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Co-pyrolysis of Corn-cob and Waste Cooking-oil in a fixed bed reactor with HY upgrading process

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Abstract

Corn cob and waste oil were co-pyrolysed in a fixed bed at the temperatures of 500℃, 550℃, 600℃, respectively, under nitrogen atmosphere. Co-pyrolysis products were investigated with focus on the physical and chemical properties of oily products characterized by means of GC–MS and elemental analyser. The results show 550℃ seems to be the optimum temperature considering maximum bio oil yields and bio oil properties. Co-pyrolysis of corn cob and waste oil produced more amount of liquid and less amount of solid residue than that of pyrolysis of corn cob solely. While weight ratio of waste oil: corn cob increases from 0 to 0.87, bio-oil yield increases dramatically from 44.7wt% to 70.62wt% with increasing acids content and decreasing phenols, acohols, ketones content. The upgraded bio-oil has the potential to be an alternative fuel for engine after upgraded by HY zeolite.

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Key words: corn cob; waste cooking oil; co-pyrolysis; fixed bed; bio oil; HY zeolite

1. Introduction

Pyrolysis is a process in which biomass is converted without oxygen into three phase products (char, bio-oil and gases) as energy production, especially the bio-oil which holds the potential to become an alternative for transportation fuels and important chemicals[1]. Recently, a new method of pyrolysis process, by adding alcohols into the pyrolysis process has been proved to attain quality-upgrading and yield-enhancing bio-oil [2]. The elevated hydrogen to carbon effective ratio (H/C_{eff}) of the feedstock is the key contributing to the effect. The H/C_{eff} ratio is defined in Eq. 1, where H, C and O are the mol of hydrogen, carbon, and oxygen, respectively.

$$H/C_{eff} = \frac{\text{mole of } (H-2O)}{\text{mole of } C} \qquad (1)$$

The isotopic study showed that all the hydrocarbon products contained mixtures of ^{12}C (from biomass) and ^{13}C(from methanol), indicating that the feeds lose their identity within a hydrocarbon pool and

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combine stochastically with other molecules. This conclusion proves that adding hydrogen to biomass conversion process via co-feeding it with other higher H/C_{eff} ratio is feasible. However, the additives (alcohols) used in the research are quite valuable resources and the optimal reactive condition between biomass and alcohol is varing to a large extent. Herein, new additives should be found to enhance the quality and yield of pyrolysis oil.

Waste cooking oil (WCO) owns a relative high $H/C_{eff ratio}$ (>2) and has been viewed as a waste resource for a long time. It is usually used as raw material to produce biodiesel. However, WCO-derived biodiesel is quite less in amount and completely not enough as an additive to petro-diesel on the market, thus limiting its application. Herein, WCO has the potential to be additives in the pyrolysis of biomass. To date, few published studies focus on the pyrolysis of WCO, except for vegetable oil or animal fatty.

Hence, the main objective of this paper is to study the effect of WCO adding to biomass feedstock on pyrolysis products. Further, the influence of temperature and WCO to biomass mass ratio on yield and quality of bio-oil was investigated. In the end, HY zeolite catalyst would be used for further upgrading of bio-oil. The governing hypothesis is that co-pyrolysis of WCO and biomass could produce higher yields of bio-oil and more hydrocarbons as well as less oxygen components than that of pure biomass pyrolysis.

2. Experimental Section

2.1 Feedstock

The pyrolysis feedstock is Tianjin-originated corn-cob and Waste Cooking Oil. Corn-cob was provided by a farm in Jing Hai country, Tianjin, China, and sieved to 8-10mm using a mill. WCO was provided by a student restaurant of University of Nankai, in Binhai. Elemental analysis of the feedstock is shown in Table 1.

Table 1. Elemental analysis of corn-cob and WCO

Feedstock	C (wt %)	H (wt %)	O* (wt %)	N (wt %)	S (wt %)
Corn-cob	42.03	5.51	51.79	0.61	0.06
WCO	64.41	10.92	23.92	0.73	0.02

*** by difference**

2.2 Co-pyrolysis Experiments

Co-pyrolysis experiments of corn-cob and WCO were performed in a fixed bed reactor system, as shown in Fig. 1. Co-pyrolysis was conducted under the temperature of 500, 550, 600 ℃ and mass ratio between WCO and corn-cob of 0.1, 0.5, 1, equivalent to H/C_{eff} of 0.1, 0.55, 0.82.

2.3 Pyrolysis Products Characterization

The elemental analysis of feedstock and solid products was carried out using Vario Micro CHBE Elemental Analyzer. Chemical compounds of liquid products were analyzed by Agilent 6890 GC-5795C MS. GC-MS chromatogram could give the area percentage of various chemical compounds, which would be a good approach for semi-quantitative analyses of bio-oil.

3. Results and Discussion

3.1 Effect of WCO to Corn-cob mass ratio and Temperature on the Product Yields

From fig.2, 550 ℃ have been concluded to be the optimal temperature for producing bio-oil under the same mass ratio, while with the increase of mass ratio, yields of bio-oil increased significantly. The maximum bio-oil yield of 69.42% achieved at 550 ℃ with a mass ratio at 1. Wiggers et al. [3] reported a bio-oil yield of 71% from the pyrolysis of soybean oil with water to oil mass ratio at 0.5:9.5 and pyrolysis temperature is 525 ℃ in a pyrolysis pilot plant. Wiggers et al. [4] obtained a bio-oil yield of 72~73% from the pyrolysis of Waste Fishing Oil (WFO) at 525 ℃ in the same condition.

Within the temperature and mass ratio domain of this study, the char yield decreased significantly with the growth of mass ratio. It may be due to greater H/C_{eff} ratio of pyrolysis feedstock [2]. At the same time, the char yield also decreased slightly by increasing the pyrolysis temperature. This should be due to higher temperature which would lead to both more complete pyrolysis of feedstock and greater decomposition of the char residue [5].

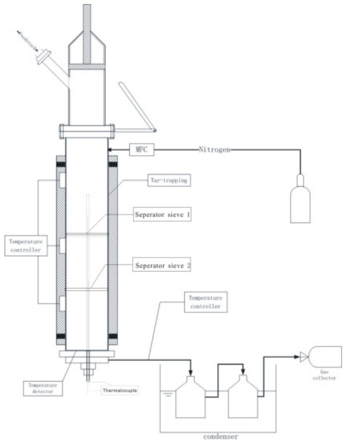

Fig.1. Schematic diagram of fixed bed

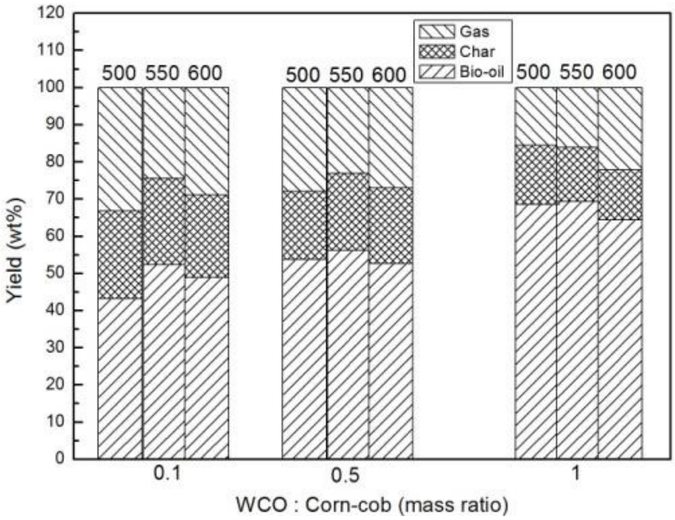

Fig. 2. Product distribution versus pyrolysis temperature (Operational conditions: nitrogen gas flow rate, 300 ml/min; corn-cob particle size, < 1 cm)

3.2 **Effect of WCO to Corn-cob mass ratio and Temperature on bio-oil**

Elemental analysis of bio oil and its calculated heating value were shown in Table 2. C (wt%) and H(wt%) multiplied with the increasing of mass ratio and temperature, which lead to the enhancing of heating value significantly. These results corresponded to conclusions from Zhang et al. [5] who have investigated the co-pyrolysis of biomass and alcohols and found that alcohols enjoys a relative high H/C_{eff}, which can be regarded as hydrogen-rich feedstock. Alcohols could provide additional hydrogen to help biomass` pyrolysis and made its bio-oil products contained more hydrogen which would enhance the bio-oil`s heating value significantly. WCO enjoys the same properties as the alcohols, so WCO could enhance the H (wt%) and heating of bio-oil from co-pyrolysis.

Table 2. Elemental analysis of liquid and char products

	1	2	3	4	5	6	7	8	9
C(wt%)	61.33	61.45	61.39	62.6	62.44	62.52	68.9	69.7	70.2
H(wt%)	8.01	8.03	8.07	8.473	8.663	8.568	9.45	10.04	9.67
HHV (MJ/kg)	26.2	26.27	26.3	27.41	27.6	27.51	31.61	32.78	32.5

3.3 Effect of WCO to Corn-cob mass ratio and Temperature on bio-oil quality from GC-MS

Over 300 components in the bio-oil are detected by GC-MS and classified into 10 groups. With the addition of WCO, acids raised highly, while phenols, alcohols and ketones decreased significantly, but other chemical compounds changed slightly. WCO addition have much greater influence on bio-oil than temperature, so under the same WCO mass ratio, chemicals compounds changed litter. Hydrocarbons as the most valuable compound in fuels, its relative amounts increased greatly with the addition of WCO and raising temperature. It may be due to the H/C_{eff} raised with the addition of WCO. While at the same time, higher temperature was benefit for deoxygenation.

3.4 Effect of HY zeolite on pyrolysis products

The #2 experiment was selected as the most suitable reaction condition between the 9 experiments, which have considered the actual production of biomass and WCO. It has been reported that Chinese could produce agricultural waste 10 times more than WCO. A commercial HY zeolite made from Nankai Catalyst Factory was used as the catalyst to upgrade the quality of bio-oil. Table 3 have shown elemental properties of upgrading bio-oil. With the addition of HY, yields of bio-oil decreased to 48.13% compared to 51.23% in the non-catalytic condition. But its C and H contents increased significantly, while O content decreased greatly. As a result, HHV of bio-oil enhanced highly.

Table 3. Yields and elemental properties of Char and Bio-oil products

	Yields (wt%)	C(wt%)	H(wt%)	O*(wt%)	N(wt%)	S(wt%)	HHV(MJ/kg)
Char	21.5	75.54	2.68	21.00	0.78	0.16	26.69
Bio-oil	48.13	73.68	10.07	15.61	0.64	-	35.92

*** by difference**

4. Conclusions

1) Yields of bio-oil increased significantly with the WCO addition, the highest yields could reach 70.62 wt%. Under the same WCO mass ratio, 550 ℃ have been testified to be the optimal temperature. Char yields decreased with the addition of WCO and temperature raised.
2) The elemental analysis of pyrolysis products shows: Oxygen content decreased with the addition of WCO and raising temperature, while the changing trend appears in contradiction to heating value. Properties of char changed slightly with WCO addition and raising temperature.
3) With the HY addition, yields of bio-oil decreased a litter, but heating value enhanced significantly. What is more, after upgraded by HY, the upgrading bio-oil has valuable potentials to become alternative liquid fuels.

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Biography

Professor Guanyi Chen, Dean of School of Environmental Science and Engineering, Tianjin University, China, focuses on bio-energy development, such as biomass gasification technology - low tar formation and emission, fast pyrolysis and bio oil upgrading, jet fuel production.