1-4-3  褐炭とチャーを同時供給した時のドロップチューブ反応器におけるタール in-situ 改質特性
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Pyrolysis and steam gasification of brown coal with in-situ tar reforming promoted by co-feeding char in a drop-tube reactor

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SYNOPSIS: A Victorian brown coal (Loy Yang, LY) was co-fed with char prepared from the same coal in the atmospheric drop-tube reactor at 900 and 950 °C in the presence of 50% steam to study in situ reforming of tar derived from rapid pyrolysis of brown coal over a char surface. This in-situ tar reforming process was investigated at different operating conditions, such as char properties, char concentration in the blended sample, temperature, solid hold-up, and steam partial pressure. Moreover, a four-lump kinetic model for the in-situ tar reforming process is proposed.

1. Introduction
Corresponding to the advanced-IGCC/IGFC technology, a triple-bed combined circulating fluidized-bed reactor system was proposed recently, which added a downer, as a pyrolyzer, to the conventional dual-bed circulating fluidized reactor system. One of the crucial expectations for this reactor system is tar decomposition at the downer, which was promoted by the circulating char/medium, so that minimizing the detrimental effects of tar on the following char gasification. Therefore we carried out the first study examining in-situ tar reforming over char surface under reaction conditions approximated in the downer where coal, char particles, and gas are concurrently flowing. In this work, a drop-tube reactor (DTR) was chosen to simulate the downer.

2. Experimental
Dried Loy Yang brown coal (LY) and two different chars were prepared, including devolatilised LY at 800 °C under nitrogen flow (LYC, surface area 524 m²/g) and LYC gasified with steam at 900 °C (GLYC, surface area 734 m²/g). The samples used in this study were prepared by blending LY and LYC/GLYC at different ratios.

The DTR included a transparent quartz tube, 2550 mm long × 8 or 15 mm internal diameter (isothermal zone, ~2100 mm long), which was heated up to 900–950 °C by eight independently controlled electric furnaces.

The sample and preheated nitrogen–steam mixed gas (200–250 °C) were supplied to the DTR. The resultant products were collected in a collection train consisting of char trap (200 °C), silica-fiber-made thimble filter (200 °C), cold traps (-73 °C), and gas bag (room temperature). We defined that the methanol soluble portion of the organic compounds condensed in the cold traps as light tar. Dichloromethane was used to wash the thimble filter and the cold traps after methanol washing. The resultant slurry was filtered to separate soot and solution. This Dichloromethane soluble portion of the organic compounds was defined as heavy tar. The soot and char were quantified by measuring the mass. The non-condensable gases (carbon oxides and gaseous hydrocarbons; CO₂ and GHCs) were collected in the gasbag. The solid carbon deposited over the inner wall of the DTR was quantified by the conventional combustion method.

3. Results and discussion
The yields of heavy tar at different concentrations of char are shown in Fig. 1, which are compared with predictions by assuming independent conversion of coal and char. The observed heavy tar yields were 0.40–0.50 mol-C/100-mol-C-sample lower than the
corresponding predicted yields at LYC ratios of 0.5, 0.75, and 0.85 in the blended samples, respectively. Therefore, the difference between observed and predicted heavy tar yields was direct evidence of nascent tar decomposition through tar–char interactions in the DTR.

Fig. 1. Heavy tar yields of in-situ tar reforming at different char ratios on a sample-fed carbon basis.

In-situ tar reforming in the DTR resulted from concurrent processes of pyrolysis, steam gasification, gas phase thermal cracking, and steam reforming. This process was influenced by the char properties, char concentration in the blended sample, temperature, and feeding rate corresponding to solid hold-up. Increasing the temperature, feeding rate, and char concentration enhanced the tar decomposition.

Fig. 2. Four-lump reaction net work for in-situ tar reforming process in the DTR.

To well understand the in-situ tar reforming process, particularly to design and simulate a real downer reactor, to predict reaction behaviour, and to optimize operating conditions, the first four-lump kinetic model for the in-situ tar reforming process is proposed. In our model the feedstock is lumped into tar (light and heavy tar), gases (COx and GHCs), char, and soot derived from the primary pyrolysis based on the assumption that the primary pyrolysis of coal has completed at the top of DTR (500–900 °C) before entering into the isothermal zone (900 °C). A simplified reaction net work among lumps in the DTR as shown in Fig. 2. For each reaction, a kinetic expression is formulated as a function of mole fraction for each lump on carbon basis and kinetic constants.

This four-lump kinetic model well predicts the product yields of the in-situ tar reforming process occurred in the DTR. The temperature shows great influence on almost every main reaction occurred during the in-situ tar reforming process in the DTR. The solid hold-up seems mainly affect on the tar–char interaction because of higher solid hold-up resulting in more chance for the tar and char contact. Under current conditions the steam partial pressure affects slightly on tar, char and gases yields. However the addition of steam suppresses the soot formation obviously.

Moreover, the quantitative correlation between kinetic constants and operating conditions are established.

4. Conclusions

This study demonstrated the potential of the downer part to decompose tar in the TBCFB reactor system by using a drop-tube reactor to simulate the reaction conditions expected in the downer. A four-lump kinetic model for the in-situ tar reforming process is proposed, which well predicts the in-situ tar reforming process occurred in the DTR.

References

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