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Comparison of yield and fuel properties of thermal and catalytic Mahua seed pyrolytic oil

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HIGHLIGHTS

- Thermal and catalytic pyrolysis of one non-edible oil seed Mahua was carried out.
- 525 °C was the optimum temperature to produce maximum pyrolytic liquid.
- Yield of pyrolytic oil was higher for catalytic pyrolysis than thermal pyrolysis.
- CaO as catalyst increased the calorific value and decreased the viscosity.
- The catalytic pyrolytic oil has closer fuel properties with that of diesel.

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ABSTRACT

In this work, the production and evaluation of fuel properties of pyrolytic oil from one non-edible oil seed Mahua was reported. Both thermal and catalytic pyrolysis using CaO was carried out. The aim of the study was to detect the optimum temperature to produce maximum pyrolytic oil and to increase the quality of oil using catalyst. It was observed that thermal pyrolysis of Mahua seed at 525 °C produced maximum yield of liquid. Hence the influence of catalyst was examined at the optimum temperature (525 °C) on liquid yield and its properties.

The catalytic effect of CaO, on Mahua seed pyrolysis at a feed to catalyst ratio of 2:1, 4:1 and 8:1 was studied. The pyrolytic liquid collected was separated into two phases. The top phase (organic) was considered as oil phase where as the bottom phase as aqueous. Maximum yield of 40.71 wt.% of oil with better fuel properties was obtained as Mahua seed pyrolyzed in the presence of CaO at the ratio of 2:1. The result confirmed that catalyst (CaO) not only increased the heating value (41–43.15 MJ kg^{-1}), viscosity (0.033–0.018 Pa s) and cold flow properties but also altered the pH (4.86–8.58) significantly when compared with thermal pyrolysis.

1. Introduction

The fuel which does not originate from fossil fuel is termed as alternative fuel. Alternative fuel is the advanced and future fuel derived from non-conventional sources of earth. Among various alternative fuels, biofuel is gaining a lot of interest due to its various advantages over other alternative fuels. Biofuels can be solid, liquid or gaseous fuel derived from biomass and hence it is CO_2 neutral fuel. Owing to their renewability; biodegradability and generating adequate quality exhaust gases, it is an approving option to be consumed as fuel [1]. The rapid growth of population and industrialization decreases the forest level and as a result increases the percentage of CO_2 level in the atmosphere. Deforestation and burning of fossil fuel causes more than 90% of global warming [2]. Plantation is the only one approach which can be an obstacle for global warming. The production of fuel from biomass is accepted as an advance and future fuel.

Among various biofuels, pyrolytic oil derived from biomass (commonly known as bio-oil) is also another alternative fuel of interest. Verities of non-edible oils were traditionally used as lightening agents in various parts of the world since many decades. The non-edible seeds are the main sources for this which contains maximum quantity of oil and fats. Mahua (*Madhuca indica*) seed is one of such oil containing seeds whose oil is being used for lightening as well as for the production of biodiesel [3]. Mahua trees are vastly available in various parts of India as well as other countries. It can grow in rainy area and all types of soils. Mahua seed holds maximum 35% of oil and 16% of protein. During expelling at most 15–20% of oil can be possible to extract whereas the rest remain in the cake and used as cattle feed or to increase the fertility of soil.

Literatures reveal that pyrolysis is one of the suitable processes to produce maximum 65% of oil from oil containing seeds [4–11]. The process pyrolysis means, heating materials at elevated

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temperature in presence of very less amount of air or oxygen. During pyrolysis the higher molecular weight compounds such as hydrocarbon, breaks to form lower molecular weight, short chain hydrocarbons. The condensable liquid hydrocarbon is known as pyrolytic oil. Pyrolysis of biomass yields three form of fuel such as solid fuel which remains at the end of the process, condensable volatiles as liquid fuel and the non-condensable gases as gaseous fuel [5]. The quality and quantity of the pyrolytic oil depends on the oil content and the composition of the feed stock. One of the advantage of pyrolytic oil that it is easier to handle, store and transport and can be a source of production of several chemicals [6]. Literature reveals, the pyrolytic liquid produced from castor seed separated into two layer such as oil and aqueous [4]. The calorific value and density of oil layer were very close to diesel. Maximum 64.5% of production of oil could be possible by thermal pyrolysis of castor seed [4]. Linseed pyrolysis produced 57.7 wt.% of liquid yield at 550 °C where, [7] 44% yield was possible at 550 °C from safflower seed at a heating rate of 5 °C min^{-1} and sweep gas (N_2) flow rate 100 mL min^{-1} [8] and maximum liquid yield observed at 500 °C during slow pyrolysis of pomegranate seeds [9]. Duman et al. found maximum pyrolytic oil yield of 44 wt% at pyrolysis temperature of 500 °C for both CWS and CSS [10]. Catalytic pyrolysis of *Pistacia khinjuk* seed was carried out with BP3189 and Criterion-424 as catalyst and a liquid yield of 66.5% and 69.2% was found for the two catalysts respectively. The thermal pyrolysis yield for the same seed was only 57.6%. The results confirmed that the use of catalyst increased the pyrolytic liquid yield both qualitatively and quantitatively [11].

A lot of work has been done on thermal pyrolysis of different seeds but a few works were reported on catalytic pyrolysis of seeds. This paper reports the thermal and catalytic pyrolysis of Mahua seed. Thermal pyrolysis was carried out to study the maximum yield of oil at minimum temperature. The effect of catalyst (CaO) in three different feed to catalyst ratio (2:1, 4:1 and 8:1) were studied to determine the optimum ratio for maximum liquid yield with better fuel properties. The aim of selecting this particular catalyst was that literature reveals catalytic cracking with CaO reduces the tar yield as well as emission of CO_2. CaO absorbs CO_2 and form $CaCO_3$ and results in zero emission of CO_2 during pyrolysis. The reactions involved are provided below [12–15]:

$$C + H_2O = CO + H_2, \Delta H^0_{298} = -131.3\ kJ\ mol^{-1} \quad (1)$$

$$CO + H_2O = CO_2 + H_2, \Delta H^0_{298} = -41.5\ kJ\ mol^{-1} \quad (2)$$

$$CaO + CO_2 = CaCO_3, \Delta H^0_{298} = -178.1\ kJ\ mol^{-1} \quad (3)$$

2. Materials and methods

2.1. Raw material

Fresh Mahua (*Madhuca indica*) seeds were collected from local market of Ganjam, Odisha, India. The seeds were sun dried for 10–12 h and grinded to less than 1 mm sized particle and stored in air tight plastic bottles for pyrolysis.

2.2. Characterization of Mahua seed

The seed was characterized for its proximate (moisture, volatile, ash and fixed carbon) and ultimate analysis (C, H, N, S, O), extractives content and thermal degradation profile. ASTM standard methods such as ASTM D 3173-3187 for moisture analysis, ASTM D 3175-89 for volatile analysis and NREL/TP-510-42622 for ash analysis were followed [16–18] whereas Variael CUBE C, H, N, S elemental analyzer made in Germany was used for ultimate analysis and the oxygen content was calculated by difference. The % extractives present in the seeds were determined experimentally using NREL standard methods given elsewhere [19]. The thermal degradation temperature of Mahua seed was decided with the help of thermogravimetric analyzer (TGA). TGA experiment was performed in a Mettler Toledo, Switzerland; TGA 851^e/LF/1100 analyzer using platinum crucible. Around 10 mg of powdered seed sample was heated at room temperature from 25 °C to 700 °C at the rate of 15 °C min^{-1} in a platinum crucible under a sweeping gas (N_2) flow rate of 40 mL min^{-1}. The weight loss result from TGA was collected with respect to temperature and time. Consequently % conversion of seed to volatiles was calculated by the ratio of the difference between the initial and remaining weight of the sample to the difference of the initial and final weight of the sample. The region of maximum conversion was accepted as the pyrolytic zone for Mahua seed.

2.3. Thermal pyrolysis

Thermal pyrolysis experiments were conducted in a stainless steel batch reactor (ID: 6 cm and Length: 21 cm) with one end opened to collect the volatiles. The reactor was heated electrically by using a cylindrical furnace where PID controller maintained the appropriate temperature with an error of ±2 °C. The reactor was loaded with 40 g of powdered seed sample and inserted vertically into the furnace and pyrolysis experiment was accomplished from 500 to 600 °C at every 25 °C augment of temperature. The generated volatiles were condensed by a water cooled condenser. The condensed liquid was collected using measuring cylinder and measured by weight basis and accordingly the optimum temperature for highest oil yield was determined. At the end of each experiment the reactor was cooled and the solid residue remaining in the reactor was accumulated as char. The % yield of products such as pyrolytic liquid and char was calculated on the basis of their feed using Eq. (4), whereas gas/non-condensable volatile was calculated by difference.

$$\%\ yield = (Product\ weight/Feed\ weight) \times 100 \quad (4)$$

It was observed that the liquid product was easily separated into two layers as per their gravity. The top layer was considered as oil and bottom as aqueous. Hence at each run the weight % yield of oil and aqueous phase was also determined.

2.4. Catalytic pyrolysis

Catalytic pyrolysis experiments were conducted at the optimum temperature determined by thermal pyrolysis, at different feed to catalyst ratio (2:1, 4:1 and 8:1) in the same stainless steel batch reactor as mentioned in the earlier section. Calcium oxide (CaO) was purchased from Loba Chemie, India, (P) Ltd. and used as catalyst (BET surface area: 37 $m^2\ gm^{-1}$, MW: 56.0074 g mol^{-1}). The catalyst was used directly without any treatment and the yield was calculated as described in the above section. The product obtained from thermal and catalytic pyrolysis was compared on the basis of yield, physical and chemical properties. Later on the process was optimized and the ratio of feed to catalyst for maximum production of pyrolytic oil was determined.

2.5. Characterization of pyrolytic oil

The pyrolytic oil was characterized on the basis of their physical properties, functional groups present and composition. The physical properties such as viscosity, density, calorific value, water content, distillation temperature, pH and cold flow properties (DSC analysis) were calculated. The presences of functional groups were determined by FTIR analysis and compositions by GC–MS analysis.