CO-PYROLYSIS OF CORN STOVER WITH LOW-DENSITY POLYETHYLENE (LDPE), AND POLYPROPYLENE (PP): OPTIMIZATION BASED ON SYNERGY

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ABSTRACT

The co-pyrolysis of lignocellulosic wastes 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 (low-density polyethylene, and polypropylene) 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 Δ W. 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 preexponential factor of the reactions in the co-pyrolysis process were also obtained using direct solution method. The activation energy of the thermal decomposition of plastic 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

NONMENCLATURE

| Abbreviations | |
|---------------|---------------------------|
| CS | Corn stover |
| HDPE | High-Density Polyethylene |

| LDPE | Low-density polyethylene | | |
|---------|------------------------------|--|--|
| PP | Polypropylene | | |
| RSM | Response Surface Methodology | | |
| TGA | Thermogravimetric Analysis | | |
| | | | |
| Symbols | | | |
| k | Specific rate constant | | |
| Т | Temperature | | |
| А | Pre-exponential factor | | |
| E | Activation energy | | |
| R | Ideal gas constant | | |

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 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 to produce 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 copyrolysis could be beneficial to the environment since plastics have been a serious threat in the environment because of their low recycling rate and non-

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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. LITERATURE REVIEW

The parameter "change in weight loss" (denoted by Δ W), which is defined as the difference between the observed weight loss from the TGA of the mixture and the sum of the observed weight loss from the TGA of the individual components multiplied by their mass fraction in the mixture, have been used by two teams of researchers to quantify the synergistic effects during the co-pyrolysis of biomass with plastic. Zhang and his colleagues [3] used this parameter on the co-pyrolysis of Douglas fir sawdust (DF) with LDPE, while Wang et al. [4] used this on the co-pyrolysis of corn stover with highdensity polyethylene (HDPE). In both studies, high positive values of \triangle W were observed at higher temperatures near 500 °C because only at this temperature range when the plastic component has started to decompose.

In this study, instead of change in the cumulative weight loss, the change in the instantaneous weight loss rate or the change in the rate of the thermal degradation was used on the quantification of the synergistic effects. Unlike with the two previous studies, the study of effects of mixture component proportions, and plastic type on the synergism during co-pyrolysis was included in the study. Lastly, this is the first study which aimed to optimize the co-pyrolysis conditions (mixture component proportions, and temperature) that will maximize the synergistic effects using only the data from thermogravimetric analysis through a combined mixture experimental design.

3. MATERIALS AND METHODS

3.1 Feedstock

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 $\,^\circ\!\mathrm{C}\,$ 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.

3.2 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 the 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

3.3 Kinetics

Direct-solution method [5] was used to determine the kinetic parameters of the co-pyrolysis of corn stoverplastic 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).

4. RESULTS AND DISCUSSION

4.1 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 sets of graphs, 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.

4.2 ΔW vs Temperature Plot at Different Proportions

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 ΔW vs plot at different proportions from (a) CS-LDPE, and (b) CS-PP. As shown in the plots, high positive values of ΔW were observed at higher temperatures between 420 and 520 °C for all the different proportions because only at this temperature range when plastic has started to decompose and interact with the biomass. At low temperatures, plastic only undergoes melting.





The synergism in the co-pyrolysis of plastics and biomass at high temperatures could be due to radical interaction between their products. This co-pyrolysis probably induced formation of secondary radicals involves depolymerization, hydrogen transfer reactions, monomers formation, intermolecular hydrogen and isomerization via vinyl groups [6].

Another mechanism of the synergistic effects in the co-pyrolysis could also be hydrogen donation. The plastic could donate hydrogen during co-pyrolysis which results

in the improvement of both yield and quality of oil and gas products [2].

4.3 Effect of Proportions on ΔW

Figure 3 shows the effect of proportions on ΔW at high temperatures (near 500 °C) for (a) CS-LDPE, and (b) CS-PP. The cubic trends on both plots could be due to the gradual increase and then decrease in the rate of the generation of aromatic compounds with the increase in plastic proportion. The increase in aromatic yield could be due to increase in effective hydrogen to carbon ratio of the system as the plastic proportion is increased while the gradual decrease in the aromatic yield as the plastic proportion is further increased could be due to the decrease in polycyclic aromatic hydrocarbons which is resulted from enhanced degradation of plastic in the presence of the oxygenated compounds produced from biomass pyrolysis [7].



Figure 3. ΔW vs Proportion Plot (a) at 490 °C for CS-LDPE, and (b) at 500 °C for CS-PP.

4.4 Response Surface Graphs for ΔW

The contour plots for ΔW were generated using the statistical model that was obtained from response surface methodology. Figure 4 shows the contour plot for ΔW from (a) CS-LDPE, and (b) 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. Based on the response graphs, high positive values of ΔW occurred at: (a) CS proportion between 0.4 and 0.6, and temperature between 470 and 495 °C for CS-LDPE, (b) CS proportion between 0.5 and 0.75, and temperature between 482 and 494 °C for CS-PP



Figure 4. Contour plots of ΔW from the co-pyrolysis of (a) CS-LDPE, and (b) CS-PP.

4.5 Optimum Co-Pyrolysis Conditions

The optimum co-pyrolysis temperature, and proportions were obtained from the numerical optimization of the statistical model from RSM. 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

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

4.6 Effect of Proportions on Activation Energy

Figure 5 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 [8].



and (b) CS-PP

5. CONCLUSION

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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