Co-Pyrolysis of Corn Stover with Plastic: Optimization Based on Synergy

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Abstract

The co-pyrolysis of lignocellulosic wastes such as Corn stover with plastic has been found to improve the both the yield and quality of pyrolysis oil and gas products. In this study, the co-pyrolysis of Corn stover (CS) with plastic (LDPE, and PP) were studied through thermogravimetric analysis. The parameter "change in weight loss rate" denoted by ΔW was used to quantify the synergistic effects on the yield during co-pyrolysis. The ΔW values were fitted using a combined mixture design to generate an RSM model relating the factors mixture component proportions, plastic type, and temperature to the response ΔW. From numerical optimization, the obtained optimum co-pyrolysis conditions are: (a) 0.60 CS proportion, 0.40 LDPE proportion, and 481.73 °C temperature for CS-LDPE, (b) 0.68 CS proportion, 0.32 PP proportion, and 492.15 °C temperature for CS-PP. The activation energy, and pre-exponential factor of the reactions in the co-pyrolysis process were also obtained using direct solution method. The activation energy of the reaction that took place from 420 to 510 °C was found to be lower in the co-pyrolysis of Corn stover and plastic than in the pyrolysis of pure plastic.

Keywords: co-pyrolysis, corn stover, plastic, optimization, combined mixture design, synergistic effect

1. Introduction

The growing concern in the depletion and negative environmental impacts of non-renewable energy sources like fossil fuels has led many researchers to focus on the development in the utilization of renewable energy sources such as biomass. Corn is one of the major agricultural crops in the Philippines. The main residue from Corn is the stover which is defined as the material left in the field after the harvest of the corn grain [1]. In 2016, around 7 million tons of Corn stover was generated in the Philippines. The co-pyrolysis of lignocellulosic residues with hydrogen-rich feedstocks such as plastics is a promising conversion process for the production oil and gas products. Having a high hydrogen content of about 14 % by mass, plastic could donate hydrogen during co-pyrolysis which leads to improvement in both oil yield and quality [2]. Furthermore, the utilization of waste plastics for co-pyrolysis could be beneficial to the environment since plastics have been a serious threat in the environment because of their low recycling rate and non-biodegradability. Thus, this study aimed to optimize conditions of the co-pyrolysis of corn stover with plastic for maximum synergistic effects on the yield of oil and gas products.

2. Materials and Methods

2.1. Feedstock Preparation

Corn stover was obtained from the Institute of Plant Breeding, University of the Philippines Los Baños. Prior to drying, it was washed with distilled water. Then, it was sun dried for two days and it was pulverized and sifted through a 1 mm sieve. Then, it was dried in an oven at 120 °C for 2 hr.

Commercially available low-density polyethylene (LDPE), and polypropylene (PP) were used in this study. These plastics were also pulverized and sifted through a 1 mm sieve.

2.2 Combined Mixture Designed Co-Pyrolysis Runs

Through a combined mixture design, an RSM experimental design where both mixture component proportions and process factors are studied, co-pyrolysis experiments using a thermogravimetric analyzer were performed considering CS proportion, plastic proportion, temperature, and plastic type. The response parameter was ΔW, which is difference between the weight loss rate from the co-pyrolysis process and the sum of the weight loss rates from the individual pyrolysis of Corn stover and plastic multiplied by their respective weight fraction in the Corn stover-plastic mixture.

2.3 Kinetics

Direct-solution method [3] was used to determine the kinetic parameters of the co-pyrolysis of Corn stover-plastic mixtures. In this method, the specific rate, k, at different temperatures were calculated at different assumed reaction order. Assuming Arrhenius relation holds, the assumed reaction order that yielded straightest ln k versus 1/T plot was then selected. The slope of the selected plot is the negative of the ratio of activation energy and ideal gas constant (-E/R) while the intercept is the natural logarithm of the pre-exponential exponent (A).

3. Results and Discussion

3.1 DTG Curves

Figure 1 shows the DTG curves obtained from the co-pyrolysis of (a) CS-LDPE, and (b) CS-PP. As shown in the two figure, the thermal decomposition of Corn stover

component occurred at lower temperatures while the thermal decomposition of the plastic component took place at higher temperatures.
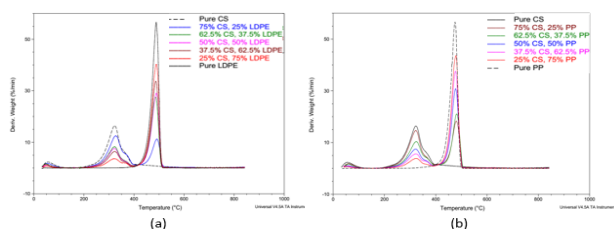

Figure 1. DTG curves from the co-pyrolysis of (a) CS-LDPE, and (b) CS-PP.

3.2 Response Surface Graphs for ΔW

A positive value of ΔW indicates synergistic effects on the rate of the thermal decomposition of the feedstock in the co-pyrolysis process. Figure 2 shows the contour plots for ΔW from (a) CS-LDPE, and CS-PP. High values of the ΔW are color coded with warmer colors toward red, while lower values are color coded with cooler colors toward blue. As shown in the plots, high positive values of ΔW were observed at higher temperatures between 420 and 520 °C since only at this temperature range when plastic has started to decompose. At low temperatures, plastic only undergoes melting.

The synergism in the co-pyrolysis of plastics and biomass could also be due to radical interaction. This co-pyrolysis induced secondary radicals formation are usual free radical formation which involves depolymerization, hydrogen transfer reactions, monomers formation, intermolecular hydrogen and isomerization via vinyl groups [4].
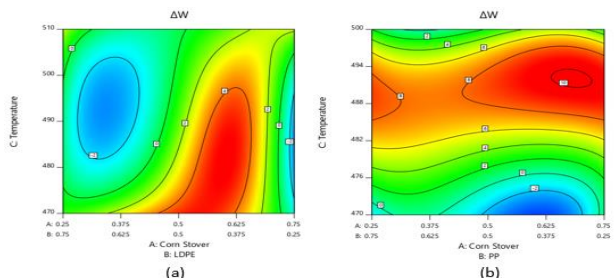

Figure 2. Contour plots of ΔW from the co-pyrolysis of (a) CS-LDPE, and (b) CS-PP.

3.3 Optimum Co-Pyrolysis Conditions

Table 1 shows the obtained optimum conditions from the co-pyrolysis of CS-LDPE, and CS-PP. Between the two mixtures, CS-PP showed a much higher predicted ΔW.

Table 1. Optimum co-pyrolysis conditions

Mixture	Optimum Conditions			Predicted ΔW, %/min
	CS Proportion	Plastic Propotion	Temperature, °C	
CS-LDPE	0.60	0.40	481.73	4.92
CS-PP	0.68	0.32	492.15	10.5841

3.4 Effect of Proportions on Activation Energy

Figure 3 shows the effect of proportion on the activation energy of the decomposition of the components in the co-pyrolysis of (a) CS-LDPE, and (b) CS-PP. As shown in the two figures, the activation energy of the decomposition of CS was not affected by the presence of plastic while the presence of CS decreased the activation energy of the decomposition of plastic. The char formed from the pyrolysis of the biomass at lower temperatures acted as a catalyst in the thermal degradation of polypropylene which resulted to a reduction in the activation energy [5].
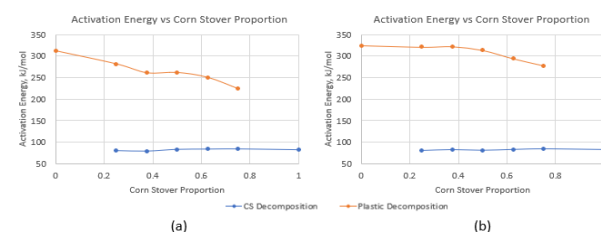

Figure 3. Effect of proportion on the activation energy of the decomposition of the components in the co-pyrolysis of (a) CS-LDPE, and (b) CS-PP.

4. Conclusions

This study has optimized the co-pyrolysis conditions of Corn stover and plastic through thermogravimetric analysis using a combined mixture experimental design. The obtained optimum co-pyrolysis conditions are: (a) 0.60 CS proportion, 0.40 LDPE proportion, and 481.73 °C temperature for CS-LDPE, (b) 0.68 CS proportion, 0.32 PP proportion, and 492.15 °C temperature for CS-PP. Kinetic Analysis showed that the activation energy of the decomposition of CS was not affected by the presence of plastic while the presence of CS decreased the activation energy of the decomposition of plastic.

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