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**Keywords:** biomass gasification, plasma catalysis, tar reforming, syngas cleaning, non-thermal plasma

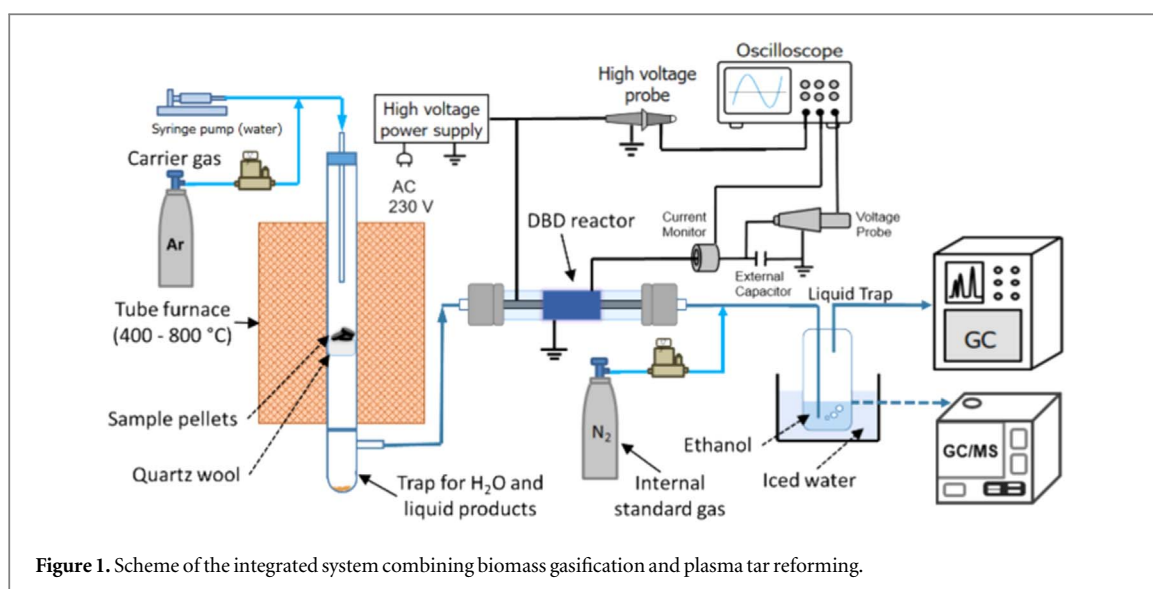
Abstract

An innovative integrated gasification and plasma-catalytic system has been developed to produce cleaner syngas from a model biofeedstock (α -cellulose). The influence of Co/ γ -Al₂O₃ catalyst on the plasma reforming of tar-contaminated syngas has been investigated using a cylindrical dielectric barrier discharge reactor. The results show that plasma-catalytic processing of the syngas from biomass gasification significantly reduces the concentration of tars by 88% and enhances the total gas product yield and the syngas ratio (H₂/CO) by up to 90%.

1. Introduction

Biomass is considered a promising source of renewable energy due to its net-zero emission of greenhouse gases. Biomass conversion for the production of fuels and higher value chemicals, therefore, offers a promising method to replace fossil fuels as the world's main energy source as we drive towards a net-zero carbon emission economy [1]. The most common pathways to producing fuels and energy from biomass include combustion, gasification and pyrolysis. Biomass gasification is a particularly attractive method as this can produce a syngas (a mixture of CO and H₂) that can be used as a feed gas for methanol and Fischer-Tropsch synthesis. H₂O is often introduced to the gasifier as an oxidiser to improve the yields of CO and H₂ through the water gas shift reaction. Other products of biomass gasification include light hydrocarbons, CH₄, CO₂, H₂O, char and tars (a complex mixture of condensable aromatic compounds). The presence of tars in syngas is particularly problematic as these can block pipelines, clog and foul components, and poison catalysts, reducing the processing efficiency and increasing maintenance costs. As typical tar concentrations in syngas streams are in the region of 0.1 g Nm⁻³ to 100 g Nm⁻³ [2, 3], the implementation of low cost and efficient processes for the removal or reforming of tars from syngas streams is, therefore, essential for the economic and sustainable production of syngas on a large scale. Mechanical/physical methods, such as dry and wet gas cleaning, catalytic cracking, and thermal treatment have been used to effectively treat tars [4]. Tar reforming by catalysis can be especially effective as this can enable conversion of the tars into syngas, thus increasing the yield. However, both thermal and catalytic methods often use high temperatures, which require a substantial amount of energy, and mechanical treatments can potentially reduce energy conversion efficiency.

Non-thermal plasma (NTP)-catalysis is a promising method for the sustainable reforming of tars from biomass gasification [3, 5–13]. NTPs can have a gas temperature as low as room temperature and are comprised of highly energetic electrons that can generate a cascade of reactive species such as radicals, ions, and excited atoms and molecules. These can significantly enhance reaction kinetics and enable thermodynamically unfavourable reactions (e.g. tar reforming) to proceed under ambient conditions. Combining NTP with catalysts can create synergistic effects that may enhance the conversion of reactants and improve product yield and selectivity. Indeed, plasma-catalysis is a demonstrably effective technique for tar reforming using various types of NTP, including dielectric barrier discharge (DBD) [9, 14–18], and gliding arc (GA) [19, 20]. DBDs are



most commonly used for plasma-catalysis as their reactor designs enable effective packing of the plasma discharge area with catalyst to optimise the plasma-catalyst interactions [21]. Furthermore, plasma processes can be switched on and off instantly, thus offering the potential to be coupled with renewable, intermittent energy sources (e.g. wind or solar energy) for localised or distributed chemical energy storage, which would improve sustainability and reduce processing costs [22]. However, most of the previous works have investigated plasma-catalytic reforming of model tar compounds (e.g., toluene, naphthalene) [3, 5–9], while very limited efforts have been made to explore the use of plasma-catalytic processes for the reforming of tars from real biomass gasification [14].

In this work, a prototype integrated gasification and plasma-catalysis system has been developed for the production of cleaner syngas from biofeedstocks. Tar-rich syngas was generated by steam gasification of α -cellulose, which was then treated by a DBD plasma (with and without a catalyst) to remove the tars. The discharge area of the plasma reactor was partially packed with $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$. The reaction performances were compared by analysing the composition of the gas and condensable liquid products.

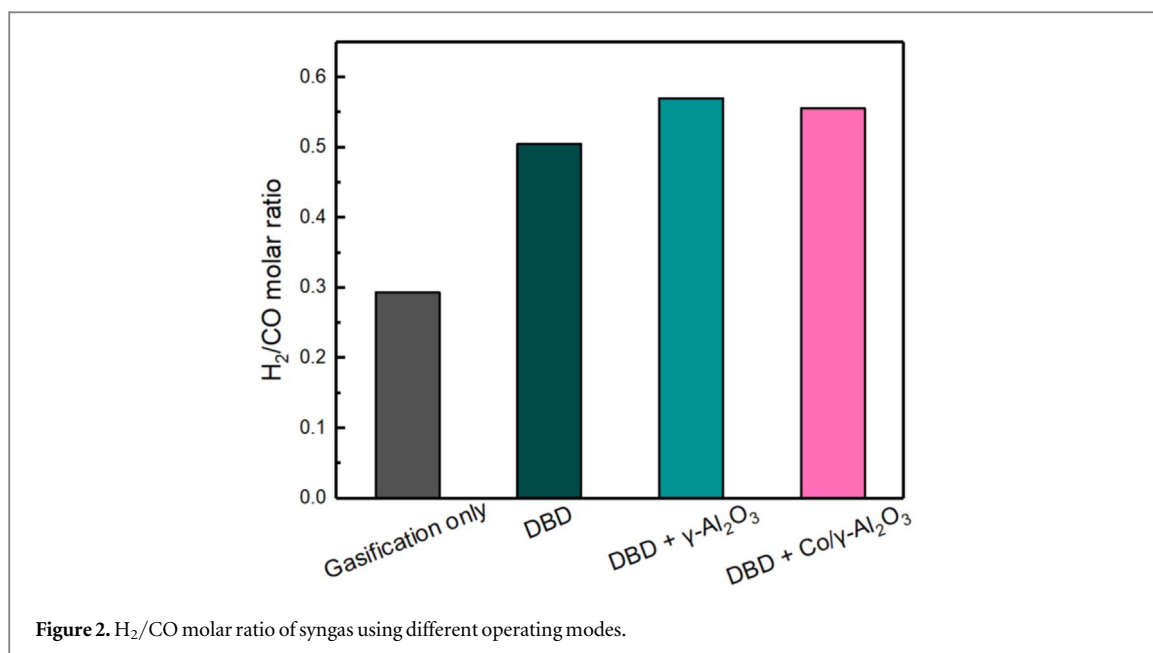
2. Experimental

2.1. Catalyst preparation

The catalyst support ($\gamma\text{-Al}_2\text{O}_3$) was first sieved to 40–60 mesh and then 10 wt% $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ was prepared by incipient wetness impregnation using cobalt (ii) nitrate hexahydrate (Acros Organics, 99%) as the metal source. The resulting slurry was sonicated at 50 °C for an hour and left to age at room temperature overnight. The catalysts and support were then dried at 120 °C for 4 h and then calcined at 450 °C for 4 h with a ramp rate of 5 °C min⁻¹.

2.2. Experimental procedure

Figure 1 shows a schematic diagram of the integrated gasification and plasma-catalysis system. The gasification process was carried out in a tube furnace (Elite) that was pre-heated to 800 °C. Deionized water was introduced into the gasifier at a flow rate of 3 ml h⁻¹ using a high-resolution syringe pump (KDS Legato 100). A 0.5 g α -cellulose pellet (Sigma Aldrich) was placed in the middle of the gasifier on a plug of cotton wool. Any gaseous products produced in the gasification were carried from the gasifier to the DBD reactor by Ar at a flow rate of 50 ml min⁻¹. Any condensable liquid products were captured in the trap below the tube furnace. A 300 mm long coaxial DBD reactor consisting of a stainless-steel rod high voltage electrode (300 mm L × 16.6 mm D.), a quartz tube (300 mm L × 25.2 mm O.D. × 2.5 mm W) and an aluminium foil tape ground electrode was used in these experiments. The discharge area of the DBD reactor (1.7 mm discharge gap and 49.6 mm in length) was partially packed using 1 g of catalyst (or support). The DBD was powered by a neon transformer with a maximum peak-to-peak voltage of 10 kV and a frequency of 22 kHz, and was operated at an input power of 25 W. N₂ gas (internal standard) was introduced into the gas stream after the DBD reactor at a flow rate of 10 ml min⁻¹. The experiments were carried out using four different operating modes: (i) gasification only, (ii) gasification with DBD, (iii) gasification + DBD packed with $\gamma\text{-Al}_2\text{O}_3$, and (iv) gasification + DBD packed with $\text{Co}/\gamma\text{-Al}_2\text{O}_3$. Gaseous products were analysed by gas chromatography (GC, Shimadzu, GC-2014) equipped



with a flame ionisation detector (FID) and a thermal conductivity detector (TCD). Any condensable liquid products in the effluent were captured in an ice-cold trap, containing ethanol as a solvent (25 ml), positioned at the exit of the DBD reactor. The condensed liquid products were analysed by gas chromatography—mass spectrometry (GC-MS, Agilent 7820A MSD 5975C) and identified using the mass spectral library from the National Institutes for Standards and Technology (NIST). Any liquid or waxy products condensed in the DBD reactor were collected by washing the catalyst and DBD with ethanol and qualitatively analysed using GC-MS.

The yield (*Y*) of the gas products was calculated as,

$$Y_{\text{product}}(\text{mmol}/g_{\text{cellulose}}) = \frac{\text{moles of product (mmol)}}{\text{mass of cellulose pellet (g)}}$$

The selectivities (*S*) of the carbon-containing gas products were given by:

$$S_{\text{CO}_x}(\%) = \left(\frac{\text{carbon in CO}_x \text{ (mol)}}{\text{carbon in cellulose pellet (mol)}} \right) \times 100\% \quad (x = 1, 2)$$

$$S_{\text{C}_x\text{H}_y}(\%) = \left(\frac{\text{carbon in C}_x\text{H}_y \text{ (mol)}}{\text{carbon in cellulose pellet (mol)}} \right) \times 100\% \quad (x = 1, 2, 3, 4)$$

The carbon balance of gas products is defined as:

$$\text{Carbon balance (\%)} = \sum S_{\text{CO}_x} + \sum S_{\text{C}_x\text{H}_y}$$

3. Results and discussion

Figures 2–4 show the syngas ratio (H₂/CO molar ratio), gas product yields, and tar product yields in the steam gasification of the cellulose pellets at 800 °C (gasification only mode). The syngas ratio was found to be 0.3, which was much lower than is typically required (H₂/CO: 1.7–2.0) for Fischer-Tropsch synthesis of liquid fuels. Co/γ-Al₂O₃ and γ-Al₂O₃ were used in conjunction with DBD plasma as an activator to improve the syngas ratio and reduce the tar formation. Figure 3 shows the effect of different operating modes on the gas product yields. There was a slight decrease in CO, CH₄ and C₂–C₄ gases detected after treatment with DBD only or DBD with catalyst, which may have resulted from further conversion of these gas products to hydrogen or recombination to condensable higher hydrocarbons. Indeed, the carbon balance of the cellulose feedstock to gas products (figure 4) dropped from 81% to 68% when passed through DBD plasma, indicating that some of the carbon-containing gases had been removed from the gas stream after interacting with the plasma. Partially packing the DBD discharge area with the Co/γ-Al₂O₃ catalyst was found to slightly improve the carbon balance to 72%, whereas packing with γ-Al₂O₃ increased the balance to 82%. Furthermore, treatment with DBD increased the H₂ production compared to gasification only (without plasma), which was further improved by partially packing the discharge area with the catalysts. This also led to notable improvements in the H₂/CO ratio of the syngas,

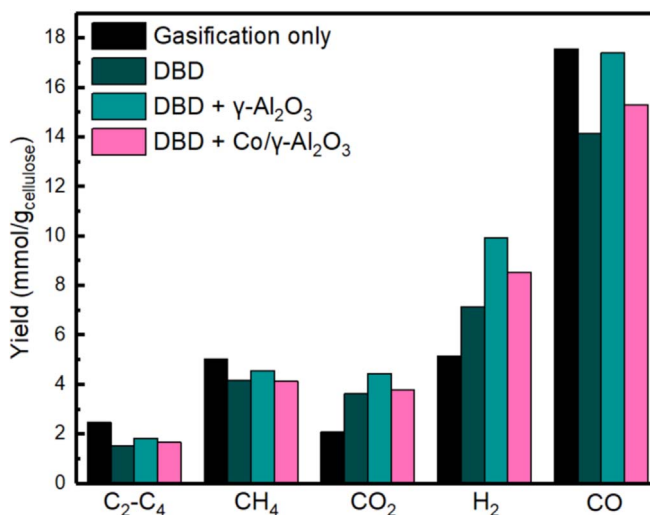


Figure 3. Yield of gas products using different operating modes.

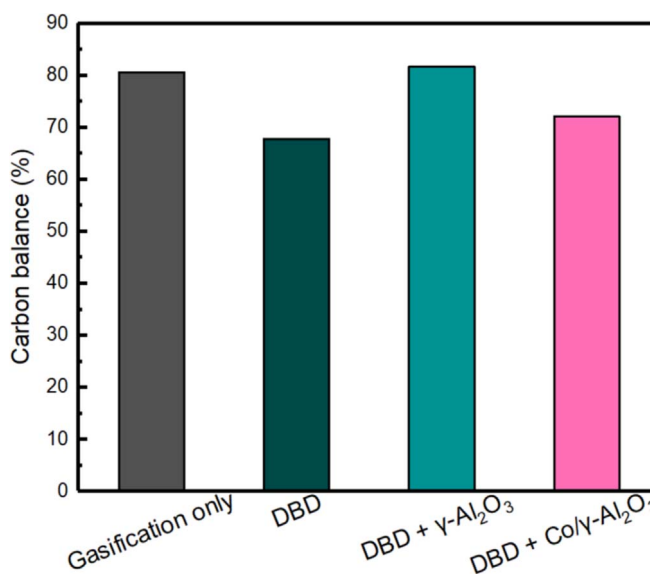
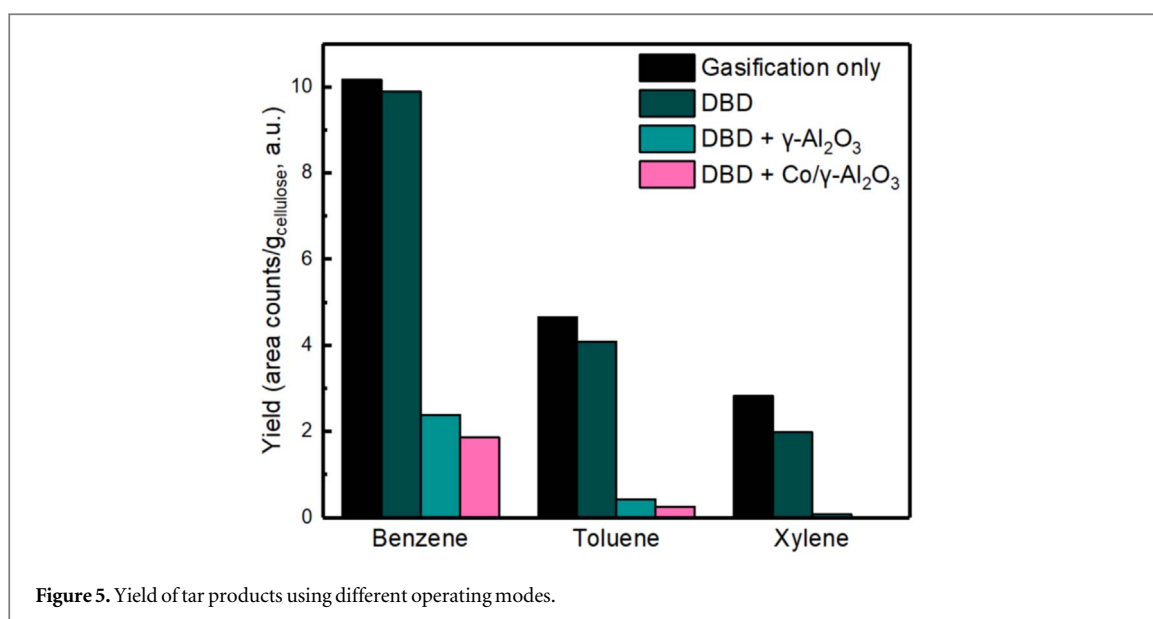


Figure 4. Carbon balance using different operating modes.

with DBD + $\gamma\text{-Al}_2\text{O}_3$ almost doubling the syngas ratio from 0.3 (gasification only) to 0.57 (figure 2). The enhancement in H₂ production by 65.2%–92.7% might be the result of a water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) and reactions of CH₄ and C₂–C₄ gases to produce larger molecules; these reactions could be facilitated by plasma activation of the reactant molecules to produce excited species that could then interact with each other in the gas phase or on the catalyst surface [23]. There was also an increase in CO₂ production when using DBD and catalysts, providing further evidence of the presence of water-gas shift reaction.

The condensable liquid products in the effluent were collected in an ice-cold ethanol trap. Any liquid or waxy products in the DBD or on the catalyst were collected by washing both with ethanol. The main condensed products identified from the post-DBD reactor effluent were monoaromatic tar compounds (i.e. benzene, toluene, and xylene isomers). Trace amounts of condensed polycyclic aromatic hydrocarbons (PAHs, e.g. naphthalene, fluorene, fluoranthene, pyrene and fluorene derivatives, etc.) were also detected. A comparison of the main tar product yields shows there was a significant reduction (88% reduction for DBD + Co/ $\gamma\text{-Al}_2\text{O}_3$) in the amounts collected after plasma-catalytic reforming process in the order: DBD + Co/ $\gamma\text{-Al}_2\text{O}_3$ > DBD + $\gamma\text{-Al}_2\text{O}_3$ > DBD (figure 5). These results are in agreement with those of other works that used supported-metal catalysts coupled with plasma to treat similar model tar compounds [14, 16], and can be attributed to the formation of surface and micro discharges and enhancement of the plasma electric field by catalyst packing that



can enhance tar decomposition [24]. Moreover, the presence of metal sites on the catalyst surface can improve charge transfer [25] and provide active sites for catalytic cracking. No traces of benzene, toluene or xylene were found in ethanol used to wash the DBD reactor and the catalysts post reaction.

4. Conclusions

A prototype integrated biomass gasification and plasma-catalysis tar reforming system has been developed as a promising and emerging method for producing cleaner syngas from α -cellulose. The results show that combining gasification with a plasma-catalytic tar reforming process significantly enhanced hydrogen production by up to 92%, reduced tar formation by 88%, and doubled the H₂/CO syngas molar ratio compared with using gasification only. This work has, therefore, demonstrated that the quality of the syngas produced by a gasifier can be improved using a plasma-catalytic reforming process, which could effectively remove tars and enrich the syngas with H₂ and enhance the syngas ratio.

Acknowledgments

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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