

Hydrothermal Pyrolysis of Food Waste for Bio-oil Production over Ceria and H-ZSM-5

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Abstract. Pyrolysis is one of thermal cracking processes that are used to convert carbonaceous materials, i.e. food waste, to energy. Effects of catalysts and the optimum operating conditions were observed to obtain the optimal condition whilst minimize pressure. The non-catalytic pyrolysis gave the highest yield of 7.98% bio-oil and 4.45% charcoal at 356 °C, 183 bars and 120 minutes of retention time. Hydrogen, oxygen and carbon content in the bio-oil produced were 10.10, 13.68 and 75.43, respectively, with heating value of 37,829.64 kJ/kg. Ceria, when used as a catalyst, was found to help reducing the final pressure by 4.13%, to compare with the non-catalytic pyrolysis under supercritical condition, and increased the yield of bio-oil by 12.9%. ZSM-5-catalysed pyrolysis showed 1.25% higher in percent yield bio-oil. The obtained bio-oil was found to possess good characteristics and possibly be a substitute for fuel oil.

Keywords: Pyrolysis, Supercritical condition, Ceria (CeO₂), H-ZSM-5

1. Introduction

Large amount of food waste is discarded all over Thailand. Food waste contains more than 70% of water content in general. Hydrothermal/Supercritical pyrolysis of biomass is a well-known process that is used to convert moisture-rich carbonaceous materials to liquid fuels. This process provides high conversion and efficiency in terms of energy due to the elimination of the drying process in the pre-treatment step. Moreover, additional solvents for liquefaction and large scale system installation are not required [1-11]. Complete reaction can be achieved in a short reaction time. Hydrothermal pyrolysis of food waste was investigated in this work. Ceria-base catalyst and ZSM-5 have been reported previously to possess some properties that could possibly help this pyrolysis process [12-18].

2. Experiments

2.1. Preparation of ceria catalyst (CeO₂)

CeO₂ was prepared by hydroxide precipitation method. Cerium (III) nitrate hexahydrate (Ce(NO₃)₃.6H₂O, Aldrich) was dissolved in 150 ml of analytical grade deionised water. It was precipitated using ammonium hydroxide (NH₄OH) to a final pH in the range of 7– 8. Ammonium hydroxide solution (10% by volume) was added drop-wise by burette (flow rate = 5 cc/min) whilst stirring for 4.0 hours until cerium hydroxide (Ce(OH)₄) was totally precipitated. Stirring was continued to ensure that the reaction completed. The precipitate was then recovered, washed with deionised water and ethanol to prevent an agglomeration of

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the particles and to get rid of the impurities from the substrates, then calcined under reducing condition (forming gas, 10% H₂/N₂) to convert to CeO₂.

2.2. Preparation of ZSM-5 catalyst

2.2.1. Preparation of gel precipitation and decantation solution

Aluminium chloride tetrapropyl (AlCl₃) and ammonium bromide (TPABr) were used as metal source and organic template, respectively, for ZSM-5 preparation. The atomic ratio of silicon/aluminium was set at 40. Upon the complete mixing, the precipitating gel was then removed from the supernatant solution by a centrifuge. The supernatant solution was mixed altogether with the milled gel mixture.

2.2.2. Crystallization

The mixture of milling precipitate and the supernatant of decant solution was charged in 500 ml stainless steel autoclave. The nitrogen was introduced into the autoclave to pressurize the system up to 3 kg/cm² gauge. Then the mixture in autoclave was heated from room temperature to 160 °C in 90 min and then up to 210 °C in 4.2 hours while stirred at 1400 rpm, followed by cooling down the hot mixture to room temperature in the autoclave overnight. The produced crystals were washed with distilled water to remove Cl⁻ away from the crystals. They crystals obtained were dried in an oven at 110 °C for 3 hours.

2.2.3. First calcination

The dried catalyst in porcelain crucible was heated in a furnace under an air ambient from room temperature to 540 °C in 60 min., and then kept at this temperature for 3.5 hours. In this step, the organic template (TPABr) was burned out and left the cavities and channels in the crystals. The calcined crystal was cooled to room temperature in a desiccator, so the crystal formed were called Na-form catalyst.

2.2.4. Ammonium ion-exchange of Na-form crystal

The ion-exchange step was carried out by mixing of sodium-form catalyst with ammonium nitrate (NH₄NO₃). The solution was heated up to 80 °C for 40 min. After that, the mixture was then cooled down to room temperature and washed with distilled water. The ion-exchange step was repeated 3 times. Then the ion-exchange crystals were dried at 110 °C for 3 hours. The Na-form crystal was thus changed to NH₄-form catalyst.

2.2.5. Second calcination

The Ammonium-form catalyst was calcined in a furnace by heating from room temperature to 540 °C in 60 min., and then kept at this temperature for 3.5 hr. After this step the crystal thus obtained was H-ZSM-5 catalyst.

2.3. Food waste preparation

This work studies bio-oil production via pyrolysis of food waste. The food waste samples were collected from canteen of Thailand Institute of Scientific and Technological Research. The proportions of food waste were categorized as shown in Table 1.

Table 1: Components and proportion (by % weight) of food waste.

Food type	Proportion	Food type	Proportion
Fish sauce	1.4	Vermicelli	4.5
Oyster sauce	1.9	Mackerel	5.8
Boiled egg	2.1	Morning glory	6.3
Tomato source	2.6	Pork	8.1
Meat ball	2.7	Bean sprouts	10.5
Omelette	3.3	Noodle	10.6
Shallots and garlic	3.5	Rice	32.5
Cucumber	4.0	Total	100.0

2.4. Method

150 g of food waste with moisture content greater than 80% was selected for this hydrothermal pyrolysis process. The reaction was carried out in a 500 ml batch reactor. The gaseous products were analyzed by GC, liquid and solid products were analyzed by Proximate and Ultimate analysis.

Effects of catalysts and optimum operating conditions, i.e. temperature, pressure and retention time, were studied. The amount of ceria catalyst was varied from 0 to 3 g. Temperature and pressure were varied in the range of 356-417 °C and 183-242 bars, respectively. The retention time was varied from 30 to 120 min.

3. Results and Discussion

3.1. Effect of the calcinations condition on the catalyst's surface area Method

3.1.1. Effect of calcinations time

Two samples of ceria were calcined at 400 °C for 1 and 3 hours to study the effect of calcination time period. Surface areas of 2 samples of ceria, calcined for 1 and 3 hours, were 9.32×10^1 and 1.10×10^2 m²/g, respectively. This result implies that the time period of calcinations has no significant effect on the catalyst's surface area.

3.1.2. Effect of calcinations temperature

Two batch of ceria catalysts were calcined for 1 hour at two different temperatures, 400 °C (A) and 500 °C (B), for comparison purpose. It was found that the ceria calcined at 400 °C showed the higher surface area, 9.315×10^1 m²/g, compared to the ceria calcined at 500 °C, 5.568×10^1 m²/g. It can be concluded that the undesired sintering of catalyst might occur at 500 °C which resulted in a reduction of surface area.

3.2. Bio-oil production

Hydrothermal pyrolysis of food waste, containing 86.34% moisture content, was operated at supercritical condition (380 °C, 242 bars) for 30 minutes. The products were 7.91 and 4.27% of bio-oil and charcoal, respectively. The heating value of the bio-oil produced was 38,059 kJ/kg and consists of 75.66% carbon, 10.30% hydrogen and 13.59% oxygen. The heating value of charcoal consists of 76.11% carbon, 4.64% hydrogen and 18.48% oxygen. The heating values of the produced bio-oil and charcoal are similar to diesel's and wood charcoal's which are 36,420 and 32,008 kJ/kg, respectively [16] implying that the products could potentially be diesel fuels and wood charcoals substitutes.

3.2.1. Effect of surface area of ceria catalyst

Both Ceria catalysts (A and B) were found to help decreasing 4.13% of the final pressure. Yield of the bio-oil in the presence of catalyst A and B were found to be increased by 12.9% and 12.0%, respectively.

3.2.2. Effect of temperature on yield of bio-oil

Non-catalytic pyrolysis was carried out at 242 bars for 30 minutes at 356, 380, 408 and 417 °C. The % yield of bio-oil was 9.12, 7.91, 5.26 and 3.89 respectively. The higher temperature resulted in lower yield of bio-oil. 356 °C of operating temperature was selected for further study as this condition gave the best yield of bio-oil.

3.2.3. Effect of pressure on yield of bio-oil

At 356 °C, the operating pressure was varied from 183, 205 and 242 bars. The yields of bio-oil were found to be 6.97%, 8.82% and 9.12% respectively. The results showed that an increase of pressure increased the amount of bio-oil produced. However, an operating pressure of 183 bars was chosen for further study due to the controlling problems of the high pressure processes (higher than 200 bars) when scaled up to industrial scale.

3.2.4. Effect of pressure on yield of bio-oil

The effect of retention time on the amount of the bio-oil produced was investigated under the selected operating temperature and pressure, 356 °C, 183 bars. The highest % yield of the bio-oil, 7.98, was achieved when the reaction was carried out for the longest period of time, 120 minutes. The % yield of charcoal produced at this condition was 4.45. These results showed that the supercritical condition may not be

required as the % yield of the bio-oil and charcoal produced under this sub-critical condition (7.91% bio-oil and 4.27% charcoal at 356 °C, 183 bars, 120 minutes) and supercritical condition (7.91% bio-oil and 4.27% charcoal at 380 °C, 242 bars, 30 minutes) are not significantly different. Table 2 showed bio-oil production yield and other properties of supercritical and sub-supercritical conditions. The heating value of bio-oil products was analyzed by Bomb Calorimeter

Table 2: Supercritical and sub-supercritical pyrolysis over ceria catalyst.

Condition	Temperature (°C)	Pressure (bar)	Retention time (min)	Bio-oil (%)	Gross heating value (kJ/kg)
Supercritical	380	242	30	7.91	38,059.00
Sub-supercritical	356	183	120	7.98	37,829.64

3.2.5. The effect of ZSM-5 catalyst

The performance of the ZSM-5 catalyst towards the hydrothermal pyrolysis reaction was tested under sub-critical condition. Table 3 showed that the pyrolysis catalysed by ZSM-5 gave the yield of bio-oil 1.25% higher compared to ceria, although, the surface area of the ZSM-5 is approximately 3 times less than the ceria's.

Table 3: Comparison between ZSM-5 catalytic and non-catalytic reaction for bio-oil production at sub-supercritical condition (356 °C, 242 bars with 150 g food waste for 120 minutes of retention time).

Catalyst	Langmuir Surface Area of Catalyst (m ² /g)	Terminal Pressure (bar)	Bio-oil (%)	Charcoal (%)
Non-Catalyst	-	183.00	7.98	4.47
Ceria	93.15	232.00	8.93	3.14
ZSM-5	28.59	183.00	8.08	7.15

4. Conclusions

Calcinating time has no significant effect on the catalyst's surface area. The highest surface area of ceria obtained at 400 °C of calcinations temperature. Ceria was found to reduce the operating pressure of the hydrothermal pyrolysis process by 4.13% , and increase the yield of bio-oil by 12.9%, to compare with the non-catalytic process under supercritical condition. The % yield of the bio-oil and charcoal produced were giving 7.91 and 4.27, respectively. The super critical condition does not promote the bio-oil production to compared with the sub-critical condition. The hydrothermal pyrolysis catalysed by ZSM-5 showed better performance, compare to Ceria.

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