Liquefaction performances of bread crusts in subcritical water

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Abstract. Hydrothermal liquefaction of bread crusts in subcritical water were performed in a micro-batch reactor. The influences of temperature (300 − 360 °C) and residence time (10-30 min) on bio-oil yield, boiling point distribution and functional groups in bio-oil were investigated. The results showed that bio-oil yield increased with increasing temperature and reaction time. Maximum bio-oil yield of 22.69wt% was obtained at 360 °C, 30min. The longer reaction time promoted the degradation of diesel to jet fuel and naphtha. The naphtha (C7-10) and jet fuel (C11-C15) increased to 29.9%, 51.82% at 30min from 20.49% and 36.14%, respectively. FT-IR analysis showed that esters, ketones, amides, acids and aldehydes were present in the bio-oil.

1 Introduction

Food waste is solid or liquid organic waste produced in the process of daily diet. Fermentation and decay will occur at the action of microorganisms. If the food waste is not properly treated, it will not only harm people's lives and health, but also cause environmental pollution and pollute the atmosphere and water sources. The main treatment process is landfill, however, it covers large amount of land, and is prone to create secondary pollution, such as the landfill leachate[1].Hydrothermal liquefaction (HTL) in subcritical water is a process that can directly convert wet organic wastes into bio-oil avoiding the energy-intensive and expensive dry step required in pyrolysis[2] . As the main component of food waste is the cereals, which are mainly composed of starch, we selected bread crusts as the research object, the effects of the reaction temperature and time on the bio-oil and solid residue yield were studied. And also the components of the bio-oil were investigated.

2 Experimental

2.1 Materials

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The bread crusts was first dried in the oven at 80 °C, and then was grinded to about 20-30 μm.

2.2 Procedures and separation of the products

The experiments were performed in a micro-reactor. The reactor is made of 316L stainless steel, and is designed to withstand a maximum temperature and pressure of 480 °C and 38MPa, respectively. A certain amount of bread crusts and deionized water were charged into the reactor, and then the sealed reactor was placed in a tube furnace to heating to the reaction temperature. After the reaction time was reached, the reactor was taken out and cooled in cold water immediately. The experimental process was shown in Fig.1. The products in the reactor were washed with 9 ml dichloromethane, and then the products was subjected to solid-liquid separation by a centrifuge. Finally, the dichloromethane in the solution was blown away with a nitrogen blower, and the rest liquid was bio-oil. The separated solid residue was dried and weighed in an oven at 80 °C.

The bio-oil yield and residue yield are calculated as the mass ratio of bio-oil to reacted bread crusts, and ratio of solid residue bio-oil to reacted bread crusts, respectively.

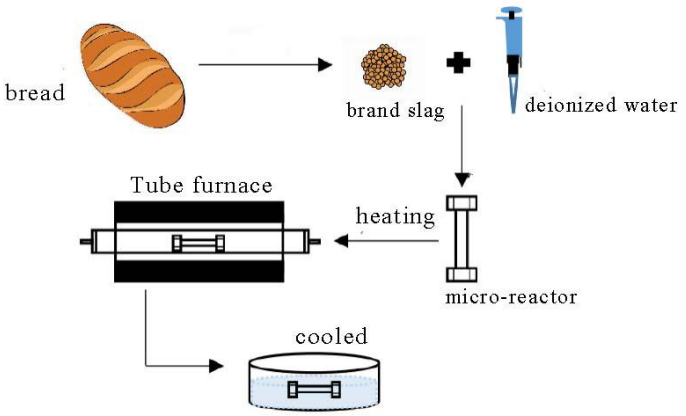

Fig.1 Experimental procedures

2.3 Analysis

Thermogravimetry analysis (TGA) (209 F3 Tarsus, Nietzsche, Germany) was used to evaluate the boiling point distribution of the bio-oil. Samples were taken at a temperature of 25°C to 550°C in an N_2 atmosphere of 60.0ml/min at 10°C/min. Fourier infrared spectrometer (FT-IR) (Shimadzu FTIR-8400S) was used to determine the functional groups contained in the bio-oil, the measurement frequency range is 4000-500cm^{-1}.

3 Results and discussions

3.1 Effect of temperature and reaction time on bio-oil yield

The effects of different reaction temperature and reaction time operated at 20MPa on the bio-oil yield and residue yield of bread residue in subcritical water are shown in Fig.2. The reactant concentration kept at 20wt%. It can be clearly observed that the bio-oil yield

increased obviously with the increasing temperature from 300°C to 360°C. And the solid residue decreased accordingly. The bio-oil yield at 300°C, 330°C and 360°C were 15.77%, 20.39%, and 22.69%, at the reaction time of 30min, respectively. Higher temperature promoted the degradation of starch and glucose in the bread crusts [3,4,5].

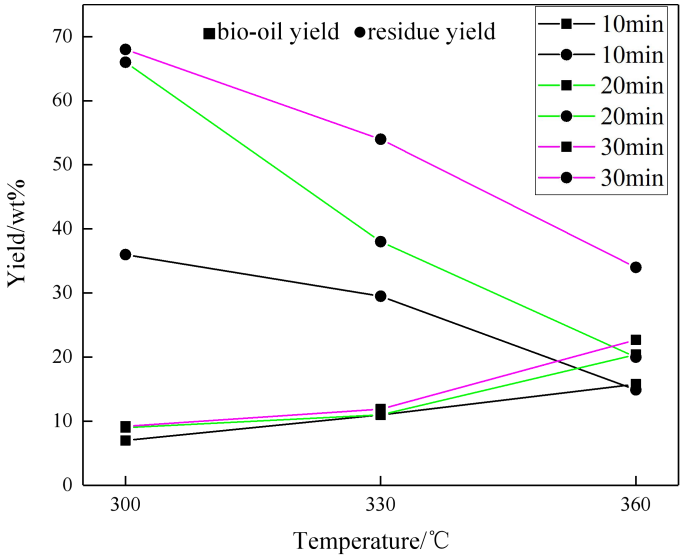

Fig.2 Changes of bio-oil and residue yield with temperature and reaction time

In the reaction time range of 10-30min, the bio-oil yield increased with the reaction, this means that the reaction was not completed before 30min. The variation trend of residue yield was opposite. Similar results were also found in the HTL of swine manure [4], military surrogate waste [1] and Dunaliella salina [6].

3.2 Boiling point distribution in the bio-oil

The boiling point distributions of bio-oil were evaluated by the TGA, which can be viewed as a miniature "distillation" [7]. Fig.3 showed the boiling point distribution and thermal conversion properties of bio-oil operated at 360°C for 20 min and 30 min. The fuel fractions with the boiling point range of 100 -200 °C, 200-300 °C, and 300-550 °C, >550 ° C were defined as naphtha, jet fuel, diesel and vacuum residue, respectively, as shown in Table 1. Results showed that the naphtha(C7-10) and jet fuel (C11-C15) increased greatly at 30 min compared with that at 20min, and the value climbed from 20.49% to 29.9%, and 36.14% to 51.82%. While the content of diesel (C16-C47) decreased from 41.78% to 16.97% from 20min to 30min. The results indicated that large molecular compounds were degraded to smaller molecular compounds with the increasing reaction time. The content of vacuum residue (>C48) were very low at 20 min and 30 min, which mean that the intermediates rarely polymerized to the coking products.

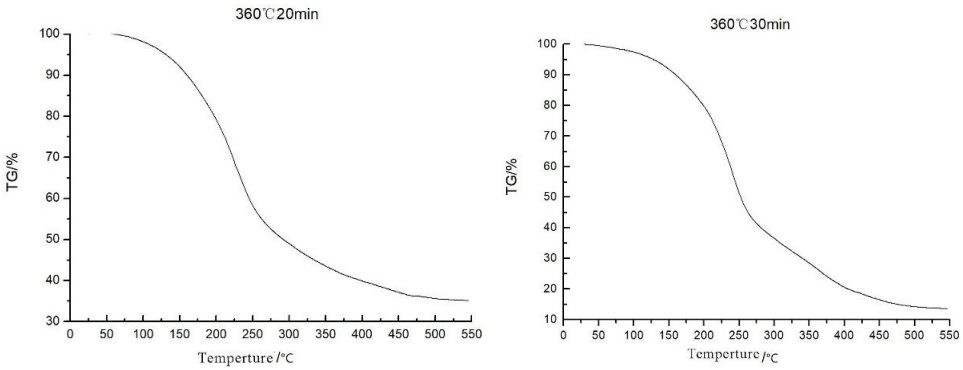

Fig.3 TG curves of bio-oil

Table 1 Boiling point distribution of bio-oil

Distillate fraction / Time/min	Naphtha (<200 °C) C7 – C10	Jet fuel (200-350 °C) C11 – C15	Diesel (350-500 °C) C16– C47	Vacuum residue (>500 °C) >C48
20	20.49%	36.14%	42.78%	0.47%
30	29.90%	51.82%	16.97%	0.73%

3.3 Functional groups in the bio-oils

The FT-IR of bio-oil is shown in Fig.4. It can be seen that the temperature and reaction time showed little influence on the vibration peaks of the infrared spectrum, which indicating that the types of functional groups in the bio-oil are similar. The vibration peaks at 3200-3500cm^{-1} indicating the O-H groups, which reflected the presence of amines, phenols, and alcohols. The 2800-2950cm^{-1} represents the stretching vibration peak of C-H. Around 1700cm^{-1} is the C=O stretching vibration peak, which means that esters, ketones, amides, acids and aldehydes may present. Around 1600cm^{-1} and 1520cm^{-1} should be the bending vibration peaks of N-H and -NH_2, which represent amides and amines. Around 1500cm^{-1} is the C=C stretching vibration peak, which represents the benzene rings. Around 1380cm^{-1} and 1460cm^{-1} are -CH_2 bending vibration peaks and -CH_3 bending vibration peaks, which represent saturated C-H. 1300cm^{-1} to 1000cm^{-1} are C-O stretching vibration peaks, which are the strongest peaks in this region. They are easier to identify and represent phenols, acids, esters, and alcohols.

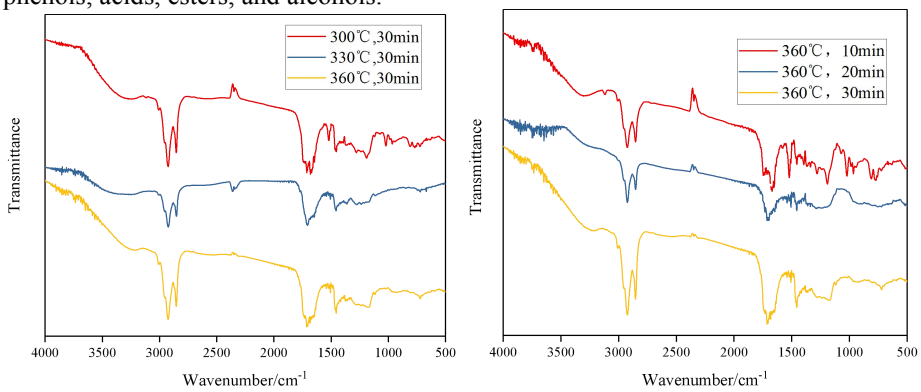

Fig.4 FT-IR spectra of bio-oil obtained at (a) 300-360°C, 30min (b) 360°C, 10-30min.

4 Conclusions

The hydrothermal liquefaction of bread crusts were operated in the micro-reactor at 300-360 °C and 10-30 min. The effects of temperature and reaction time on the bio-oil yield and components of the bio-oil were investigated. The results showed that temperature and reaction time showed positive effect on the bio-oil yield. At 360 °C, 30 min, maximum bio-oil yield of 22.69wt% can be obtained. Longer reaction time promoted the degradation of diesel to jet fuel and naphtha. The naphtha (C7-10) and jet fuel (C11-C15) increased to 29.9%, 51.82% at 30min from 20.49% and 36.14%, respectively. FT-IR analysis showed that esters, ketones, amides, acids and aldehydes were present in the bio-oil.

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