Temperature dependence of non-thermal plasma assisted hydrocracking of toluene to lower hydrocarbons in a dielectric barrier discharge reactor

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Abstract

Non-thermal plasma (NTP) is an attractive method for decomposing biomass gasification tars. In this study, the removal of toluene (as a gasification tar analogue) was investigated in a dielectric barrier discharge (DBD) reactor at ambient and elevated temperatures with hydrogen as the carrier gas. This study demonstrated that higher temperature in the presence of a DBD opens up new (thermal) reaction pathways to increase the selectivity to lower hydrocarbons via DBD promoted ring-opening reactions of toluene in H_2 carrier gas. The effect of plasma power (5 – 40 W), concentration (20-82 g/Nm^3), temperature (ambient-400 ^{o}C) and residence time (1.43-4.23 s) were studied. The maximum removal of toluene was observed at 40 W and 4.23 s. The major products were lower hydrocarbons (C_1-C_6) and solids. The synergetic effect of power and temperature was investigated to decrease the unwanted solid deposition. It was observed that the selectivity to lower hydrocarbons (LHCs) increased from 20 to 99.97 %, as temperature was increased from ambient to 400 ^{o}C, at 40 W and 4.23 s. Methane, C_2 (C_2H_6 + C_2H_4), and benzene were the major gaseous products, with a maximum selectivity of 97.93% (60 % methane, 9.93 % C_2 (C_2H_6 + C_2H_4), and 28% benzene). It is important to note that toluene conversion is not a function of temperature, but the selectivity to lower hydrocarbons increases significantly at elevated temperatures under plasma conditions.

1. Introduction

Biomass can be used as an alternative source of "green" energy and chemicals. Biomass can be converted into fuels and value-added chemicals by thermal, physical or biological processes. Thermochemical processes are useful for producing fuels, chemicals, combined power and heat. Among thermochemical processes, gasification is a promising technique for producing alternatives, green fuels for transport and power generation. In this method, partial oxidation of solid biomass is performed at temperatures of 700 to 800 ^{o}C, to produce gaseous fuels or synthesis gas [1, 2]. The product gas contains high concentrations of CO and H_2. Its composition depends upon various parameters such as the nature of the feedstock, method of gasification, operating conditions, etc [2]. The syngas (CO + H_2) can be used as fuel in gas turbines, gas engines, and it can be used to produce valuable chemicals. However, the product gas from gasifier also has impurities such as chlorine, sulphur, nitrogen and tar compounds [3]. Among these, tar creates a significant problem by condensing in filter, heat exchangers and engines at low temperatures after the exit of biomass gasifier, leading to attrition and choking. Therefore, it is necessary to decompose or remove the tar compounds from the product gas [4].

There are numerous techniques that can be implemented to remove tars, such as mechanical separation, thermal cracking, and catalytic cracking. Tar components can be reduced using mechanical separation techniques such as Venturi scrubbers, rotational particle separators, water scrubbers, ESP, and cyclones. However, these techniques only capture or remove the tar compounds from gasifier product gas, thereby producing secondary pollution. In addition, the associated chemical energy of the tar is wasted [5]. Thermal and catalytic techniques may be used to crack tar compounds, but these methods have some drawbacks. In thermal cracking, for instance, operating cost is significantly increased by maintaining the high temperature [6].

When using catalytic cracking, tar compounds can be cracked into valuable gaseous compounds at lower temperatures than in thermal decomposition [7]. However, many catalysts

have high affinities for chlorine and sulphur, which can poison them. The main contaminants in typical gasifier product gas are sulphur, chlorine and nitrogen compounds [8]. Therefore, it is difficult to remove tar compounds completely, due to their complexity and variability and unavailability of efficient and proven method.

Non thermal plasma (NTP) is widely considered to be an attractive solution for the decomposition of volatile organic compounds (VOCs) and the production of fuels and chemicals [9]. Downstream NTP treatment of tar has received considerable attention due to its easy operation and compact design [10]. In NTP systems, the reactive species are derived from the carrier gas via the impact of high energy electrons (1-10eV) [11]. This produces a variety of reactive species (electrons, radicals and excited species), which can interact with the tar to decompose the tar compounds. Various techniques have been employed to decompose the biomass tar, often using toluene as a tar analogue. Combined plasma and catalysis techniques can also be used to crack gasification tars. The plasma can reduce the catalyst's activation energy and thereby increases the rate of decomposition of reactants, raising the yield and possibly the selectivity of valuable gaseous products [12, 13]. Tao et al (2013) investigated the plasma-assisted catalytic decomposition of a tar model compound (toluene) in a He carrier gas using DC non-thermal pulsed plasma [14]. They reported that using plasma before the catalytic steam reforming reactions enhanced the decomposition of toluene. It was observed that the decomposition of toluene rises from 32 % to 57 % when using NTP before the catalyst bed [14].

In another study, the presence of moisture increased the toluene decomposition efficiency in air in a gliding arc discharge reactor [15]. In previous studies, it has been observed that removal and energy efficacy of tar compound increases by adding the steam [16-19]. The decomposition efficiency of toluene increased due to oxidation of toluene through OH radicals, which can

provide new reaction routes for the direct and indirect removal of toluene [17]. However, addition of steam increases the operational cost and process complexity.

In this study, a DBD reactor was used to remove toluene in H_2 carrier gas. In our previous work we reported almost complete conversion of tar (toluene) in CO_2 carrier gas, but with significant formation of problematic solid residue occurred [20]. Toluene decomposition in H_2 has not been reported in the literature, even though the product gas from gasification contains significant amounts of H_2 (25.2-49.5 %) [21]. Therefore, for a better understanding of tar removal from product gas, it is necessary to study the effect of H_2 on toluene conversion and product selectivity in the NTP.

Toluene is one of the main stable compounds produced during biomass gasification process at higher temperatures [22], and has been used in various experimental studies as a tar analogue to investigate the removal efficiency [17, 18, 23-25]

The performance of the DBD reactor was also studied by varying power, toluene concentration, temperature, and residence time. The present study reveals that the operation temperature plays an important role in toluene conversion to lower hydrocarbons in H_2 carrier gas under NTP conditions.

2. Material s and methods

2.1 Experimental setup

Fig.1 shows a schematic of the experimental setup. The coaxial dielectric barrier discharge

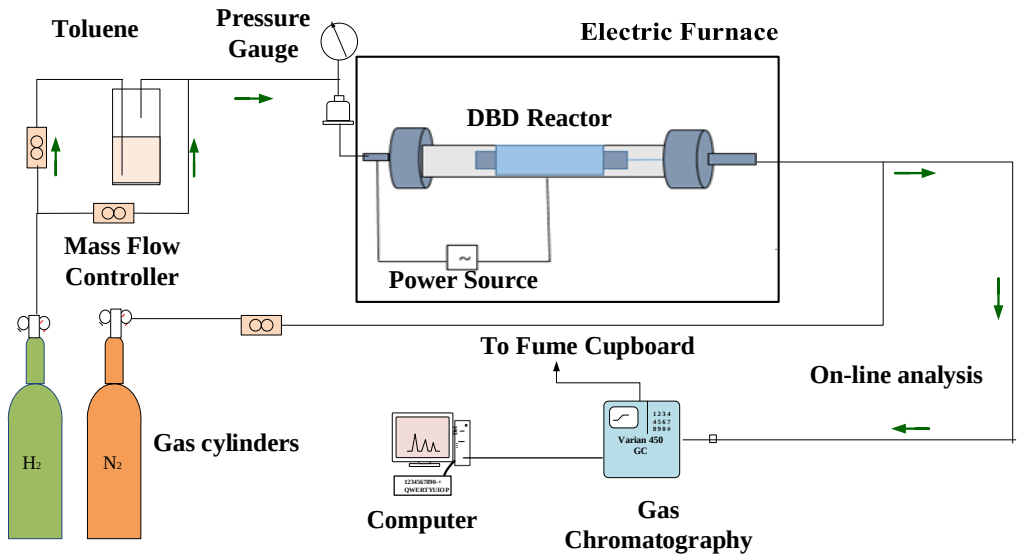


Fig.1. Schematic diagram of the experimental setup

(DBD) reactor consisted of two coaxial quartz tubes one inside the other. The two metal electrodes, one outside the external cylindrical quartz tube (330 mm length, 18 mm outer diameter, 15 mm inner diameter) and the other inside the inner tube (outer diameter 12 mm, inner diameter 10 mm). The inner and the outer metal mesh electrodes were made from 316 stainless steel. The length of the external mesh was 45 mm resulting in a discharge region of about 2.86 cm^3. The plasma was produced in the annular space between the coaxial cylindrical tubes. A variac was used to control the input voltage of the plasma generator which delivers power to DBD reactor. The voltage (0-20 kV peak-peak) and current signals were measured using an oscilloscope (TPS 2014B, Tektronix) to calculate the power transferred to the reactor. In this study, the power supplied to the DBD reactor was varied from 5 to 40 W, at a frequency of about 20 kHz.

Computer-controlled mass flow controllers regulated the flow rate of H_2 and N_2 from gas cylinders (BOC, UK, 99.99%), respectively. H_2 gas was saturated with toluene by passing through a bubbler (see Fig.1). The bubbler was placed in an ice bath to minimize the effect of diurnal fluctuations in ambient temperature on the rate of evaporation of toluene. The gas flow

rate was varied from 40.6 ml/min to 120 ml/min. To monitor the change of flow rate as a consequence of plasma chemical reactions, a constant flow of nitrogen (6.0 mL/min) as reference gas was added to the exit of the reactor. All values are stated at STP. To study the effect of temperature on the performance of plasma chemical reactions, the plasma reactor was placed inside a furnace which can adjust the temperature between ambient and 400°C.

The product compositions were monitored by a Varian 450-GC equipped with a TCD (Thermal conductivity detector) to measure CH_4 and H_2, and a FID (Flame ionization detector) to measure lighter hydrocarbons (LHC) including C_2 (C_2H_4, C_2H_6), C_3 (C_3H_6, C_3H_8), C_4 (C_4H_8, C_4H_{10}), C_5 (C_5H_{10}, C_5H_{12}), and C_6H_6).

2.2 Definitions

The removal efficiency of toluene was defined as follows:

$$d_T = \frac{\text{toluene in the input stream (mole/min) - toluene in the outlet stream (mole/min)}}{\text{toluene in input stream (mole/ min)}} \times 100$$

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

$$\text{LHC selectivity (\%)} = \frac{\sum (\text{m} \times \text{moles of } C_mH_n)}{7 \times \text{ Moles of } C_7H_8 \text{ converted}} \times 100$$

Where n and m are the carbon and hydrogen number respectively in the molecules

The SIE (specific input energy) shows the energy density applied to the plasma system

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

The energy efficiency was calculated as follows:

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

3. Results and Discussion

3.1 Effect of Power

The effect of power on the removal efficiency of toluene is shown in Fig.2 (a), below. Plasma power was varied from 5 to 40 W (SIE =7.39-59.11 kJ/L). The initial concentration of toluene was 33 g/m^3, and the residence time was 4.23 s. It was found that toluene decomposition efficiency increased with increasing plasma power, and the maximum removal of toluene was 99.5 % at 40 W and 4.23 s. The similar effect of power on the decomposition of toluene was reported in previous experimental study [20, 26].

The energy efficiency and selectivity to LHCs are also shown in Fig.2 (a). The energy efficiency of the plasma decomposition clearly decreases with increasing plasma power. There are diminishing returns as the input power is increased. Similar trends have been reported for the decomposition of tar analogue [16]. However, the overall selectivity of LHC increases from 11.20 to 20 % as the power was increased from 5 to 40 W, which suggested that the aromatic ring was broken down at higher plasma power. Fig.2 (b) demonstrated that the selectivity of LHCs (C_1-C_5) increased with increasing plasma power

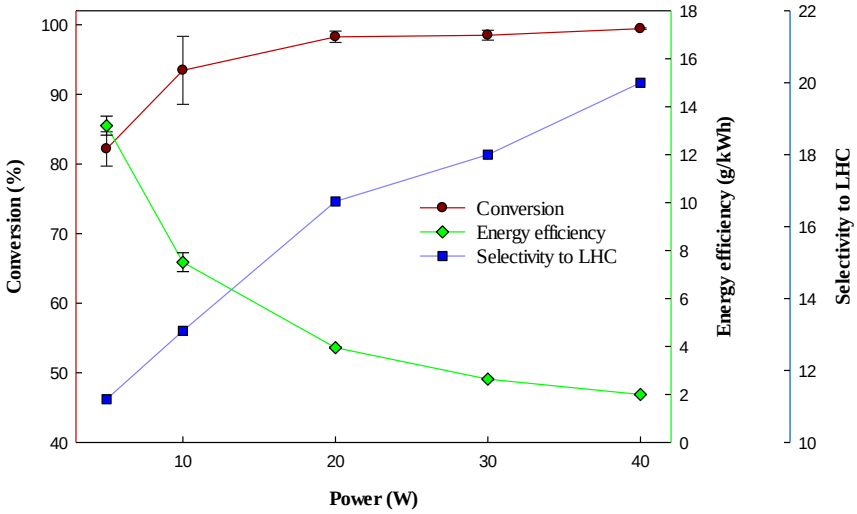


Fig. 2(a) Effect of plasma power on the conversion, energy efficiency and selectivity to LHC; bars represent standard deviation. Reaction conditions: concentration = 33 g/Nm^3; Temperature=ambient; flow rate 40.6 ml/min; residence time= 4.23 s; and SIE=7.39-59.11 kJ/L.

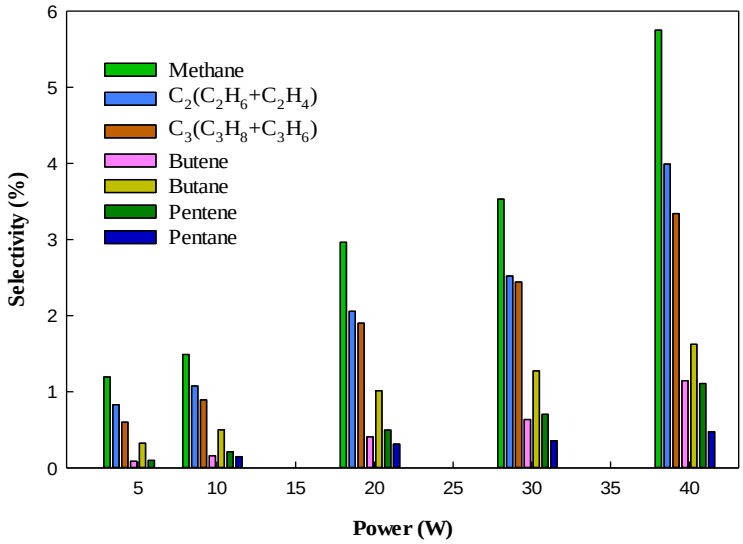


Fig.2 (b) Selectivity of different LHC at 4.23 s. Reaction conditions: concentration = 33 g/Nm^3; Temperature=ambient; residence time= 4.23 s; ; and SIE=7.39-59.11 kJ/L.

In a DBD plasma, the mean electron energy is in the range of 1-10 eV. The Maxwellian electron energy distribution function (EEDF) shows the higher the average electron energy is, the more

electrons with higher energy will be produced [27]. These energetic electrons can generate active radicals, ionic and excited atomic and molecular species through electron-impact dissociation, ionization, and excitation of the source gases, i.e., H_2 and toluene, which can initiate plasma assisted toluene decomposition/hydrocracking in H_2 carrier gas. The bond dissociation energy of H_2 is 4.5 eV [28]. In a toluene molecule, the C-H bond dissociation energy (3.7 eV) of the methyl group is lower than the dissociation energy of the C-H bond, and C-C and C=C of the aromatic ring [28]. The bond dissociation energy of the C-C bond between the aromatic ring and the methyl group is also higher (4.4 eV) [29, 30].Therefore, initially, the toluene could be decomposed via H-abstraction from methyl group, as well as aromatic ring by electron impact dissociation of C-H bond in the molecule to form benzyl radical, because the C-H bond in the methyl group and aromatic ring has lower dissociation energy. Moreover, the energetic electrons could break the C-C bond between benzene ring and methyl group, generating phenyl and methyl radicals [17]. The benzyl and phenyl radicals could agglomerate to form solid residue. Meanwhile, these radicals (phenyl, and methyl radicals) could combine with H radicals or react with H_2 to produce methane and benzene, respectively. The agglomeration of methyl radicals can form higher hydrocarbons (such as C_2, C_3, C_4, C_5 hydrocarbons) [31, 32]. Another route for the decomposition of toluene is the cleavage of the aromatic ring, which can produces LHCs ($<C_6$) directly by plasma assisted hydrocracking of aromatic ring in an NTP[33]. “Therefore, both H radicals and energetic electrons contribute to the decomposition of toluene in H_2 carrier gas. In an NTP, the formation of these chemically reactive species is necessary for the tar decomposition/hydrocracking reactions. In the cracking of a toluene molecule, the removal of methyl group, and the decomposition of aromatic ring are important [33]. An increase in plasma power/voltage can increase the electric field strength and the electron energy, which increases the number of reactive species in a DBD plasma. The increased electric field strength, the electron density, and the higher energetic electrons at high

power/voltage could all contribute to the enhanced toluene conversion and the increased selectivity of LHCs in an NTP.

It was observed that the NTP reactions strongly depended upon input energy. Hence, the specific input energy (SIE) is the main factor affecting the performance of the plasma process. It is reported that, even at 725 ^{o}C, the toluene conversion remains below 20 %, although the complete decomposition occurs by 900 ^{o}C [25]. It was observed that the most favourable required temperatures for toluene conversion was above 650 ^{o}C [22].

The decomposition of toluene with respect to SIE can be written as

$$r = -d[C_7H_8]/\,dSIE = k_{SIE}[C_7H_8]^n \quad (1)$$

Here n shows the reaction order and k_{SIE} is the energy constant in the given reaction. The natural log of remaining fraction of the toluene with respect to SIE in H_2 carrier gas is shown in fig. 3. It can be observed that the cracking of toluene in H_2 carrier gas can be represented by the following equation.

$$ln\frac{[C_7H_8]}{[C_7H_8]_0} = -k_{SIE} \times SIE$$

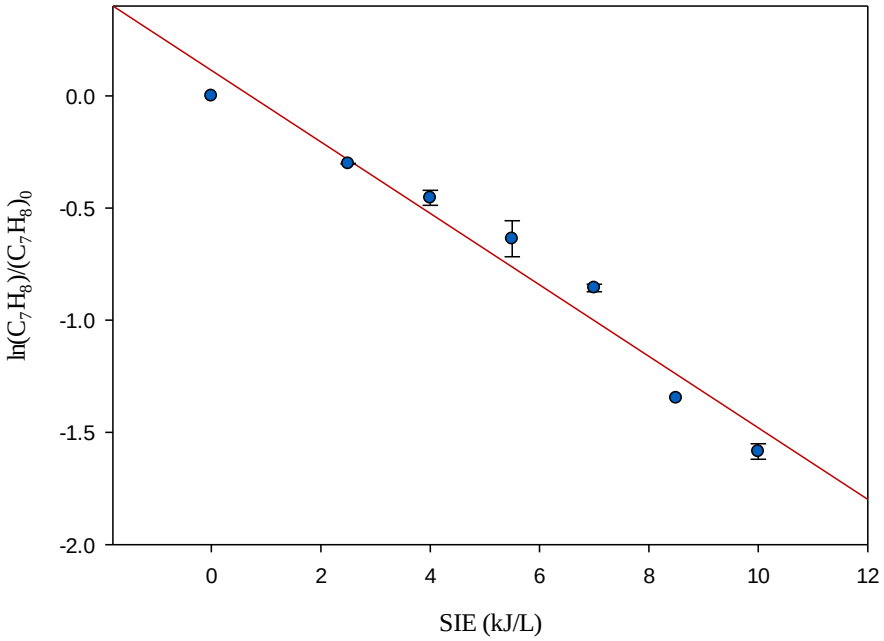


Fig.3 Effect of specific input energy (SIE) on the remaining fraction of toluene (Reaction conditions: concentration = 33 g/Nm^3; Temperature=ambient; and residence time=1.43 s)

The values of the R^2 here is 0.96. Therefore, the cracking of toluene in dielectric barrier discharge reactor as a function of SIE exhibits first order behaviour and the value of the energy constant (k_{SIE}) is 0.16 (L/kJ). It was reported that electron impact plays a key role in NTPs in similar reactions [30, 34].

3.2 Effect of concentration

The toluene concentration was varied between 20 and 82 g/Nm^3, to observe the effect on the conversion of toluene. Fig. 4 shows that the removal of toluene decreased from 98.5 % to 78% by increasing the concentration from 20 to 82 g/Nm^3. The trend is consistent with previous experimental results in which decomposition efficiency of toluene decreased with increasing the concentration in a DBD plasma, and that for benzene in a gliding arc plasma [16, 20].

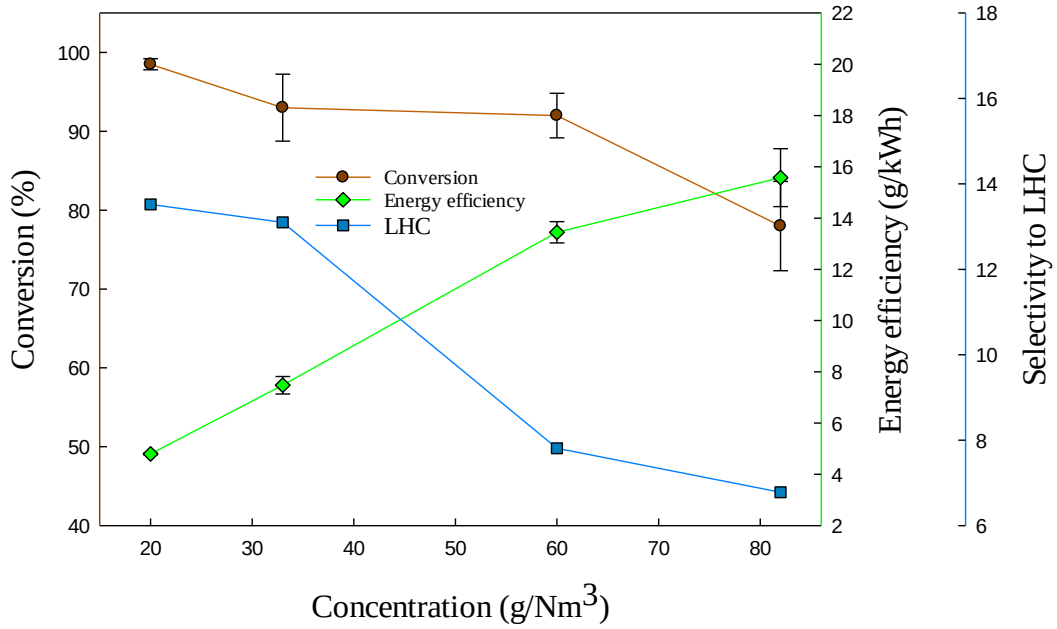


Fig.4 Effect of concentration on the conversion of toluene and energy efficiency of the plasma process; bars represent standard deviation. Reaction conditions: input power=10 W; residence time=4.23 s; flow rate 40.6 ml/min; ambient temperature. ; and SIE=14.77 kJ/L

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

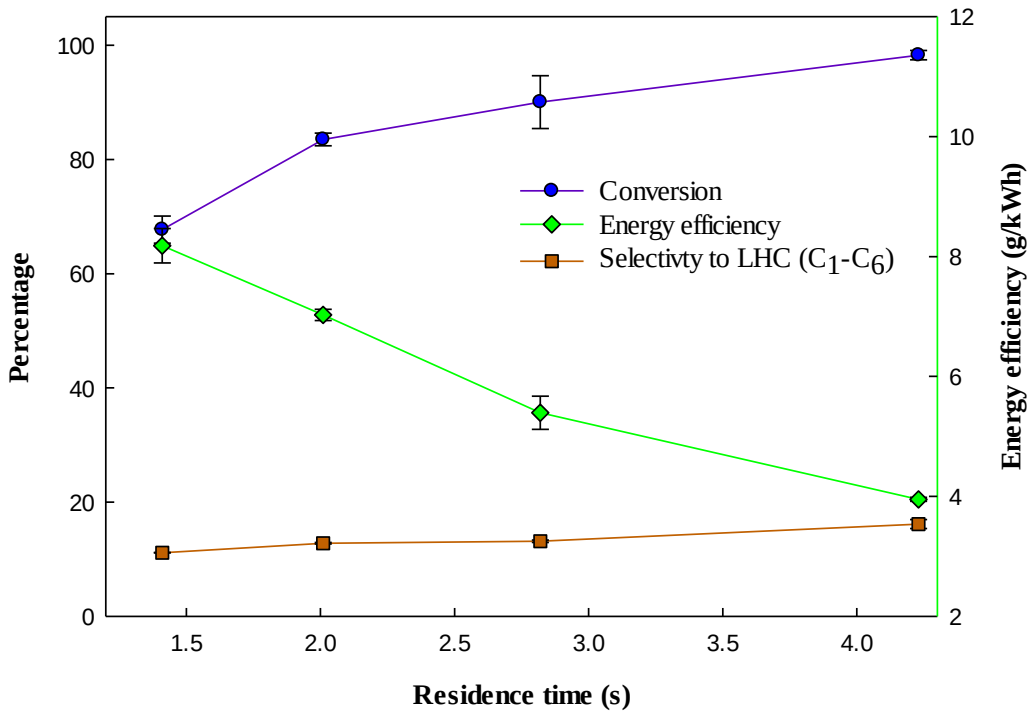
Therefore, as the concentration of toluene increases, the ratio of plasma-activated reactive species to toluene molecules will decrease, which will reduce the toluene conversion. Due to this reason, the selectivity to LHCs also decreases with increasing the concentration of toluene (Fig.4).

Fig.4 also shows the effect of the concentration of toluene on the energy efficiency of plasma. The energy efficiency increases from 4.79 g/kWh to 15.6 g/kWh by changing the concentration from 20 g/m^3 to 82 g/Nm^3. As the concentration is increased, it also increases the total amount of decomposed toluene, and so the energy efficiency of the plasma process.

The trend is similar to previous work in which GAD (Gliding Arc Discharge) plasma [16] and RGD (Rotating Gliding arc Discharge) plasmas [24] were used.

3.3 EFFECT OF RESIDENCE TIME

The removal efficiency of toluene is also influenced by residence time. Fig. 5 (a) shows the effect of residence time on the conversion of toluene at 20 W. It can be observed that decomposition of toluene increases with increasing residence time. The removal of toluene continuously increases from 67 % to 98 % as the residence time increases from 1.43 s to 4.23 s at 20 W (SIE: 10-29.6 kJ/L). At high residence time, the tar compound and carrier gas are subjected to plasma discharge zone for longer time, which can increase the collision between reactive species and tar compound. Therefore, increasing residence time promotes the conversion of toluene due to high number of collision between tar compounds and reactive species [24]. The maximum conversion attained was 98 % at the highest residence time used here (4.23 s).



(a)

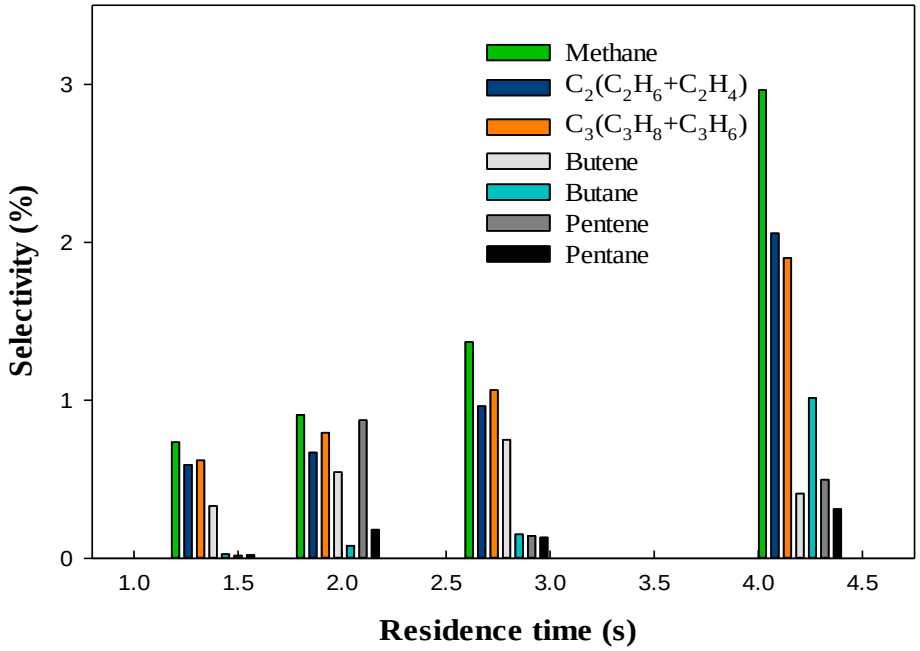


Fig.5 Effect of residence time (a) on the conversion of toluene, energy efficiency and selectivity to LHC; bars represent standard deviation (b) Selectivity to individual lower hydrocarbons. Reaction conditions: concentration = 33 g/Nm^3; flow rate 40.6-120 ml/min; Temperature=ambient; and Power=20 W; and SEI=10-29.6 kJ/L

The energy efficiency and selectivity towards the lower hydrocarbons (C_1-C_6) are shown in Fig. 5 (a). The energy efficiency of the process decreases with increasing residence time. It can be seen that energy efficiency decreases from 7.9 g/kWh to 3.9 g/kWh with increasing residence time from 1.43 s to 4.23 s. A similar trend of decreasing flow rate has been reported on the conversion of benzene [16].The residence time is associated with the flow rate, and for high residence time flow rate needs to be reduced. At low flow rate, the amount of tar compound subjected to plasma reactor also decreases, which decreases the total amount of decomposed toluene. Therefore, at high residence time, energy efficiency of the system decreases due to reduction in the total amount of decomposed toluene. Fig.5 (b) shows that

selectivity of LHC (C_1 –C_5) increases with residence time. The H_2 carrier gas spends more time in the plasma discharge with increasing residence time, which produces more H reactive radicals. These H radicals may contribute to increases the selectivity of lower hydrocarbons by reacting with toluene and its fragments.

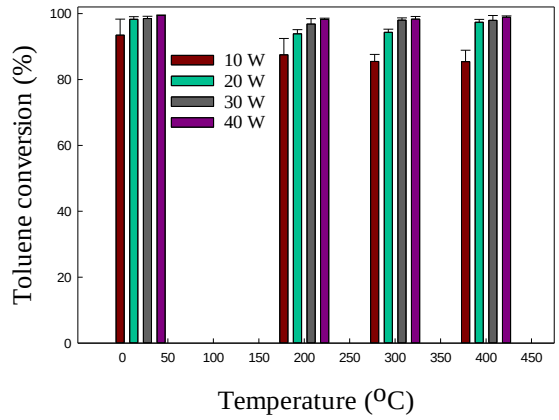
During the decomposition of toluene, a solid yellow residue was found inside the plasma zone. In some reports, these deposits were described as polymeric substances, or carbonaceous deposits [35, 36]. It was also reported that solid particles formed during the cracking of toluene in air, leading to the formation of solid deposits on the surface of the catalyst, thereby decreasing catalytic activity [37]. Moreover, formation of these solid residues can also clog the reactor. Therefore, it is very important to avoid the deposition of solid residue. However, in current study we have observed that the formation of solid residue completely disappeared (fig. 6 b) at elevated temperature in the presence of H_2 carrier gas.

3.4 Effect of temperature

Experiments were conducted to investigate the effect of temperature on product distribution and solid residue formation, at various powers (5-40 W) and a specific residence time (4.23 s). Fig. 6 (a), below, shows that removal of toluene is not affected by increasing the temperature. However, Song *et al.* (2002) reported that decomposition of toluene increased at elevated temperatures [38]. In other research, it was demonstrated that elevated temperature increased the removal efficiency of VOC in a non-thermal plasma reactor, and it was explained on the basis of increased kinetic reaction rate of O radicals [39]. However, in those experiments air was used as the carrier gas instead of H_2. In this research, at 40 W, almost complete removal of toluene was obtained at all temperatures.

Fig. 6 (b) shows the effect of temperature on the total selectivity to lower hydrocarbons at various levels of power and 4.23 s, it can be seen that total selectivity significantly increases

with increasing temperature at each level of power. At 400°C and 40 W, the selectivity rises from 20 % to 99.97 %, without the formation of solid residue. At 400°C and 4.23 s, the minimum selectivity towards LHC reaches to 81 % even at 10 W, which shows the high conversion of toluene to LHC, at high temperature, in the presence of H_2 carrier gas. There are three different types of reaction involve in hydrocracking of aromatics: (a) hydrogenation-dehydrogenation (b) isomerization and (c) cracking.



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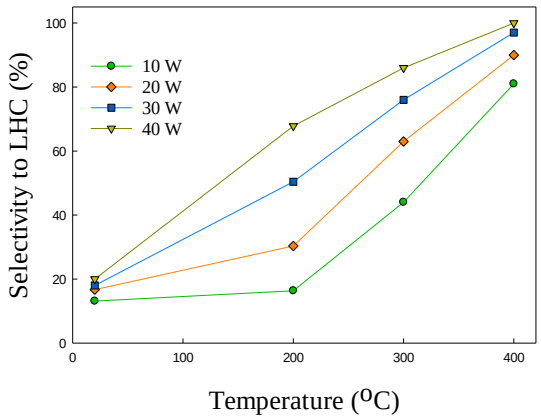

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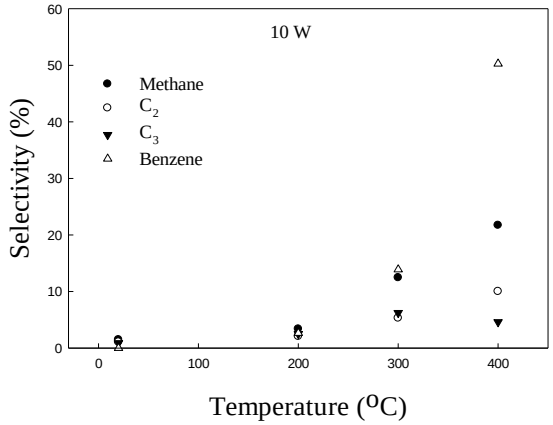

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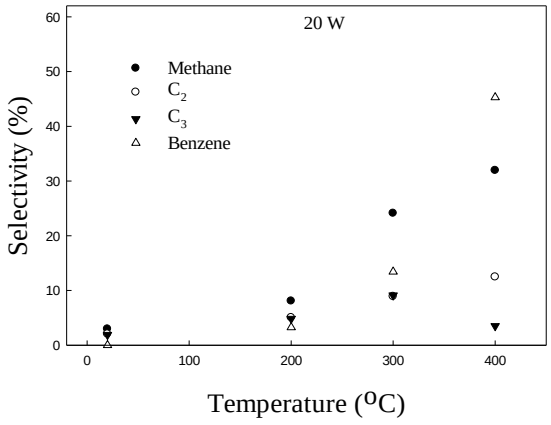

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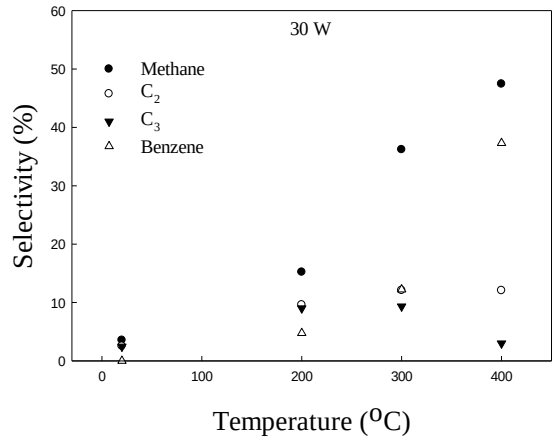

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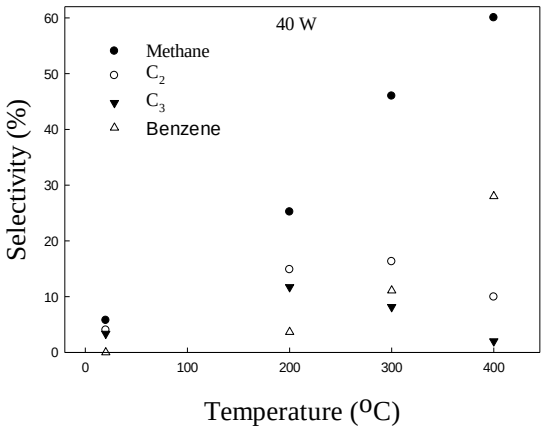

(f)

Fig.6 Effect of temperature on: (a) the conversion of toluene; (b) Total selectivity LHC; (c) Selectivity to various LHCs at 10 W;(d) selectivity to various LHCs at 20 W;(e) selectivity to various LHCs at 30 W; and (f) selectivity to various LHCs at 40 W. Reaction conditions: concentration = 33 g/Nm^3; flow rate 40.6 ml/min; residence time=4.23 s; and SIE=14.77-59.11 kJ/L

The cracking reaction can be categorized as primary (ring-opening), secondary and tertiary [40]. Hydrogenation and isomerization take place at lower temperature because of lower activation energy, whereas the rate of cracking (ring-opening) increases with increasing temperature [41].

Fig. 6(c), (d), (e), and (f) show the effect of temperature on the selectivity of individual LHCs at 10, 20, 30 and 40 W, respectively. Fig.6 (c) shows that, at 10 W, selectivity of benzene and methane reaches 50 % and 21% respectively, with increasing temperature up to 400 ^oC. However, the selectivity of C_2 (C_2H_6 + C_2H_4) and C_3 (C_3H_8+C_3H_6) remains below 11%. It has been reported that formation of benzene increases rapidly when increasing the temperature to 400^oC [42]. The high selectivity to the aromatic compounds may be due to a radical exchange reactions during the hydrocracking of toluene at high temperature [43]. It can be observed from fig. 6(f) that the selectivity of methane increases to 60%, whereas selectivity of benzene

reduces to 28%, at 40 W and 400°C. This happened due to the high population of energetic electrons at high power. In the absence of plasma, the selectivity of methane was reported to be nearly 10% at 450°C by hydrocracking of toluene [41]. It was reported that higher temperatures (>850 °C) are required to produce CH_4 and C_2H_4 as the major gaseous products [44, 45]. However, in this study, selectivity to methane reaches 60 % at 400 °C, due to the additional effect of non-thermal plasma.

The selectivity of C_2 (C_2H_6 + C_2H_4) increases to 16.3 % by increasing the temperature up to 300°C, afterwards it decreases to 9.93 % at 400 °C. Similarly, the selectivity to C_3 (C_3H_8+C_3H_6) increased when increasing the temperature from ambient to 200 °C, after which it decreased, from 200 to 400 °C. This occurred because of formation of methane in the presence of excess H_2 at high temperature [46]. Hence, the synergetic effect of plasma and temperature enhance the selectivity to lower hydrocarbons rather than solid residue. Plasma causes the production of reactive H radicals which hydrocrack toluene into lower hydrocarbons, when operating at elevated temperatures. It has been reported that adding steam reduces the formation of solid carbon and heavy hydrocarbons [47], which increase the operational cost and process complexity. However in this study, it was noted that problem can instead be resolved using hydrogen gas, which is already present (27-53 %) [48] in fuel product gas. The installation of a DBD reactor at a suitable location after the gasifier exit, where the temperature was high enough, could therefore have a substantial impact on tar mitigation.

4. Conclusions

In this study, the decomposition of toluene was studied in a dielectric barrier discharge (DBD) reactor using H_2 as carrier gas, as a proxy for biomass gasification tars. For the first time, this study investigated that elevated temperature in the presence of a DBD opens up new (thermal) reaction pathways to raise the selectivity to lower hydrocarbons via DBD promoted ring-opening reactions of toluene. H_2 was selected as a carrier gas because it is the major component

in most steam gasifier effluents. Experiments were performed at various levels of power (5-40 W) and residence time (1.43-4.23 s), at ambient and elevated temperature (20-400 ^{o}C), to determine the conversion and selectivity towards valuable gaseous products.

The main findings are as follows:

i. The removal efficiency of toluene can be as high as 99.5 % in this design of DBD reactor. The toluene is converted to lower hydrocarbons (C_1-C_6) and solid residue.

ii. The rate of decomposition of toluene increases with power input and residence time. At ambient temperature, solid residue was formed in the reactor, which would create various problems over time.

iii. Toluene conversion is not a function of temperature, but the selectivity is under plasma conditions, which is different from conventional chemical process. The selectivity towards lower hydrocarbons increases with increasing temperature, reaching 99.9 % at 400^{o}C, without formation of solid deposits and heavy hydrocarbons (>C_6). Clearly, there are benefits of combining thermal and non-thermal effects in this particular application. Here, adding in thermal effects allows high selectivity to LHCs, without solid residue formation: both desirable outcomes.

iv. Formation of methane, C_2 (C_2H_6 + C_2H_4) and benzene increases with increasing temperature. Here, the maximum selectivities observed were 60%, 9.93 % and 28%, respectively, at 400^{o}C and 40 W (the highest values used).

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