DBD plasma enhanced catalytic reforming of toluene to hydrogen-rich syngas

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Introduction

Biomass tar is a great challenge limiting the further development of biomass pyrolysis and gasification. The removal and reforming of tar are necessary for the commercial application of biomass gasification. The most common methods for tar destruction include thermal cracking, catalytic reforming and plasma treatment. However, direct thermal cracking and catalytic reforming need to be carried out at a high temperature, which requires high energy consumption (Chen et al, 2009). Plasma treatment is widely used for hydrocarbon reforming due to the advantages of fast ignition, universal applicability to hydrocarbons, less deactivation of catalysts, compact structure and light weight (Bromberg et al, 2000). Combining plasma with catalysts seems to be a more promising alternative, improving the conversion efficiency of tar and the selectivity of syngas. Various model compounds such as toluene, naphthalene and phenol are mostly used to replace the actual tar because of its complexity (Bona et al, 2008). In this paper, toluene was used as a model compound of biomass tar, and the reforming of toluene to produce syngas was carried out using dielectric barrier discharge (DBD) plasma. The effects of discharge power, oxygen content in carrier gas and steam/carbon ratio (S/C) on toluene reforming were studied to provide optimized parameters for tar reduction.

Materials and methods

The Ni/ZSM-5 catalyst with a Ni loading of 0.5 wt.% was prepared using fusion method in this study.

The coaxial DBD plasma generator contains a stainless-steel rod and a quartz tube wrapped with a 60-mm-long stainless-steel wire. The discharge gap is 1 mm. The reactor was installed vertically in a tube furnace. The DBD plasma reactor was connected to an AC high-voltage power supply with a maximum peak to peak voltage of 30 kV and a frequency of 10 kHz. The discharge time and temperature were 30 min and 573 K, respectively. Toluene and water were injected into the DBD reactor through two injection pumps. The flow rate of toluene was 30 μL/min. 1.0 g of catalyst held by quartz wool was placed in the discharge zone. After the reaction, the condensable products were absorbed using two impingers filled with methanol in an ice-water bath. The condensable liquid products were analyzed using gas chromatography-mass spectrometer. The non-condensable gaseous products were analyzed by gas chromatograph.

Results and discussion

The conversion efficiency of toluene increased with the increase of discharge power under the same composition of carrier gas, which can be seen from Fig. 1. It might be attributed to the fact that the produced electric field was stronger at higher discharge power and more electrons reacted with toluene. Fig. 1 also shows the oxygen content in carrier gas has some influence on toluene conversion. The conversion efficiency of toluene increased initially and then decreased with the oxygen content in carrier gas increasing. The highest conversion efficiency of toluene (87.97%) was achieved when the oxygen content was 3 vol.% and the discharge power was 90W. Appropriate oxygen content in carrier gas is essential for toluene reforming. As for the energy efficiency, it had the same trend as the conversion efficiency of toluene with the variation of carrier gas. The energy efficiency also reached the maximum when the oxygen content was 3 vol.%. The difference was that the effect of discharge power on energy efficiency followed an order of 75W>39W>90W. It indicates that it is not beneficial to increase the conversion efficiency of toluene by enhancing the discharge power continuously.

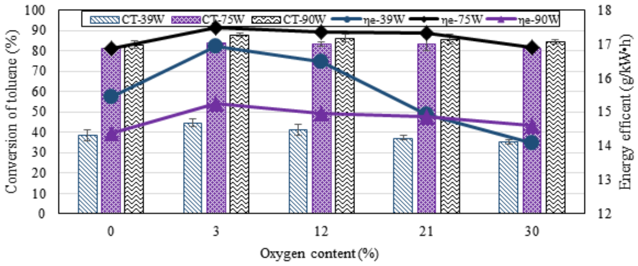
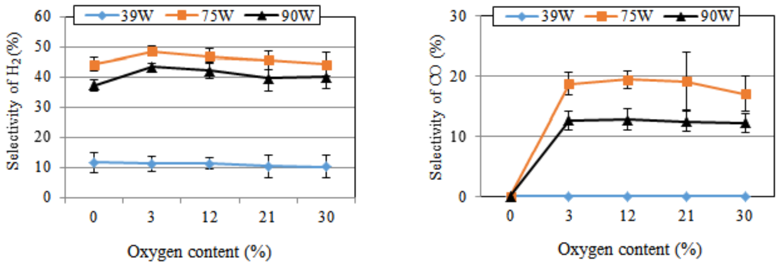


Fig. 1 Effects of discharge power and oxygen content in carrier gas on the conversion efficiency of toluene.

H_2 and CO were found as the main gas products of toluene reforming. The results showed that the effect of discharge power on the selectivity of H_2 followed the rule of 75W>90W>39W. When the discharge power were 75W and 90W, the selectivity of H_2 increased firstly and then decreased with the increase of oxygen content in carrier gas, as can be seen from Fig. 2a. When the oxygen content was 3 vol.%, the selectivity of H_2

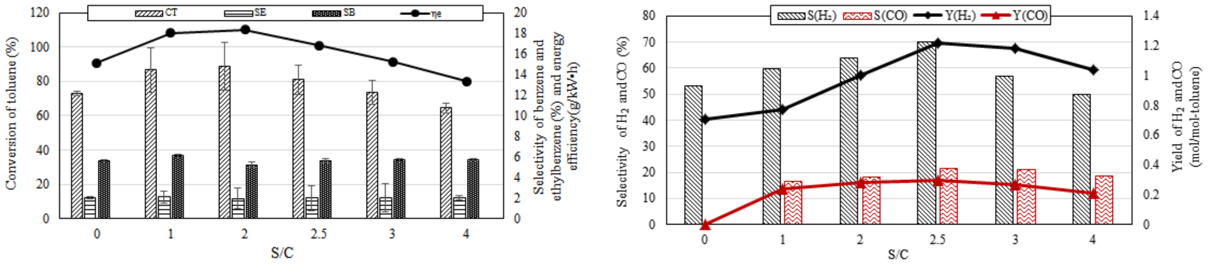
reached the maximum of 48.4% and 43.3%, respectively. However, when the discharge power was 39W, the selectivity of H_2 decreased with oxygen content increasing. The discharge power and carrier gas also affected the selectivity of CO. It can be seen from Fig. 2b that CO was almost not detected when the discharge power was 39W. However, when the discharge power was 75W and 90W, CO was generated. The selectivity of CO under 75W was higher than that under 90W. With the increase of oxygen content in carrier gas, the selectivity of CO first increased and then decreased. When the oxygen content in carrier gas was 12 vol.%, the selectivity of CO reached the maximum of 19.4% and 12.7%, respectively.



(a) (b)

Fig. 2 Effects of discharge power and oxygen content in carrier gas on the selectivity of H_2(a) and CO(b).

The effect of S/C ratio on toluene reforming was conducted in order to better understand the influence of steam on toluene reforming. It can be found that the conversion efficiency of toluene and energy efficiency increased firstly and then decreased with the increase of S/C ratio from 0 to 4 at a fixed toluene flow rate of 900μL. When S/C ratio was 2, the conversion efficiency of toluene and energy efficiency reached the maximum, as shown in Fig. 3a. However, the selectivity of benzene and ethylbenzene reached their minimum of 5.2% and 1.9% when S/C ratio was 2, which showed that most of the converted toluene did not generate benzene and ethylbenzene. The selectivity of H_2 and CO showed similar trend with the increase of S/C ratio and reached their maximum when S/C ratio was 2.5. The yield of H_2 and CO had the same variation as their selectivity.



(a) (b)

Fig. 3 Effect of S/C on the conversion efficiency of toluene, selectivity of benzene and ethylbenzene and energy efficiency (a), effect of S/C on the selectivity of H_2 and CO (b).

Conclusion

The results suggested that discharge power, carrier gas composition and S/C ratio had remarkable influence on toluene conversion, selectivity of benzene, ethylbenzene, H_2 and CO. The increase of discharge power promoted toluene conversion and reduced the selectivity of undesired liquid by-products. Appropriate carrier gas composition could promote toluene conversion and the selectivity of syngas while reduce the formation of undesired liquid by-products. In addition, the conversion of toluene and the selectivity of H_2 and CO increase firstly and then decrease by increasing the S/C ratio from 0 to 4, while the selectivity of benzene and ethylbenzene decreased firstly and then increased. At the S/C ratio of 2, the conversion efficiency of toluene was the highest and the selectivity of benzene and ethylbenzene was the lowest. However, when the S/C ratio was 2.5, the selectivity of syngas reached the maximum.

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