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Thermo-chemical conversion of mango seed kernel and shell to value added products

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ABSTRACT

Mango (*Mangifera indica*) is one of the popular fruits in India and many other tropical countries also. Mango seed weight is 30 – 45% of the total fruit weight which completely goes off as waste. In this study, Mango seed kernel (MSK) and Mango seed shell (MSS) were selected as a feed for pyrolysis for the production of bio-chemicals. Conventional pyrolysis of MSK and MSS was carried out in the range between 673 to 873 K temperatures at a heating rate of 25 K min^{-1}. The optimum temperature for maximum yield of pyrolytic liquid was 823 K and 848 K for MSK and MSS with the corresponding yield of pyrolytic liquid of about 32.37% and 52.57% respectively. The composition analysis of MSK and MSS pyrolytic liquid revealed the presence of various valuable chemicals. It was noticed that MSS pyrolytic liquid contains about 27.63% D-allose, which is a rare sugar, whereas MSK contains 13.27% of levoglucosan along with furfural, furan, alcohol, aldehyde, benzene and various alkanes.

1. Introduction

Mango (*Mangifera indica*) is most popular fruit grown in tropical and subtropical countries and is one of the most common edible fruit all over the world. Mango and mango products such as pickles, nectar, chutney, canned pulp and slices have gained worldwide popularity. The waste products from this fruit (i.e., mango peel and seed) have not been put to any serious use till date. Mango seed which accounts for 30 – 45% of the total fruit weight depending on its variety is the major waste product from mango processing industry [1]. In India, mango is known as the “king of fruits” and India itself accounts for 15.03 million tons of mango production which contributes to 40.48% of the world mango production. Total mango production of the world in 2010 was around 37.12 million tons [1,2]. The weight of Mango seed accounts for more than 30% of the total fruit weight. The fat content is around 10% of the weight of the seed. The fatty acid composition (oleate and stearate) of matured mango seed varies with its variety [3]. Ali et al. and Abdalla et al. reported that the extraction of lipids was possible using methanol as solvent in solvent extraction process from different variety of mango seed kernel [4,5]. Along with these extractives, hemicelluloses, cellulose and lignin are the other constituents of mango seed kernel and shell. Upon thermal treatment, these offer various chemicals along with char. Literatures reveal pyrolysis of seeds can be a sources various valuable bio-chemicals [6–15]. Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydro-glucose held together in a giant straight-chain molecule. These anhydro-glucose units are bound together by β-(1,4)-glycosidic linkages [16]. The degradation reaction of cellulose is characterized by the decrease in polymerization degree. Thermal degradation of cellulose can either proceed through gradual degradation, decomposition and charring on heating at lower temperatures or through rapid volatilization accompanied by the formation of levoglucosan during pyrolysis at higher temperatures. The glucose chains in cellulose are first cleaved to glucose and from this, during second stage, glucosan is formed by the splitting of one molecule of water [16]. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the binding material holding together the cellulose units and fibre. Hemicellulose decomposes readily forming furan and furan derivatives. Lignins are polymers of aromatic compounds. It is a macro-molecule, which consists of alkyl-phenols and has a complex three-dimensional structure. Pyrolysis of lignin yields more than 51% of phenol and methyl phenol derivatives which constitute the dark oil [17]. The extractives content in biomass also plays a significant role in the product distribution of biomass pyrolysis. Lignin and extractive content of the biomass determine the possibility of formation of the tarry liquid. If

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the lignin or extractive content of the biomass is less, the pyrolysis product results in lesser amount of tarry liquid and so it may be considered for extraction of valuable chemicals instead [18].

The present study reports the best use of one of the agricultural waste such as mango seed kernel (MSK) and mango seed shell (MSS) for the production of various valuable chemicals using pyrolysis technique.

2. Materials and methods

2.1. Preparation of raw materials

Mango seeds were collected from the fruit juice stall of IIT Guwahati, Assam, India. The seeds were properly washed in tap water to remove the remaining fruit pulp. Then the seeds were sun dried for 48 h followed by oven drying for another 24 h at about 333 ± 5 K. The seed kernel was separated from the seed shell manually with the help of knife and both the kernel and shell were grinded to powder by using a mixer grinder (Bajaj, India). The mango seed kernel (MSK) and mango seed shell (MSS) were passed through sieve and a particle size of 75 μm (ASTM 200 mesh) were collected and stored in air-tight polythene bags for further use.

2.2. Characterization of MSK and MSS

2.2.1. Proximate and ultimate analysis

Proximate analysis of MSK and MSS was carried out using standard methods reported elsewhere [6–9], whereas, Eurovector EA3000 (CHNS) elemental analyzer determined the amount of C, H, N (ultimate analysis). The high heating value (HHV) was determined using the formula given by Demirbas [9].

$$HHV = \{33.5[C] + 142.3[H] - 15.4[O] - 14.5[N]\} \times 10^{-2}\ MJ\,kg^{-1} \quad (1)$$

2.2.2. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR analysis of the MSK and MSS were carried out using Excalibur Bio-Rad spectrophotometer (model FTS 3500 GX) attached with DRS (Diffuse Reflectance Spectroscopy). Prior to FTIR analysis, KBr was oven dried at 333 K for 1 h and powdered by using mortar pestle. The powdered KBr was mixed with samples (1:100) and placed in the sample holder and the IR spectra were collected at scan rate of 40 with a step size of 4 cm^{-1} within the range of 400 to 4000 cm^{-1}.

2.2.3. EDX analysis

Finely powdered MSK and MSS were analyzed to identify the presence of various minerals which varies according to the soil characteristics of the place of growth of Mango tree. The mineral content of MSK and MSS were determined using LEO 1430 VP SEM/EDX analyzer.

2.3. Pyrolysis of MSK and MSS

Pyrolysis of MSK and MSS were carried out in the temperature range between 673 and 873 K, at a heating rate of 25 K min^{-1} using a semi-batch reactor made up of stainless steel (Length: 21 cm, ID: 6 cm). The reactor was filled with 40 g of feed samples and heated by a self-fabricated electrical heated cylindrical furnace where the set temperature was maintained by a PID controller. The generated volatiles were condensed by a water cooled glass condenser. The liquid product was collected in a measuring cylinder and weighed. At the end of the process, the reactor was cooled and the remaining char was collected from the reactor and weighed. The weight% yield of pyrolytic liquid, char, gas and conversion of feed to products were calculated using Eqs. (6)–(9).

$$\%\text{Liquid yield} = (\text{Liquid weight}/\text{Feed weight}) \times 100 \quad (6)$$

$$\%\text{Char yield} = (\text{Char weight}/\text{Feed weight}) \times 100 \quad (7)$$

$$\%\text{Gas yield} = 100\text{-}(\%\text{Liquid yield} + \%\text{Char yield}) \quad (8)$$

$$\%\text{Conversion} = (\text{wt. of raw material-wt. of char})/\text{wt. of raw material} \quad (9)$$

2.4. Characterization of MSK and MSS pyrolytic liquid

2.4.1. FTIR analysis

The functional groups present in MSK and MSS pyrolytic liquid were determined using DRS attached Excalibur Bio-Rad spectrophotometer (model FTS 3500 GX) FTIR analyzer within the range of 400–4000 cm^{-1} at scan rate of 40 with a step size of 4 cm^{-1}. One drop of liquid sample was added to KBr pellet and the IR spectra were collected and analyzed.

2.4.2. GC–MS analysis

The composition of MSK and MSS pyrolytic liquid obtained at the optimum temperature were determined and discussed. The GC–MS analysis was performed using Perkin Elmer Clarus680 GC/600C MS analyzer. The GC was programmed at 313 K for 0.5 min with the total run time of 30 min. The temperature was increased at the rate of 10 K min^{-1} to 573 K. Elite 5 MS column of diameter 0.250 μm, length 30 m was used. Exact 1 μL volume of sample was injected into the column with a carrier gas (Helium) flow rate of 0.6 mL min^{-1}.

3. Results and discussion

3.1. Physical properties of MSK and MSS

The physical properties of MSK and MSS are discussed from the outcomes of proximate, ultimate and EDX analysis. The proximate and ultimate analysis is displayed in Table 1. From the analysis, it was observed that the 48 h sundried and 24 h oven dried MSK and MSS hold 11% and 10.42% of moisture respectively. Both MSK and MSS were rich in volatile matters followed by fixed carbon and ash content. Volatile matters are responsible for the formation of gaseous products such as carbon monoxide, carbon dioxide, methane, free nitrogen etc. along with condensable volatiles during thermochemical conversion (pyrolysis). Fixed carbon is the combustible residue left after the expulsion of volatiles. Fixed carbon along with the ash constitutes the char that formed during pyrolysis. More amount of fixed carbon in the biomass yield a higher amount of char during pyrolysis. Proximate analysis confirmed that MSK was rich in fixed carbon compared to MSS, thus, more amounts of char may be expected out of MSK pyrolysis. Ash is that part of a material which doesn't burn. The amount of ash in both MSK and MSS was very less therefore making them a suitable feed for pyrolysis to produce more liquid products.

Table 2 shows the various minerals present in MSK and MSS determined by EDX analysis. It was noticed that MSK was comparatively less rich in minerals whereas, MSS contains various minerals. Among all, magnesium was higher in MSS followed by Fe, Co, Ni, Cu and Zn, which can be extracted using various techniques as value added products. The presence of such minerals act as catalysts during pyrolysis to enhance the rate of various reactions [19].

FTIR analysis characterized the raw materials as shown in Fig. 1. The IR peaks observed in the range of 3200–3400 cm^{-1} indicated the presence of moisture in the sample which could be due to the