Bio-oil Production from Ablative Pyrolysis of Corncob Pellets in a Rotating Blade Reactor

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Abstract. Fast pyrolysis serves as an alternative and eco-friendly method to convert biomass into valuable bio-oil and char. Bio-oil is a potential source for generating renewable biofuels. In this study, corncob pellets were pyrolysed in a laboratory rotating blade ablative pyrolysis reactor. Effects of plate temperature (450 – 550°C) and nitrogen flowrate (5 – 15 L/min) were investigated on pyrolysis product yields at a fixed rotating speed of 6 Hz. Temperature and inert gas flowrate were shown to affect product distribution and yields. Maximum bio-oil yields of almost 50% w/w on dry basis were obtained at 550°C and flowrate of 5 L/min. Composition of the bio-oil contained predominantly oxygenated hydrocarbons. From analysis of chemical and physical properties, the bio-oil derived from corncob pellets showed good fuel quality, comparable to those bio-oils reported in the literature.

1. Introduction
Corn is an important industrial crop in the northern region of Thailand. Large amount of corn residues such as corncobs are generated after harvest. Some of these residues have been disposed of improperly such as burning openly in farms. This practice may lead to wildfires, accidental fires to agricultural lands, causing local atmospheric pollution [1]. These biomass residues may be utilized for renewable energy. The use of biomass for energy and chemicals has tremendous potential to reduce the problems caused by our dependence on fossil fuels [2]. A simple physical upgrade of corncobs by densification has been proposed [3]. The ago-residues can be further improved to produce liquid biofuel via fast pyrolysis.

Fast pyrolysis is an effective thermochemical process for biomass conversion, in which biomass is rapidly heated in the absence of oxygen, and operated at reaction temperatures between 300 and 700°C [4], generating a majority of condensable vapours, solid char, and permanent gases. After quenching and rapid condensation of the vapours, a dark brown liquid called bio-oil is formed [5]. The bio-oil can either be combusted in boilers, engines and turbines to generate heat and power or upgraded to produce transportation fuels and chemical stocks [6], [7].

There are many types of fast pyrolysis reactor, including bubbling fluidized bed, circulating fluidized bed, free fall, auger, and ablative reactors. For most pyrolysis reactor configurations, the biomass feedstock needs to be processed into small sizes of around 2 mm or less to minimize heat transfer resistances throughout the material [8]. Fortunately, the ablative pyrolysis reactor provides an opportunity to use large particles of biomass which can potentially offer saving on processing costs [9, 10]. In ablative pyrolysis, the biomass is directly in contact with hot surface. There is a steep temperature gradient at the biomass surface, undergoing severe decomposition or sublimation and leading to the formation of a thin layer of reacting solid, shown schematically in Figure 1. The reacting layer moves towards the inside of the cold biomass. The conversion takes place only at the
surface rather than the entire biomass particle, and the reaction rates are not limited by heat transfer throughout the whole particle [11]. In this work, a laboratory scale rotating blade ablative reactor was designed, developed and tested with corncob pellets. The goal was to experimentally verify if high yield of bio-oil can be produced. Operating factors that affect bio-oil yield were also parametrically evaluated.

![Diagram of ablative pyrolysis mechanism](Figure 1. Basic principle of contact ablative pyrolysis mechanism.)

2. Materials and Methods

2.1. Feedstock

Corncob pellets as feedstock in the experiment were supplied from Mae Cham agricultural cooperative in Chiang Mai, Thailand. The pellets were about 8–10 mm in size and kept in airtight zipper bags prior to use. The composition and energy content of the feedstock are given in Table 1 below.

| Proximate analysis (% w/w) | Moisture | Ash | Volatile | Fixed carbon |
|----------------------------|----------|-----|----------|--------------|
| 10.7                       | 5.5      | 67.3| 16.5     |

| Ultimate analysis (% w/w) and energy content | C | H | O | N |
|----------------------------------------------|---|---|---|---|
| HHV(MJ/kg)<sup>b</sup>                      | 49.1 | 6.3 | 44.1 | 0.4 | 20.1 |

<sup>a</sup> dry basis  
<sup>b</sup> estimated from HHV (MJ/kg) = (C% x 0.3578) + (H% x 1.1356) + (N% x 0.0594) – (O% x 0.0854) – 0.974 [12]

2.2. Experimental setup

A rotating blade ablative reactor was designed and developed for fast pyrolysis of biomass. The ablative reactor was made of steel, cylindrical in shape with 260 mm in diameter, 80 mm high and 10 mm thick. The rotating blade had two propellers which were at 53° angle with a horizon, connected to axle shaft of motor. The rotational speed was adjustable by an inverter. The top of the reactor was a movable cover with static seal by graphite gasket placed between the cover and the reactor chamber. The hot plate formed the bottom of the reactor, directly heated by liquefied petroleum gas flame. Temperature of the hot plate was measured using a type K thermocouple and controlled manually via a gas regulator.

An experimental setup (shown in Figure 2) was composed mainly of a biomass hopper, nitrogen feeding, the ablative reactor, condenser and cooling water, bio-oil collection, and pyro-gas collection. The biomass hopper of 1.5 L capacity was made of brass steel material. It was connected with a nitrogen feeding to the ablative reactor. Downstream of the reactor was a counter-current, double-pipe glass condenser connected with oil and gas collection systems. Installation of a vacuum pump was connected to the system for driving pyrolysis vapours out of the reactor chamber.
2.3. Experimental procedure

Prior to the start of each experiment, preheating was initiated and nitrogen was fed to the reactor to purge any oxygen or air inside. The biomass feedstock was loaded to the hopper, with the bottom valve closed and upper vent of the hopper open while feeding nitrogen in order to sweep any oxygen or air in the hopper. The required nitrogen flow rate was adjusted. Once the hot plate reached the set temperature, the rotating blade was set in motion and the biomass pellet was released from the hopper. Ablative contact between the hot plate with the biomass initiated fast pyrolysis. Volatile vapours were released and carried quickly by the nitrogen out of the reactor chamber to the cooling water condenser, where bio-oil was condensed. The remaining incondensable vapours flowed through the gas conditioning unit and collected in a gas bag. Each experimental run lasted for about 5-10 min in which no further release of volatile vapours was observed. The remaining solid char was then collected and kept in a closed container while all bio-oil samples were stored in a refrigerator for further analysis. Effects of the hot plate temperature (450 – 550°C) and nitrogen flowrate (5 – 15 L/min) on pyrolysis product yields were investigated at a fixed rotating speed of 6 Hz. Each experimental condition was carried out and repeated at least in triplicate. The aim was to find out the optimum condition for obtaining highest bio-oil yield.

2.4. Product analysis

Pyrolysis product distribution and yields were determined. Each yield was relative to the initial loading of biomass. Elemental composition of the bio-oil and solid char were evaluated using a Thermo Scientific, CHNS/O analyser model Flash 2000. Gas chromatography and mass spectrometry (GC/MS) was used to determine chemical composition of the bio-oil. Pure acetone was used as solvent. The GC/MS analysis was performed using an Agilent Technologies model 7890A GC equipped with an Agilent Technologies 19091s-433 column (30 m x 0.25 mm x 0.25 µm) and an Agilent Technologies MS model 5975C. The carrier gas was helium at a flowrate of 1 L/min. The column temperature was initially held at 40°C for 5 min, then gradually increased to 280°C at 10°C/min, and finally maintained at 280°C for 10 min. The injector and detector temperatures were set at 250 and 280°C, respectively.

3. Results and discussion

3.1. Effects of nitrogen flowrate and hot plate temperature

Figure 3 shows mass balances, product distribution and yields of the ablative pyrolysis experiments. Bio-oil, solid char and incondensible gases were obtained. It was generally accepted that in fast pyrolysis, bio-oil is dominant, while char and gases are by-products. All cases of accumulative mass were found to be above 96% which were in acceptable level. Incremental mass loss may have related to losses during collection of liquid and solid samples, as well as undetectable gases. With regards to product yield, nitrogen flowrate and hot plate temperature appeared to have significant effect. It was observed that for a given flowrate, bio-oil yield was increased with increasing hot plate temperature. This was expected, since higher plate temperature resulted in higher temperature gradient.
and higher heating rate to the biomass sample, hence greater decomposition of the biomass and more volatile release may have occurred [11]. At the lowest temperature considered here, char yields were higher than bio-oil yield. This was possibly due to low heating rate, leading the reaction to become intermediate or slow pyrolysis. For a fixed temperature, increase in flowrate was found to decrease the yield of bio-oil. It was probable that higher flowrate may have reduced overall heat transfer to the biomass due to convection. The highest yield of the bio-oil obtained here was about 50% w/w on dry basis. This was smaller than those reported in the literature [11] in which 70% was typically obtained for similar configuration of reactor. It should be noted that at high flowrate, gas yields were increased, at the expense of both bio-oil and char yields. This was probably due to combination between secondary char decomposition and secondary thermal cracking of pyrolysis vapours [13].

![Graph](image)

**Figure 3.** Effects of nitrogen flowrate and hot plate temperature on product distribution and yields, (a) for 550°C, (b) 500°C, (c) 450°C.

3.2. **Characteristic of the bio-oil**

Ultimate analysis and heating value of the bio-oil were determined and compared with literature data for bio-oils produced from ablative and fluidized bed pyrolysis of various agro-residues, shown in Table 2. It was found that the percentages of carbon, hydrogen and oxygen and the heating value were in similar range to other bio-oils. However, H/C and O/C atomic ratios were larger. This indicated that the bio-oil from this work had lower aromaticity and lower degree of deoxygenation, compared to other bio-oils. Taking into account the bio-oil heating values and their yields, the energy recovered in the form of liquid fuel was accounted for about 45% of the biomass energy input. Chemical compounds of the bio-oil from the ablative pyrolysis process were also identified using GC/MS. The results are shown in Figures 4 a and b. It was observed that the bio-oils were composed
of complex mixture of oxygenated hydrocarbons. The compounds observed in this investigation consisted of long chain products such as phenols, aromatics, esters, aldehydes, alcohols, organic acids and ketones.

**Table 2.** Comparison of elemental composition of bio-oils from this work with those in the literature.

| Ref           | This work | [9]       | [14]      |
|---------------|-----------|-----------|-----------|
| biomass       | corncob pellet | pines     | rice husk |
| reactor       | ablative   | ablative  | fluidized bed |
| C             | 33.22      | 37.53     | 35.95     |
| H             | 10.64      | 8.38      | 9.81      |
| O             | 55.86      | 54.05     | 53.94     |
| N             | 0.28       | 0.03      | 0.59      |
| H/C           | 0.32       | 0.22      | 0.27      |
| O/C           | 1.68       | 1.44      | 1.50      |
| HHV (kJ/kg)   | 18.35      | 17.38     | 18.52     |

**Figure 4.** GC/MS analysis result and organic compounds of the bio-oil.
4. Conclusion
Agro-residues have great potential to produce bio-liquid fuels. Bio-oil from fast pyrolysis of agro-residues is of great interest in providing alternative source of renewable energy and biofuel. In this work, fast pyrolysis of corncob pellet in a rotating blade ablative reactor was reported. Pyrolysis products were found to be strongly affected by the hot plate temperature and sweeping gas flowrate. Optimum condition was identified at 550°C and flowrate of 5 L/min. High yields of bio-oil (50% w/w dry basis) was realized. The GC/MS analysis showed that the ablative pyrolysis of corncob pellets generated bio-oil with various phenolic compounds, and aromatics. In the present work, it was shown that corn residues were promising renewable sources for bio-oil production.

5. Reference
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