficiency and aerosol formation from the decomposition of gas-phase benzene, *IEEE transactions on industry applications*, 41 (2005) 206-214.
- [8] S.A. Nair, A.J.M. Pemen, K. Yan, F.M. Van Gompel, H.E.M. Van Leuken, E.J.M. Van Heesch, K.J. Ptasiński, A.A.H. Drinkenburg, Tar removal from biomass-derived fuel gas by pulsed corona discharges, *Fuel Processing Technology*, 84 (2003) 161-173.
- [9] Y.N. Chun, S.C. Kim, K. Yoshikawa, Decomposition of benzene as a surrogate tar in a gliding Arc plasma, *Environmental Progress & Sustainable Energy*, 32 (2013) 837-845.
- [10] K. Urashima, J.-S. Chang, Removal of volatile organic compounds from air streams and industrial flue gases by non-thermal plasma technology, *IEEE Transactions on Dielectrics and Electrical Insulation*, 7 (2000) 602-614.
- [11] H. Kohno, A.A. Berezin, J.-S. Chang, M. Tamura, T. Yamamoto, A. Shibuya, S. Honda, Destruction of volatile organic compounds used in a semiconductor industry by a capillary tube discharge reactor, *IEEE Transactions on Industry Applications*, 34 (1998) 953-966.
- [12] H.M. Lee, M.B. Chang, Abatement of gas-phase p-xylene via dielectric barrier discharges, *Plasma chemistry and plasma processing*, 23 (2003) 541-558.
- [13] B.d. Darwent, Bond dissociation energies in simple molecules, NSRDS-NBS NO. 31, U. S. DEPT. COMMERCE, WASHINGTON, D. C. JAN. 1970, 48 P, (1970).
- [14] H. Huang, D. Ye, D.Y.C. Leung, F. Feng, X. Guan, Byproducts and pathways of toluene destruction via plasma-catalysis, *Journal of Molecular Catalysis A: Chemical*, 336 (2011) 87-93.
- [15] F. Saleem, K. Zhang, A. Harvey, Role of CO₂ in the Conversion of Toluene as a Tar Surrogate in a Nonthermal Plasma Dielectric Barrier Discharge Reactor, *Energy & Fuels*, (2018).
- [16] F. Zhu, X. Li, H. Zhang, A. Wu, J. Yan, M. Ni, H. Zhang, A. Buekens, Destruction of toluene by rotating gliding arc discharge, *Fuel*, 176 (2016) 78-85.
- [17] S. Liu, D. Mei, L. Wang, X. Tu, Steam reforming of toluene as biomass tar model compound in a gliding arc discharge reactor, *Chemical Engineering Journal*, 307 (2017) 793-802.
- [18] Y.-F. Guo, D.-Q. Ye, K.-F. Chen, J.-C. He, W.-L. Chen, Toluene decomposition using a wire-plate dielectric barrier discharge reactor with manganese oxide catalyst in situ, *Journal of Molecular Catalysis A: Chemical*, 245 (2006) 93-100.
- [19] A. Cenian, A. Chernukho, V. Borodin, Modeling of Plasma-Chemical Reactions in Gas Mixture of CO₂ lasers. II. Theoretical Model and its Verification, *Contributions to Plasma Physics*, 35 (1995) 273-296.
- [20] A. Amano, O. Horie, N.H. Hanh, Reaction of toluene with hydrogen atoms at elevated temperatures, *Chemistry Letters*, 1 (1972) 917-920.
- [21] A. Amano, H. Tominaga, H. Tokuhisa, Mechanism of Thermal Hydrogenolysis of Toluene, *Bulletin of The Japan Petroleum Institute*, 7 (1965) 59-63.
- [22] M.A. Arribas, A. Martinez, The influence of zeolite acidity for the coupled hydrogenation and ring opening of 1-methylnaphthalene on Pt/USY catalysts, *Applied Catalysis A: General*, 230 (2002) 203-217.

337 [23] P. Castaño, J.M. Arandes, B. Pawelec, M. Olazar, J. Bilbao, Kinetic modeling for assessing the
338 product distribution in toluene hydrocracking on a Pt/HZSM-5 catalyst, Industrial & Engineering
339 Chemistry Research, 47 (2008) 1043-1050.
340 [24] J. Freel, A.K. Galwey, Hydrocarbon cracking reactions on nickel, Journal of Catalysis, 10 (1968)
341 277-289.

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