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# Microwave assisted fast pyrolysis of corn cob, corn stover, saw dust and rice straw: Experimental investigation on bio-oil yield and high heating values

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ABSTRACT

In the present research, microwave assisted pyrolysis of biomass feed stocks such as corn cob, corn stover, saw dust and rice straw were carried out at constant microwave experimental conditions. GC–MS and bomb calorimeter analyses were carried out to identify the compounds present in bio-oil and higher heating values (HHV), respectively. Amongst all, corn cob gave the highest bio-oil yield up to 42.1% (wt) with a higher bio-oil HHV of 22.38 MJ/kg at the given experimental conditions. GC–MS analysis of corn cob based bio-oil showed the presence of ethyl ether, phenol, aliphatic hydrocarbons, furfural, furan derivatives and acids in major proportions. Higher HHV of bio-oil from corn cob was due to the presence of ethyl ether and 2-bromo-butane with a relative proportion of 15.63% and 4.60%, respectively. Addition of $MgCl_2$ compound as a catalyst during corn cob pyrolysis yielded only in selective formation of furfural compound, and bio-oil yield in this case was found to be similar (40%, wt) to that of pyrolysis of corn cob in absence of catalyst. The results suggested that the corn cob can be used a potential biomass feed stock to produce bio-oil in major quantity, which can be further distilled to produce fuel oils.



## 1. Introduction

In recent years, much attention has been given to explore an alternative energy source to meet the raising global energy demands and to create a pollution free environment. Biomass being inexpensive material and considered as high energy renewable feed stock for second generation bio fuels which makes it affordable to sustainably produce fuel oils and variety of platform chemicals, thus helping to overcome the huge dependency on depleting fossil fuels. Biomass fast pyrolysis is of particular interest as it leads to the production of bio-oils (in higher amount), gaseous products and minimal amount of solid bio char [1–2]. The technique involves thermal decomposition or depolymerisation of large molecules of solid biomass at a shorter residence time, typically in the temperature range of 400–500 °C in an inert environment (i.e. in the absence of oxygen), yielding gaseous products and char [3–4]. The condensable gases present in the gaseous products are cooled to get energy rich bio-oils which can be further distilled to get fuel oils and valuable chemicals. The obtained carbon rich char can be used effectively for several practical applications such as fuels, soil conditioners, adsorbents for water treatments and as an agent to improve the fertility of acidic soils [5].

Amongst all pyrolysis techniques, microwave assisted fast biomass pyrolysis is a fast growing and widely used technique to process lignocellulosic biomass feed stocks such as corn cob, corn stover, sawdust, rice straw, bagasse, douglas fir, rice straw, wheat straw, wood pellets, agricultural and forestry crops and residues etc. [4]. This technique offer several advantages over conventional pyrolysis technique as it provides instantaneous and uniform heating of raw materials, high heating efficiency, flexibility to use different feed stocks, minimal raw material pre-treatment requirements, processing of large size particles, and requires only shorter residence time (i.e., fast process) [6–7]. Fast heating of raw materials by microwaves are due to the polar molecules present in the materials undergoing continuous rotation (dipole rotation) under the influence of microwave electromagnetic radiation [8–9]. The rotating molecules collide with other molecules present in the material and transfer their energy in the form of heat. This technique is energy efficient and also used to pyrolyze other materials like waste tyres, waste engine oils, and plastics [10–11].

Most of the biomass pyrolysis studies have been conducted on lignocellulosic feed stocks, which typically comprise of cellulose (40–50%), and hemicellulose (30–40%) carbohydrate polymers, lignin (10–30%) phenolic polymers and low concentrations of other compounds [12]. Analysis of several reports suggests that during the initial stages of pyrolysis reactions (i.e., below 300 °C), the cellulose component of biomass undergoes two different depolymerisation pathways to form

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levoglucosan and glycolaldehyde [13–14]. Above 300 °C, both these compounds degrades subsequently and yields volatiles of low molecular weight compounds acetaldehyde, acetol, acetic acid, furfural and methyl furfural, non-condensable gases (methane, ethane and carbon monoxide) and minimal amount of char [14]. Simultaneously, hemicellulose also decomposes in the temperature range of 200 °C to 260 °C and leads to the formation of more volatiles and minimal amount of char [13–14]. The third component lignin decomposes in the temperature range 280 °C to 550 °C, and forms majorly char and phenolic compounds along with lower amount of non-condensable gases [15]. During pyrolysis reactions, each of these biomass components follows different reaction pathways and posse's different reaction rates and yields multiple compounds with varying quantity. Hence, the bio-oil is considered as a complex mixture; and its quantity and the composition vary from biomass type and the conditions employed for the pyrolysis reactions [14, 16]. Few reports also have been published with the use of catalyst during biomass pyrolysis to improve the quality or to increase the bio-oil yield. Compounds such as KAc, $Al_2O_3$, $MgCl_2$, $ZnCl_2$, $H_3BO_3$, and $Na_2HPO_4$ were used as catalyst [17]. Research work on the role of catalyst during biomass pyrolysis reactions is still emerging and fundamental or mechanistic understanding has to be developed to understand the formation of complex chemical composition of bio-oils. Corncob is a lignocellulosic agricultural by-product which was used to get the bio fuels and the variety of chemicals. The results showed that it was typically consist of cellulose: 38.8%, hemicellulose: 44.4% and lignin: 11.9% in the dry matter [18]. Corn stover typically consists of 38% cellulose, 26% hemicellulose, and 19% lignin [19–20], and rice straw consists of 37% cellulose, 24% hemicellulose and 14% lignin [21].

In the present research, the microwave assisted fast pyrolysis of different feed stocks (corn cob, corn stover, rice straw and saw dusts) were performed at constant microwave assisted experimental conditions. A comparative analysis based on bio-oil yields, higher heating value (HHV) and the compounds present in bio-oil were carried out to identify an energy rich biomass feed stock amongst the biomass used. Gas chromatography–mass spectrometry (GC–MS) analysis was carried out to identify the different compounds present in the bio-oil. Also Bomb calorimeter analysis was carried out to get the higher heating values for the produced bio-oils from the different feed stocks.

## 2. Experimental

### 2.1. Materials

Biomass feed stock such as corn cob, corn stover, wood saw dust (saw dust) and rice straw were received as fresh from farm fields (Tamilnadu, India), and these materials were used without any pretreatment. All the biomass was initially air-dried for 2 days. Corn cob was crushed and grounded to get a size fraction of 2–4 mm; corn stover was cut in to pieces of size ~2 mm × 2 mm; rice straw was cut in to 2 cm length, and fine particles of sawdust was collected from a wood mill. Before the start of pyrolysis experiments, all the biomass was dried at 125 °C for 6 h using a tray drier to remove the moisture. Fig. 1(a–d) shows all the dried biomass feed stocks used in our present pyrolysis experiments. Reagent grade magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) was obtained from Merck and used without purification.

### 2.2. Microwave assisted pyrolysis of biomass feed stocks

Pyrolysis of biomass feed stocks (corn cob, corn stover, saw dust and rice straw) was carried out in a microwave cavity oven (Panasonic model, India). The heating area of the oven is 46.1 cm × 28.9 cm × 37.7 cm and has a maximum output power of

**Fig. 1.** Biomass feed stocks used in the present study (a) corn cob (b) corn stover (c) saw dust (d) rice straw.