Reduction of tar from biomass gasification using a dielectric barrier discharge reactor

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Abstract. A non-thermal plasma reactor was used to investigate its effectiveness in reducing the by-products from biomass gasification. Biomass is used for generating heat and power through gasification, which is a process of converting solid fuel to gaseous fuel at temperatures of 700 to 900 °C by operating a reactor in sub-stoichiometric conditions. This gas mixture can be utilized for liquid fuel synthesis or for fuel cells. However, the by-product of gasification consists of tar, which consists of oxygenates, ringed-aromatics, phenolic compounds, and polyaromatic hydrocarbons (PAH). Depending on the composition, the condensation temperature can be as high as 450 °C, fouling downstream equipment. In this study, a dielectric barrier discharge (DBD) reactor with a coil as the inner electrode was used to reduce toluene, a model tar compound. Toluene was injected into a mixing chamber that was heated to 900 °C, evaporating the toluene, and is entrained by nitrogen into the DBD reactor. High voltage is injected into the DBD reactor to initiate ionization, decomposing the toluene into lighter hydrocarbons. A sampling bottle submerged in an ice bath collects the residual toluene, and the resulting decomposition rate is as high as 70%.

1. Introduction
Biomass is increasingly being used for generating heat and power through gasification, which is a process of converting solid fuel to gaseous fuel at temperatures of 700 to 900 °C by operating a reactor in sub-stoichiometric conditions [1]. In stoichiometric conditions, sufficient (or excess) amount of air is supplied for reaction of oxygen with solid fuels, and combustion is the main reaction where the products are mostly carbon dioxide and water. In sub-stoichiometric conditions, the amount of air into the reactor is less than required for the stoichiometric conditions, such that the there is a partial oxidation of the solid fuels (as opposed to combustion) produces syngas that consists of carbon monoxide, methane, hydrogen, and other hydrocarbons [1, 2]. This gas mixture can be utilized for liquid fuel synthesis [3, 4] or for fuel cells [5]. The scale and type of the gasifier affects the concentration of the by-product, also known as tar, which can be substantial and causes operational issues by fouling downstream equipment. Tar consists of compounds including oxygenates, ringed-aromatics, phenolic compounds, and polyaromatic hydrocarbons (PAH) [6–8]. The condensation temperature of tar depends on its composition, which can be as high as 450 °C [9, 10], making prevention measures difficult.

There are several methods to reduce tar, which include the use of low temperature pre-treatment methods, catalysts and scrubbers [7, 11]. Low temperature pre-treatments involve the carbonization of
biomass at temperatures of 300 to 400 °C before gasification. Results showed that the syngas from the
gasification of carbonized biomass contains 58% less tar than biomass which were not pre-treated [12].
Several catalysts are commonly used to reduce tar, such as nickel, cobalt, alumina, platinum, rubidium
and etc. However, the catalysts are known to deactivate during the reduction of the tar [13]. Recently,
dielectric barrier discharge (DBD) reactors initiate non-thermal plasma (NTP) to reduce tar content.
NTP has been known to convert toluene (C₇H₈, a model tar compound [14, 15]) by 90%, producing H₂,
CO, and CO₂ at a power consumption of 90 W and a temperature of 300 °C [16]. Naphthalene was also
used as a tar model compound in a reforming experiment, using a gliding arc discharge reactor (a form
of NTP) with the addition of steam. Results showed that the naphthalene conversion rate was 85%,
producing acetylene yield of 33%, with a total gas yield of 72% with a steam-to-carbon ratio of 2. The
advantage of NTP is its’ lower reaction temperature, allowing process and material requirements to be
less stringent. In this study, a dielectric barrier discharge (DBD) reactor was used to investigate its
effectiveness in reducing toluene, a compound that is classified as a Class 3 tar [17].

2. Methodology
Figure 1 shows a schematic of the experimental set-up. Toluene (5 to 7 g) was injected using a syringe
into a mixing chamber of 0.2 m in diameter and 0.1 m in height. The injection rate of toluene is timed
with a stopwatch, to ensure similar amount of toluene is injected into the mixing chamber within a period
of time for each experimental run. The mixing chamber is heated up to temperatures of 900 °C such that
the injected toluene evaporates. The toluene vapor is entrained by nitrogen (as a carrier gas) at a flow
rate of 10 LPM, giving a toluene concentration of 17%. The gas mixture of toluene and nitrogen then
flows into the DBD reactor.

The detailed dimensions and construction of the DBD reactor is described in [18], and is connected
to a high voltage (HV) supply shown in figure 2. A detailed description of the HV supply and set-up is
available in literature [19, 20]. The discharge power of the DBD is determined via a correlation with the
power consumption, recorded by a power meter, and is varied between 1 to 56 W to determine its effect
on the reduction rate of toluene.

When the voltage is high enough and the resonance frequency is achieved, ionization is initiated in
the gap between the dielectric barrier and the ground electrode. Electrons begin to accelerate to the
ground electrode, colliding with the toluene and nitrogen gas mixture.

The ionisation intensity of the DBD reactor is varied according to discharge power of between. A
sampling bottle filled with silica is submerged in an ice bath to collect the by-products from the reaction
with the DBD. The sampling bottle is weighed (in grams) before and after the experimental run to
determine the rate of decomposition or reduction. The results show that the higher the discharge power
(from 0 to 56 W), the higher the decomposition rate of toluene (from 28 to 55%).

M₀ is the initial weight of the toluene collected (in grams) after 20 s of the experiment, while Mᵰᵢ is
the weight of toluene collected (in grams) after each subsequent 20 s (e.g., t₀ = 20 s; t₁ =40 s; t₂ =60 s…)
The reduction rate of toluene is thus determined by:

\[ \text{Reduction rate of toluene (%) } = 1 - \left( \frac{Mᵰᵢ}{M₀} \right) \] (1)
3. Results and Discussion
Figure 3 shows the reduction rate of toluene with respect to time and discharge power of DBD reactor. After $t = 100s$, the little or no discharge power ($\sim 1W$), the decomposition rate of toluene in the sampling bottle is at 32%. When the discharge power of the DBD increases to 26 W, the reduction rate increases to 50%, and is at its highest at 41 or 56 W, with a reduction rate of 62%. After 200 s, the reduction rate reaches 70% at a discharge power of 56 W.
Figure 3. Decomposition rate of toluene with respect to time and discharge power of DBD reactor.

The results show that with increasing discharge power, there is an increasing number of excited electrons due to the higher ionization intensity. The higher number of electrons collide to initiate the breakdown of the toluene into lighter hydrocarbons. Reports have shown that the decomposition of toluene produces benzoic acid, benzaldehyde, benzyl alcohol and nitrophenol [21]. Real time monitoring of the lighter hydrocarbons showed that initially acetone was produced, and was decomposed into other organic byproducts such as methanol and acetic acid [22]. Other results suggest that when toluene is decomposed, the major gases that are produced are H₂, CO and C₂H₂, yields of 34.9%, 39% and 73.9% respectively [23].

The aforementioned elements and reactions can corrode the electrodes in the DBD reactor (figure 4), hence causing the surface to become uneven and the non-thermal plasma to be unstable, with sharp edges on the electrodes promoting sparks instead of the non-thermal plasma that is more effective in reducing tar formation.

A non-concentric DBD reactor was used in this study, with the advantage of a longer operating lifetime. When the surface of the electrode is corroded, the system could be tuned off temporarily so that the electrode is rotated to other new surface areas (figure 4). Operation of the non-thermal plasma is resumed for decomposition of the pollutants. Thus, the operating lifetime of the tar reduction device is extended.
Figure 4. Corroded surfaces of electrodes and other surfaces which could be rotated for continued use.

4. Conclusions
A non-thermal plasma system in the form of a dielectric barrier discharge (DBD) reactor has been shown to reduce the toluene content by as much as 70%. The non-concentric DBD used in this study has the advantage of a longer operating lifetime. If a surface of the electrode is corroded due to reactions with the toluene or other tar compounds, a new surface for reducing tar is available by extracting and rotating the electrode. A stable non-thermal plasma is now able to be generated for the decomposition of tar. The operating lifetime of the device is prolonged, since the reduction of tar continues until the entire surfaces of the electrodes have been corroded and exhausted. Future work includes the use of the device for the decomposition of other gases, such as biogas, and also pre-commercial trials in pilot scale gasifiers.

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