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Comparative Study of Production of Bio-fuel from Mango Seed Kernel Using Pyrolysis and Chemical Conversion Processes

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ABSTRACT

The conversion of mango seed kernel into biofuel was performed through thermal pyrolysis and chemical transesterification process in this present study. The research also involved a comparative analysis of product yield and physico-chemical properties of the resulting biofuel. The pyrolysis experiment was performed in a 22 cm length and 15 cm diameter fixed bed external heating reactor at a temperature ranging from 150 – 350°C using a full-size sample. The major components of the experimental setup included a furnace, fixed-bed external heating reactor, water-cooled condenser, K-type thermocouples, and collectors for liquid and char. Instead of electricity, low-grade waste biomass was used for heating. This process achieved a maximum biofuel yield of 30.18 wt.%. For the chemical process, initially vegetable oil was extracted through a solvent extraction method, mixing the samples in a 1:2 ratio with hexane and stirring the mixture at a temperature between 25 – 50°C for a duration of 3 – 12 hours, resulting in a 17.3 wt.% yield of vegetable oil. After that, the obtained vegetable oil was transesterified using potassium hydroxide as a catalyst at 60°C for 1 – 1.5 hours. A maximum of 75 – 80 wt.% of extracted vegetable oil was converted into biofuel. The produced biofuels were evaluated for their suitability as alternative fuels by analyzing their physico-chemical properties including viscosity, density, pour point, flash point, and gross calorific value.

Keywords: Bio-fuel; Mango Seed Kernel; Pyrolysis, Transesterification; Product Yields; Fuel Properties.

1 Introduction

The world has been facing increasing energy demand and emphasizing the urgency for sustainable and environmentally friendly solutions. Fossil fuels including natural gas, oil, and coal account for 80 – 85% of total global primary energy production but as these resources are finite, several studies have predicted that they will eventually be depleted over time [1], [2]. However, using these resources is scary because of their high rate of consumption and release of greenhouse gases that contribute to environmental issues [3] including global warming, climate change acid rain, and health issues from the discharge of toxic compounds [4], [5].

In addition, the rise in population, urbanization, and economic development has led to increased waste generation. According to World Bank, if the current rate of waste generation continues it is expected to increase by approximately 70% by 2050 [6] – [8]. From the research studies, carbon dioxide (CO_2) emissions are directly linked to the consumption of fossil fuel and are responsible for worldwide climate changes [9]. To address these challenges, researchers assert that carbon-neutral biomass presents a promising resource for energy production, especially in the form of biofuel [10]. Such substances hold special significance because they are renewable, widely accessible, biodegradable, non-toxic, and environmentally sustainable [11]. They not only help to reduce dependence on fossil fuels but also support the objectives of the Kyoto Protocol which aim to mitigate greenhouse gas emissions [12]. This biofuel is increasingly being acknowledged worldwide as a green fuel because of its low sulfur content, biodegradable properties, and high flash point [13].

The tropical and subtropical climate of the South Asian region is ideal for the prolific growth of fruits like mangoes. Bangladesh is currently in the seventh position globally in terms of mango production [14]. In 2012, global mango production was estimated at approximately 46.7 million MTs and this figure is further increasing [15]. According to authorities from the Department of Agricultural Extension (DAE), the yearly mango production in Bangladesh is expected to reach around 2.55 million MTs in 2023 [16]. In fruit processing industries around 40 – 50% of mangoes are processed into juice and other by-products, while the seeds and peels are typically discarded as waste [17]. Depending on the variety, mango seeds account for 30 – 40% of the fruit's weight [18]. Mango seeds are comprised of two main parts: seed shell and seed kernel. The shell is the outer layer of the seed; it covers the kernel. The shell makes up about 5 – 15% of mango while the kernel accounts for 10 – 20% [19] –[21]. The chemical composition of the mango seed includes lignin, hemicelluloses, and cellulose are primary constituents in the shell while starch and fat are in the kernel [22].

Previously, researchers have produced biofuel from various non-edible biomass sources such as jatropha, microalgae, neem, karanja, rubber seed, mahua, silk cotton tree, castor, pongamia pinnata, and others. These biofuels have shown to be viable alternatives to conventional fuels [23] – [29]. Sultana and Ashraf [29], Saka et al. [30], Julio et al. [31], and Narayansamy et al. [32] have investigated various extraction and chemical processing techniques for biofuel production from mango seeds. They also analyzed different catalyst's impact on product yield and the properties of resulting biofuel. Additionally, Ganeshan et al. [33], Lam et al. [34], Lazzari et al. [35], and Andrade et al.

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[36] conducted experiments on the pyrolysis of mango seed shell or kernel in a fixed-bed reactor and examined the product yield of biofuel, gas, and char.

Previous experiments entailed milling the samples into the form of powder and utilizing electricity during heating, which was energy-inefficient and incurred additional labor costs. As a result, the main objective of the current research is to produce biodiesel from mango seed kernels through the pyrolysis and transesterification process, including the construction of a pyrolysis reactor that can produce biofuel from mango seed kernels without using electricity. This study also aims to compare the product yields and physico-chemical characteristics of the biofuel obtained from both processes.

2 Materials and Methodology

2.1 Materials

In this study, mango seed kernel was utilized as feed material, which was collected from Khulna City, Bangladesh. Initially, the seeds were properly rinsed with water and detergent to wash away any remnants of mud, sand, or additional surface impurities. Upon washing, the seeds were sun-dried to remove any additional moisture. Once fully dried, each of the seeds was meticulously split using a knife to retrieve the kernel, which originally measured around 4 – 6 cm. Fig. 1 depicts the sample that was prepared for both pyrolysis and transesterification. Although the full-sized kernel was employed in pyrolysis, for transesterification the kernels were pulverized into smaller fragments as this increased the surface area and facilitated the extraction of the oil.

2.2 Experimental Set-Up and Procedure

2.2.1 Pyrolysis Experiment

The pyrolysis of mango seed kernels was carried out using a fixed-bed external heating reactor designed to produce biofuel. The major components of the experimental setup were a fixed-bed external heating chamber, reactor inside the heating chamber, water-cooled condenser for condensing the pyrolytic vapor, K-type thermocouples with display, liquid collecting pot, N_2 gas cylinder with flow control valve and pressure regulator, char collecting bag and fan. Fig. 2 illustrates a diagram of the experimental setup offering a visual representation of the configuration. The setup included a furnace constructed from galvanized steel, which measured 61 cm in length and 36 cm in diameter. Inside this chamber, an aluminum reactor of 22 cm in length and 15 cm in diameter was positioned. The size of the reactor was finalized after analyzing the size taken by different researchers for their experiments [4], [26], [37], [38]. In each pyrolysis run 0.5 kg of pre-treated mango seed kernel was placed into the reactor chamber via the top opening. Before initiating the pyrolysis experiment, the reactor was purged with N_2 gas for 2 – 3 minutes to create an inert atmosphere. The experiments were conducted by changing the temperature between 150 – 350°C with an interval of 50°C, with the inside temperature of the reactor closely monitored using K-type thermocouples. Although higher temperatures and rapid heating using electricity can produce higher biofuel yields, a relatively low temperature (150-350°C) and slow heating were used in this study due to the use of low-grade waste biomass for heating. Additionally, maintaining a high temperature using waste biomass is quite impossible.

(a) (b)

Fig. 1 Prepared feedstocks of mango seed kernel for (a) pyrolysis (b) transesterification

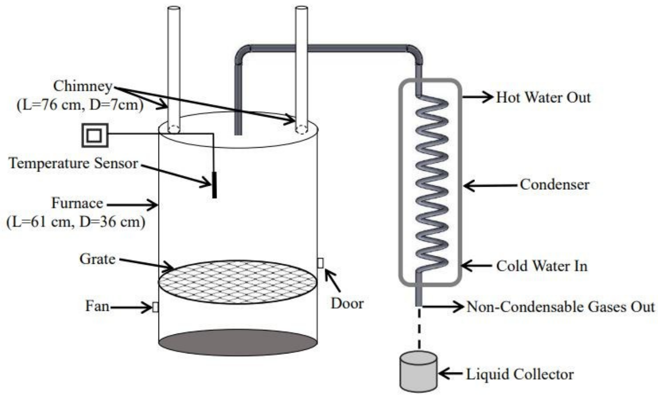

Fig. 2 Schematic diagram of pyrolysis system

Lazzari et al. [35] investigated the rise in liquid yield during the pyrolysis of mango seed kernels at temperatures ranging from 200°C to 450°C and Dyjakon et al. [39] examined the physico-chemical properties of mango, lychee, and avocado seeds at temperatures between 200 – 300°C, observing that higher temperatures led to increased production and higher heating values.

During the combustion of low-grade waste biomass, which served as the heating source, the produced smoke was vented through two chimneys, each measuring 76 cm in length and 7 cm in diameter. The volatile gases coming from the reactor were then cooled by passing through a water-cooled copper condenser, where the condensable gases were converted into liquid and collected in a pot. Non-condensable gases were flared into the open air separately. The heating process continued until all gases were completely released from the biomass indicating the completion of the pyrolysis reaction and the total duration was recorded as the reaction time for the process. Initially, as the temperature increased, the production of liquid also increased until it reached its maximum level, after which it began to decrease. The maximum liquid production occurred at an optimum temperature of 250°C, as the raw material undergoes significant breakdown at this temperature. However, beyond 250°C, liquid production decreased while gas production increased. The decline in liquid production and rise in gas production are likely due to secondary decomposition processes and the transformation of some oil vapors into permanent gases. After the pyrolysis reaction was complete heating was ceased and the set-up was allowed to cool. The reactor was then opened to extract char residue and weigh it after putting it into a sample bag. Similarly, the weight of the obtained liquid was also measured. The weight of pyrolytic gas was determined by subtracting the combined weight of char and liquid from the initial weight of the feedstock. The system was then prepared for subsequent runs ensuring a systematic and efficient approach to the experimental process.

2.2.2 Transesterification Experiment

The production of biofuel from mango seed kernels involves two main steps: firstly, extracting vegetable oil from the kernels and secondly, converting that vegetable oil into biofuel. Vegetable oil was extracted from mango seed kernel using hexane through a solvent extraction method. Each test involved mixing 100gm of the sample with hexane at ratios of 1:2.5 or 1:2 (w/v), followed by agitation. Agitation was conducted at temperatures ranging from 25 to 50°C for 3 – 12 hours to optimize the chemical reaction throughout the solvent and sample for maximizing oil extraction. Before agitation, the material was submerged in hexane for approximately 48 hours. After that, the vegetable oil was separated using evaporation and filtration techniques. A flow chart illustrating the biofuel production process through transesterification is provided in Fig. 3.

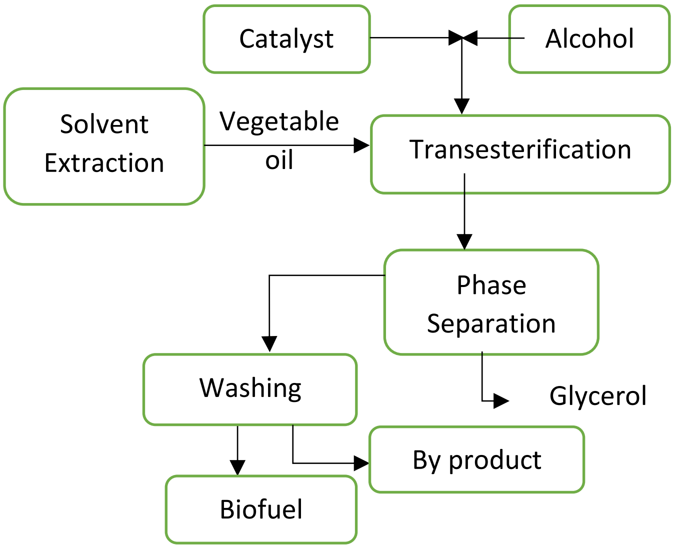

Fig. 3 Transesterification process to produce biofuel

For producing biofuel from the extracted vegetable oil transesterification process was utilized. This reaction was conducted at 60°C for 1 hour where the vegetable oil was forcefully agitated with a methanol-KOH solution. To drive the reaction toward biofuel production, a methanol-to-oil molar ratio of 6:1 was used by adding an excess of methanol. Zhang et al. [40] determined the required amount of KOH in kilogram for the transesterification using the formula, KOH = 0.013 × Volume of vegetable oil (liters). Therefore, KOH was incorporated at a level of 1.5% of the oil's weight. At a constant temperature, the reaction was continued for 1 – 1.5 hours and then it was left for 24 hours to settle. This settling resulted in biofuel floating on top, while glycerin accumulating at the bottom. Both biofuel and glycerin were carefully separated. Filtration was also carried out to remove free fatty acids, enhancing the quality of the biofuel.

2.3 Product Analysis Procedure

Characterization is essential to assess the efficiency and acceptability of the produced biofuel for different purposes. Standard ASTM test procedures were used to examine various types of physico-chemical characteristics, such as viscosity, pour point, density, gross calorific value (GCV), and, flash point. The oil's density indicates how aromatic it is, while its kinematic viscosity shows its flow characteristics. Density and viscosity measurements were performed using the ERASPEC Fuel Analyzer-ES10. The flash point, which is the minimum temperature at which the fuel momentarily ignites without sustaining a flame, was determined using the Pensky-Martens AIM 509 (Closed) apparatus. The pour point, indicating the temperature at which the biofuel ceases to flow, was assessed using the AEX 503 device. Finally, the calorific value, representing the energy or heat released upon combustion, was measured with the GDY-1C Oxygen Bomb Calorimeter.

3 Results and Discussion

3.1 Proximate Analysis

Mango seed kernel's proximate analysis identifies their compositional attributes, including moisture content, volatile matter, ash content, and fixed carbon content. These tests were conducted following ASTM standards. The result of this analysis for mango seed kernel is presented in Table 1.

Table 1 Proximate analysis of mango seed kernel

Parameters	**Mango Seed Kernel**
Volatile Matter (%)	67.53
Ash Content (%)	3.9
Moisture Content (%)	11.13
Fixed Carbon (%)	17.44

3.2 Product Yields

The biofuel obtained through the pyrolysis and transesterification of mango seed kernel is illustrated in Fig. 4. Pyrolysis experiments were conducted at temperatures ranging from 150°C to 350°C at 50°C increments, resulting in the production of three distinct types of products: liquid, solid, and gas. The maximum yield of pyrolytic liquid and solid were 30.16 wt.% and 65.23 wt.% at a temperature of 250°C and 150°C, respectively. The yields of pyrolytic liquid varied significantly with temperature and were affected by various factors which include the feedstock layout, temperature of operation, reactor size as well as type, heat transfer efficiency from the reactor surface to the biomass, feed size of particles, and vapor time of residence [37].

(a) (b)

Fig. 4 Biofuel derived from mango seed kernel (a) pyrolysis (b) transesterification

In contrast, 13.8% of the vegetable oil was recovered using the solvent extraction method from the mango seed kernel. Subsequently, through the transesterification process 75 – 80% of this vegetable oil was converted into biofuel. It is recommended that using Soxhlet instead of Hexene and reducing the feed size can potentially improve the vegetable oil recovery.

3.3 Properties of Produced Bio-fuel

The biofuel derived from the pyrolysis of mango seed kernel was dark red-brown and had a strong acrid odor. Notably, if the water content exceeds 30 – 40 wt.% phase separation can occur [41]. The pyrolytic liquid was homogeneous and in the liquid storage bottles, there was no phase separation. In contrast, the biofuel produced via transesterification exhibited a yellowish color. Several physico-chemical characteristics of the obtained biofuel through pyrolysis and transesterification including density, kinematic viscosity, flash point, pour point, and calorific value were measured and compared. The results are summarized in Table 2.

The density of the liquid obtained through pyrolysis (875.4 kg/rn^3) exceeds that of diesel but closely resembles biodiesel fuels, such as those derived from jatropha (880 kg/rn^3), neem (878 kg/rn^3), and waste cooking oil (910 kg/rn^3). In contrast, liquid obtained through transesterification (778.8 kg/rn^3) is lower than diesel, jatropha, neem, and waste cooking oil. Generally, fuels with higher density result in lower fuel consumption, while those with lower density require more to produce the same heat output. The kinematic viscosity of biofuel produced through pyrolysis and transesterification is 2.86 and 1.74 cSt, respectively, at 40°C, which is similar to diesel (2 – 4.5 cSt at 40°C) but lower than those of jatropha (4.8 cSt), neem (5.81 cSt), and waste cooking oil (4.9 cSt).

Lower viscosity is beneficial for easier handling and transportation. The viscosity of biofuel can vary widely depending on the feedstock, process conditions, and the efficacy of low-boiling component collection [42]. The flash point of biofuel from pyrolysis and transesterification is 112°C and 70°C, respectively, which are higher than diesel (50 – 95°C). In contrast, jatropha (135°C) [43], neem (175°C) [7], and waste cooking oil (150°C) [44], the flash points of biofuel from pyrolysis (112°C) and transesterification (70°C) exhibit significantly lower. This is because biomass-derived liquids are less refined and contain a variety of components with a wide distillation range. The pour point of biofuel through pyrolysis and transesterification is –11°C and –9°C, respectively. Although these pour points are lower than diesel, the practical experience of the present study suggested that this was not problematic. However, despite these promising properties, the gross calorific value of the biofuel from pyrolysis is 18.8 MJ/kg, and from transesterification is 22 MJ/kg which is considerably lower than that of diesel (42–46 MJ/kg), jatropha (39.5 MJ/kg), neem (26.65 MJ/kg), and waste cooking oil biodiesel (35.5 MJ/kg) due to the presence of moisture and oxygenated chemicals.

Even though, the liquid oils obtained from pyrolysis and chemical conversion have certain challenges that may affect combustion, engine efficiency, and emissions [37], appropriate treatment is necessary to make them suitable for use in engines.

4 Conclusions

This study focused on producing biofuel from the mango seed kernels exploring its viability as an alternative fuel. Pyrolysis was carried out in a fixed-bed external heating reactor at a temperature ranging from 150 – 350°C for full-sized samples. For the chemical process initially, vegetable oil was extracted through a solvent extraction method, mixing the samples with hexane in a 1:2 ratio and the mixture was agitated between 25 – 50°C for a duration of 3 – 12 hours. The obtained vegetable oil was subsequently turned into biofuel via the transesterification process, utilizing potassium hydroxide as the catalyst at 60°C for 1 – 1.5 hours. The results of this experiment likely provide insights into product yields, chemical composition, and potential applications of the biofuel produced.

- The maximum yield of biofuel from full-sized mango seed kernel through pyrolysis was 30.18 wt.% at a temperature of 250°C.
- The chemical conversion process extracted 17.3 wt.% vegetable oil from mango seed kernel, with a maximum of 75 – 80 wt.% of this oil was converted into biofuel.
- Analysis of the physico-chemical properties revealed that both the biofuels were dense with moderate viscosity and had favorable pour and flash point.
- The calorific value of biofuel produced through pyrolysis and transesterification process was 18.08 MJ/kg and 22 MJ/kg, respectively.
- The biofuel derived from mango seed kernel can be utilized either as a low-grade biofuel or as a blend with conventional liquid fuel.

As a waste product from mango processing industries and an alternative energy source, future studies can focus on how companies can implement this process economically. This

Table 2 Comparison of properties of biofuel derived through pyrolysis and transesterification with conventional diesel, and other biofuel sources

Properties	Mango seed kernel oil		Diesel	Jatropha Biodiesel [43]	Neem Biodiesel [7]	Waste Cooking Oil [44]
	Pyrolysis	Trans-esterification				
Density (kg/m^3), 30°C	875.4	778.8	820 to 860	880	878	910
Kinematic Viscosity (cSt)	2.86	1.74	2 to 4.5	4.8	5.81	4.9
Flash Point (°C)	112	70	50 to 95	135	175	150
Pour Point	–11	–9	–40 to –1	2	8	2
Calorific Value (MJ/kg)	18.08	22	42 to 46	39.5	26.65	35.5

approach would not only reduce environmental pollution and dependency on fossil fuels but also create job opportunities. Additionally, future research will explore how to optimize product yields using heterogeneous catalysts, upgrade the biofuel, test different biomass sources for biofuel production, and conduct emission and engine performance testing.

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