Co-pyrolysis of cellulose and polyethylene: Prediction of pyrolyzate yields using response surface methodology

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INTRODUCTION

Pyrolysis is a promising technology for the treatment and utilization of polymeric materials, which are converted into gas, oil, and char under high temperature and the absence of oxygen. The production of value-added chemical feedstocks (sugar, phenol, and hydrocarbon) is enhanced by controlling the synergistic effect between lignocellulosic biomass and plastic (Kumagai S., Fujita, K. et al., 2016). However, there is still a lack of comprehensive understanding about pyrolyze yields at different conditions because there are numerous combinations of plastic and biomass. Therefore, it is necessary to establish the mathematical model for obtaining certain results without conducting experiments and instructing the directional conversion of wastes to chemical feedstocks in further large-scale pyrolysis experiments. Response surface methodology (RSM) is a combination of mathematical and statistical techniques, which is based on the fit of a polynomial equation to the experimental data and can include the interactive effects among different variables (Bezerra M., Santelli, R. et al., 2008). Therefore, we applied RSM to predict yields of major pyrolyzates besides the gas, liquid, char yields based on a case study of cellulose and PE co-pyrolysis.

MATERIALS AND METHODS

Materials

Commercial cellulose and high-density PE were ground, sieved (less than 75 μm), and kept in a glass desiccator. The pulverized cellulose and PE (0.1 g) with the desired weight ratio were placed in microtubes and mixed by shaker for 5 min to obtain homogenous mixtures.

Design of co-pyrolysis conditions

The variable central composite design based on two factors and five levels was applied to determine co-pyrolysis condition via Design Expert 12 software (Stat-Ease Inc., Minneapolis USA), and its design principle was shown in **Fig. 1**. It was required at least 15 experiments for covering the entire conditional area where the center point of the experimental domain (600 °C with 50% of PE addition) was repeated three times for reducing the pure error.

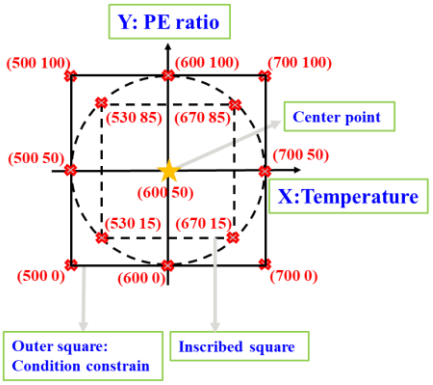

Fig. 1 Principle of central composite circumscribed design based on co-pyrolysis experiment.

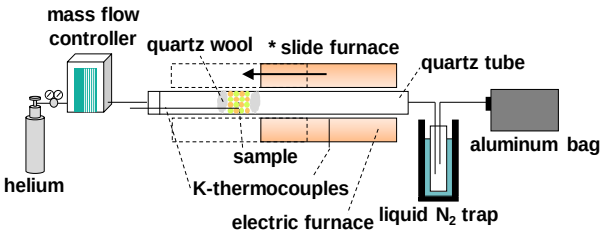

Fig. 2 Experimental setup of horizontal tube reactor.

Pyrolysis experiment and product analysis

The sample was pyrolyzed at preset temperature for 15 min with 50 mL/min of helium using a horizontal tube reactor as shown in **Fig. 2**. Gases were analyzed by GC/MS and GC/FID using standard gases. The liquid yield was determined by the weight difference of cut tube, joint, and trap before and after rinsing with 10 mL of tetrahydrofuran (THF) solution. The THF solution containing liquid products were analyzed by GC/MS and GC/FID with naphthalene as the internal standard. The solid (THF insoluble fraction) yield was measured by the weight difference of the THF-rinsed cut tube before and after combustion at 900 °C. The char yield was calculated from the weight difference of the cut tube before and after combustion at 900 °C.

RESULTS AND DISCUSSION

The gas yield was increased from 4.4% to 18.5% with the increases in co-pyrolysis temperature and PE ratio. The liquid and char yields were decreased from 33.9–38.3% and 4.4–5.1% to 5.8–10.9% and 0% with the addition of more PE, respectively. The yields of gas, liquid, and solid (coke and wax) could be sufficiently described by the quadratic model ($R^2 > 0.96$) because their results presented the curved trend. Co-pyrolysis could increase gas and liquid yields and decrease the solid yield compared with the theoretical value. The interaction between cellulose and PE did not affect char formation, which was suitable for the linear model ($R^2 = 0.97$). To more specific, the addition of PE had different synergistic effects on LG yield with the rise in temperature, which could be fitted to the cubic model ($R^2 = 0.99$). Cellulose would remarkably promote PE decomposition and increase the hydrocarbon yield with the rise in temperature, which could be described by the cubic model ($R^2 = 0.91$). The CO yield could be well-described by the quadratic model ($R^2 = 0.98$) because co-pyrolysis promoted the CO formation. The CH_4 yield could be well-described by the cubic model ($R^2 = 1.00$) because there were different synergistic effects. Moreover, the statistical analysis also verified the significance and accuracy of the models.

CONCLUSION

This study aimed to establish the mathematical model for obtaining certain results without conducting pyrolysis experiments. In this case, the product yield prediction models from co-pyrolysis of cellulose and polyethylene at 500–700 °C were established by response surface methodology. The different polynomial equations can predict the product yields with high accuracy. This work shows that response surface methodology is a promising way to effectively predict pyrolyzes distribution, which will help instruct the directional conversion of wastes to chemical feedstocks in further large-scale pyrolysis experiments.

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