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Utilizing manilkara zapota seed oil for biodiesel production and conducting an investigation into its properties and characteristics

Kanthavelkumaran N.*, Mathu Kumar S., Iyyappan S. and Suthan Raja Prasad N.N.
Mechanical Engineering, Ponjesly College of Engineering Alamparai, Nagercoil, Tamil Nadu, India
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*to whom all correspondence should be addressed: e-mail: kanthavelpriya@gmail.com
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Graphical abstract

Sapota Tree, Fruit and Seeds

Biodiesel Glycerin Separating Procedure

Abstract

Biodiesel can be derived from the oils of fruit seeds for powering diesel engines, and this study focuses on extracting biodiesel from Manilkara Zapota seeds, which are readily available and not intended for human consumption. The primary aim is to underscore the use of non-edible oils as a cost-effective raw material for biodiesel production. The research indicates a successful production yield of 92.45% using a 0.76% catalyst, an excess of 6 methanol equivalents in comparison to the oil, a temperature of 62°C, and a reaction time of 90 minutes. The biodiesel obtained from Manilkara Zapota seed oil predominantly comprises methyl esters of oleic, stearic, and palmitic acids, presenting a viable alternative to fossil diesel for unmodified diesel engines. Optimal performance variables for maximum conversion efficiency were determined as a 40°C reaction temperature, 6:1 alcohol-to-oil ratio, 120 minutes of experimental duration, and a 0.5wt.% NaOH catalyst. Among these variables, the alcohol-to-oil ratio was identified as the most influential, contributing 84.34% to the overall performance. The thermal profile of Manilkara Zapota Seeds biomass exhibited multistage decomposition behavior. The synthesized Manilkara Zapota Methyl Ester (MZME) derived from seed oil, using the optimized performance variables, complies with the ASME D 6751 and EN14214 Biodiesel Standards.

Keywords: Ethanol, fermentation, fruit waste, manilkara zapota seed oil, thermogravimetric, yeast, wine

1. Introduction

Combustion of fossil fuels stands as the primary contributor to CO_2 emissions, leading to environmental damage. With the surge in industrialization, increased energy consumption, depleting fossil fuel reserves, and growing apprehensions about environmental pollution, vegetable oils, both edible and non-edible, emerged as potential substitutes for conventional liquid fuels owing to their abundant availability. Despite their conceptual viability, these vegetable oils failed to gain broad acceptance mainly due to their higher costs compared to petroleum-based fuels (Wu Xuan and Leung Dennis 2011). Concerns regarding climate change and the diminishing reserves of fossil fuels have triggered a substantial global upswing in the demand for biofuels. The primary drawback associated with utilizing natural resources for fuel is the significant elevation in atmospheric CO2 levels resulting from the use of petroleum-based fuels, thereby contributing to global warming. Biofuels, such as bio-ethanol, have been advocated as credible substitutes or alternatives in addressing concerns about greenhouse gas emissions and climate change (Hassan and Kalam 2013, Jeswani *et al.* 2020). Moreover, the issue of open-air waste disposal, which harms the nearby natural ecosystem, has prompted research into cost-effective and efficient waste-to-energy solutions (Samadi *et al.* 2020).

Technologies for renewable energy, such as biogas, liquid fuels, and solid biomass, have grown significantly in the last several years. Because they come from biomass rather than the geological processes that produce oil and fossil fuels, biofuels are different from fossil fuels. These phrases are frequently used synonymously when discussing biomass and biofuels (Popp *et al.* 2014, Singh and Gu 2010). The process of producing bioethanol requires biomass that contains a range of free sugars that can be transformed into soluble sugars in the future. There are three main types of feedstock: lingo cellulosic biomass (LCB), starchy crops (such as outputs from sugar refineries), and each type of feedstock provides a different kind of sugar. Historically, first-generation bio-ethanol technologies have

used conventional starch-rich feedstocks such corn, potatoes, and sugarcane (Khandaker *et al.* 2018, Shah and Sen 2011). However, these face various economic and social challenges, leading to a growing interest in second-generation bio-ethanol processes (Eisentraut 2010).

Lignocellulosic biomass, encompassing materials like corn stover, sugarcane bagasse, straws, stalks, and switch grass, plays a crucial role in second-generation processes (Kang *et al.* 2014, Hassan *et al.* 2019). These methods serve as a vital alternative for bio-ethanol production and can readily adapt to current engines with higher octane ratings (Calero *et al.* 2015). Alcohol, particularly bio-ethanol, is a preferred fuel additive for enhancing the cold flow characteristics and reducing the viscosity of biodiesel; its use in conjunction with biodiesel also contributes to lower smoke emissions (Kanthavelkumaran *et al.* 2015). Plant materials with high sugar content, such as sugarcane, pineapple, and potatoes, serve as significant sources for bioethanol production, yielding substantial amounts of bioethanol as byproducts. This has diverted scientific investigations from exploring the potential of vegetable oils as alternative fuels. Nevertheless, researchers' interest in vegetable oils as a potential replacement for diesel engine fuel persists due to the factors described above. Globally, extensive investigations have focused on the intriguing qualities of vegetable oils as alternative fuels. Various oils derived from woods and farms have emerged as promising candidates. As of 2022–2023, India has been importing petroleum products, incurring a substantial cost of $50 billion USD annually. The potential for substantial savings becomes evident as India could save USD 2.8 billion by transitioning just 5% of its oil fuel to biofuel. Notably, there has been a 6.57% decline in the demand for imported petroleum products.

Figure 1. Manilkara Zapota Tree, Fruit and Seeds

Figure 1 shows the Manilkara Zapota tree, fruit and collection of seeds. Manilkara Zapota Seed Oil is produced in this research and also conducting an investigation into its properties and characteristics.

2. Methodology

Producing biodiesel from Manilkara zapota (sapodilla) seeds involves a series of steps, primarily focused on extracting oil from the seeds and converting it into biodiesel through a process called transesterification. Here's a detailed and clear method:

Biodiesel Production from Manilkara zapota Seeds

2.1. Materials and equipment

Manilkara zapota seeds, Oil extractor (e.g., oil press), Hexane or another solvent for oil extraction, Reactor vessel with stirring mechanism, Methanol or ethanol, Sodium hydroxide (NaOH) or potassium hydroxide (KOH) catalyst, Water separator, Wash tanks, Biodiesel dryer, pH testing strips and Safety equipment (gloves, goggles, etc.)

Maintain equipment cleanliness.

Ensure ventilation during transesterification.

Adhere to safety guidelines.

This streamlined process emphasizes key stages in biodiesel production from Manilkara zapota seeds, promoting clarity and efficiency. Adjustments may be made based on specific conditions and safety considerations.

2.2. Esterification

The elevated free fatty acid (FFA) content in the oil is the primary factor influencing reaction times of 120, 150, and 180 minutes. Specifically, Manilkara Zapota was found to have an FFA of 5.91 mg KOH/g. typically, oils with higher FFA require a two-step acid-base transesterification process. According to various sources, this transesterification reaction usually necessitates a reaction period ranging from 120 to 180 minutes to effectively convert the oil into biodiesel. The procedure involves filling a round-bottom flask with 200 g of Manilkara Zapota seed oil, the methanol and H_2SO_4 mixture, and heating it to 50°C while maintaining continuous stirring. After 120 minutes, the mixture is transferred to a separating funnel and allowed to undergo phase separation for an additional hour. Following the separation of the lower layer (oil) from the upper layer (methanol), the oil is introduced into a rotary evaporator maintained at a temperature range of 65 to 70 degrees Celsius. This step aims to remove any excess methanol from the oil with a low free fatty acid (FFA) concentration. Subsequently, the low FFA content oil undergoes a purification process by passing through a separating funnel twice, employing distilled water in the purification steps.

2.3. Yeast for wine

Saccharomyces cerevisiae, a wine yeast obtained from a stock culture, was employed in the fermentation experiments. This yeast culture, previously utilized in the production of wine from various fruits and substrates (Hassan *et al.* 2019), was selected for this study. The process for gathering and processing one kilogram of mature Zapota fruits is outlined below:

The process began by using a knife to halve the Zapota fruits, facilitating the efficient removal of the pulp according to a practical guideline. Simultaneously, a hundred grams of healthy Vitisvinifera, var. Bangalore blue grapes were selected and rinsed under tap water to initiate the culture. Using a juicer, the grapes were crushed in a mixer-cum-grinder (TTK Prestige Limited, Bangalore, India) to extract the juice. Following this, the juice's volume was measured, and it was filtered through cotton cheesecloth. An equal amount of water was then added to the juice, along with an additional glass of water. The resulting mixture was brought to a boil on a hotplate for ten minutes and subsequently allowed to cool to room temperature, approximately 282°C. Prior to use, the grape juice underwent additional chilling. The Saccharomyces cerevisiae culture obtained from the stock was grown in a laminar airflow condition after being inoculated with Klenzoides from Mumbai. The fermentation process,

conducted in the presence of yeast, involved breaking down two molecules of glucose into four molecules of ethanol and four molecules of carbon dioxide. This fermentation occurred under atmospheric pressure and at the optimal temperature of 37°C.

2.4. Prepare the starter culture

It was first incubated for 24 hours at 30°C. Following the fermentation process, the wine was bottled and the sediment that had settled at the bottom of the bottle was separated from the top liquid using racking. Room temperature was used for the duration of this experiment (Mowlds and Kavanagh 2008)."Stacking the shelves" is the term for the procedure used to get the Zapota wine's total soluble solids (TSS) level down to two or three degrees Brix. In order to eliminate the sediment that had built at the bottom, this process was done three times, with a 20-day gap between each time. Prior to the last racking, bentonite (0.04%) was added to the mixture to help with clarifying and remove any leftover residues. For enhanced clarity post the final racking, SMS (Sulfite Metabisulfite Solution) was employed. Subsequently, the wine bottles underwent filling, corking, labeling, and sealing with beeswax, followed by the application of a preservative (100 g/ml) before bottling.

A series of analytical biochemistry tests were conducted to determine various properties of the Zapota must and wine. These included assessments for pH, ethanol content, ascorbic acid, lactic acid, β-carotene, total soluble solids, total soluble phenols, total sugar content, and titratable acidity (TA). The DPPH-scavenging activity of both the must and wine was also evaluated, with these attributes assessed in accordance with established practices.

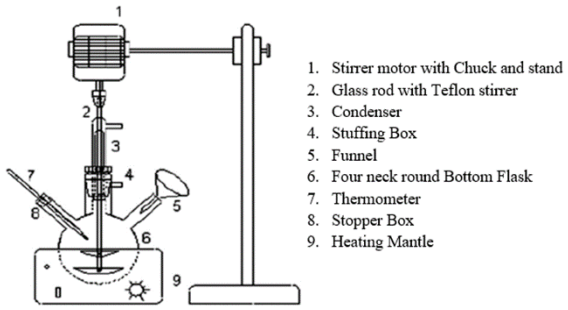

Figure 2. Experimental setup – Transesterification Process

Manilkara Zapota seeds were harvested and stored in a dry and cool environment until needed for biodiesel production. The biodiesel manufacturing process involved the use of pelletized potassium hydroxide (KOH) and pure analytical grade methanol. Only intact seeds were selected for use, and they were thoroughly dried to eliminate any remaining moisture (KarabasHulya 2013). Crude oil was then extracted from the dry seeds using mechanical screw pressing equipment. After separation and drying, the collected oil constituted approximately 25% of the crude seeds. Various qualities of the extracted oil, including density, viscosity, and flash point, were assessed using different tools in accordance with ASTM guidelines. The configuration of the batch-type tansesterification reactor utilized in the investigation is depicted in Figure 2.

2.5. Transesterification Process

Elevated levels of free fatty acid (FFA) in non-edible oils render them unsuitable for conventional transesterification procedures. It is recommended to employ a one-step transesterification procedure with a base catalyst if the oil's FFA level is less than 2.5%. However, if the FFA content exceeds 2.5%, a two-step transesterification procedure is generally a more suitable option.

In the case of Manilkara Zapota Seed Oil (MZSO), the determined level of Free Fatty Acid (FFA) was found to be 3.26% in this specific investigation. As this exceeds the 2.5% criterion, biodiesel production will be carried out using a single-step base catalyst transesterification process. The following parameters have been selected for the biodiesel production process in this anlysis.

In a batch reactor, 100 grams of Manilkara Zapota oil were introduced and heated to sixty degrees Celsius. To ensure thorough mixing, the stirrer operated consistently at 500 rpm. A precisely measured quantity of solid catalyst (KOH) was dissolved in a premeasured amount of methanol to form the methoxide solution. The methoxide solution was then gradually introduced into the reactor, heating the oil to 60°C. The commencement of the reaction was identified at the moment the methoxide was added (Sureshkumar *et al.* 2008).

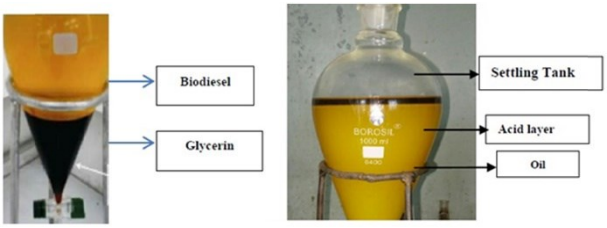

Figure 3. Biodiesel Glycerin Separating Procedure

The process flowchart illustrating the production of biodiesel from ManilkaraZapota oil is presented in Figure 4. To collect and recycle any evaporated methanol, a condenser was attached to one of the four necks of the reactor. Once the predetermined reaction period concluded, the reactor was removed from the heating mantle, and the reaction products were transferred to a 500 ml separating conical funnel. After allowing it to settle for a full day, the denser glycerol layer at the bottom of the funnel was removed using a drainage valve. The remaining crude biodiesel derived from ManilkaraZapota oil underwent a careful cleaning process at 40ºC using distilled water to eliminate contaminants, catalysts, and unreacted methanol. The biodiesel yield as a percentage was determined using the following formula:

The efficiency of synthesized Biodiesel: Y = (grams of methyl ester produced / grams of oil used in reaction) × 100

In Figure 3, images illustrating the biodiesel preparation process are presented. Furthermore, Figure 4 illustrates the procedural flow chart for the experimental synthesis of biodiesel from Manilkara Zapota Seed Oil, employing a two-step transesterification method.

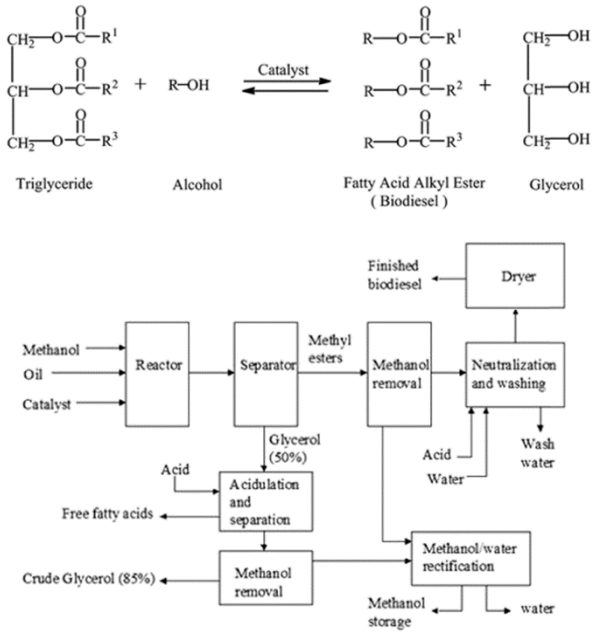

Figure 4. Process flow chart - Biodiesel Production from Manilkara Zapota Oil

2.6. Drying of biodiesel

Drying plays a pivotal role in the biodiesel production process to eradicate any remaining moisture or water content. The presence of excess moisture in biodiesel can lead to various issues such as microbial growth, compromised fuel quality, and an increased risk of corrosion in fuel systems and engines. Several conventional methods for dehydrating biodiesel are employed in this regard.

2.7. Heat and evaporation

To facilitate the evaporation of water content, this procedure involves gradually heating the biodiesel to a temperature slightly below its boiling point. Subsequently, the evaporated water and biodiesel are typically separated, often employing condensation techniques. Due to the sensitivity of biodiesel to elevated temperatures, it is essential to exercise caution to prevent overheating.

2.8. Desiccant dehumidification

This technique involves the utilization of desiccant materials, such as silica gel or molecular sieves, to extract moisture from biodiesel. Typically, a column or chamber filled with the desiccant material is employed to pass the biodiesel through. The desiccant gradually absorbs moisture, efficiently drying the biodiesel in the process.

2.9. Centrifugation

Centrifuges can be employed to separate water from biodiesel. The centrifugal force causes water to separate from the biodiesel, collecting at the bottom of the centrifuge chamber, from where it can be subsequently drained out.

2.10. Vacuum drying

Lowering the pressure inside a vacuum chamber and adding biodiesel is the process of vacuum drying. As a result, water will evaporate at a lower temperature and have a lower boiling point. After that, the water vapor in the chamber is evacuated, leaving the biodiesel dry.

2.11. Use of drying agents

Chemical drying agents, such as magnesium sulfate (Epsom salt) or calcium oxide (quicklime), can be introduced to biodiesel to absorb moisture. After allowing for a settling period, these agents are mixed with biodiesel and subsequently extracted along with the absorbed water. The choice of the drying process is influenced by factors such as the production scale, available equipment, and specific requirements for the biodiesel product. Ensuring proper drying is imperative to guarantee the quality and stability of biodiesel before it is deemed ready for use as a fuel.

There may be some leftover methanol and water in the ester layer once the purification procedure is finished, which needs to be eliminated. This is important since methanol has the ability to lower fuel's flash point and corrode fuel hoses. Water content is particularly problematic because it can raise the fuel's acidity and encourage the growth of biological organisms. In order to remedy this, 15 to 30 minutes of distillation at 100°C were spent on the ester layer. The water and methanol content of the biodiesel product were successfully eliminated by this distillation method. An acid-catalyzed transesterification process was followed by an alkaline-catalyzed transesterification process to produce the final biodiesel product.

After the purification and distillation processes were concluded, the biodiesel fuel was stored in preparation for subsequent analysis and utilization.

3. Results and discussion

3.1. Fermentation parameter

The two microbial enzymes employed in this investigation exhibited impressive efficacy in converting starch from fruit peels, yielding results comparable to those reported in numerous other studies. Earlier research has documented the saccharification of various agricultural residues using enzymes from diverse microorganisms. For instance, Karakastsanis and Liakopoulu-Kyriakides achieved a 96% starch conversion in corn by simultaneously employing amylase and glucoamylase. Dettori Campus *et al.*, utilizing amylases from Bacillus species, reported an 80% starch conversion in barley, corn, and rice. Following enzymatic saccharification, Sharma *et al.* achieved a maximum production of 63 g L^{-1} of reduced sugar and 0.426 g^{-1} of ethanol through fermentation in a blend of banana peels and kinnow waste.

In addition to enhancing fermentation efficiency and ethanol production from fruit hydrolysates, Hammond *et al.* demonstrated increased sugar recovery and ethanol production specifically from bananas. The biochemical composition of Zapota pulp is detailed in Table 1. Among the fruit pulps studied, the mixed fruit pulp sample exhibited the highest yield at 35.86%, followed by banana pulp at 28.45%, and mango pulp at 26.5%. Optimal yeast fermentation of the enzymatic hydrolysate of acid-

pretreated mixed fruit pulps was observed at a 48-hour incubation period, resulting in a peak ethanol production of 35.86% and a fermentation efficiency of 70.33%. Peel samples, when incubated for 42 hours, demonstrated the highest yields, with mango at 9.68% and banana at 13.84%. The ethanol yield observed in banana fermentation aligns with the findings of Sirkar *et al.*

Fermentation studies revealed that the ethanol yield from fruit pulp hydrolysates, obtained through both pretreatments (LHW and DAP) without enzymatic hydrolysis, was notably lower compared to hydrolysates obtained through regular saccharification—approximately 25% less. This result corresponds with a prior study by Hammond *et al.*, which reported a 13.4% reduction in ethanol output when ripe banana pulp underwent fermentation without enzymatic hydrolysis. In a study on fermentation employing flocculating yeast, Joshi *et al.* discovered that residual banana peels could sufficiently supply sugar for the process, establishing them as a economically viable source of ethanol.

Table 1. Biochemical composition of Zapota pulp

Sl. No	Parameters	Pulp
1	Ash	0.46±0.03(g/100g)
2	Total Sugar	34.18±2.26(g/100g)
3	Phenol	0.35±0.11(g/100g)
4	Ascorbic Acid	7.67±0.26(mg/100g)
5	Moisture	70.08±2.24(%)

These findings highlight that the ethanol fermentation process, utilizing yeast cells in coconut milk or pineapple juice, demonstrates biocatalytic efficiency comparable to or even exceeding that observed in commonly used materials like molasses or thick juice. This study investigated whether crude Manilkara Zapota oil could serve as a suitable feedstock for biodiesel synthesis by examining its physicochemical characteristics and fatty acid composition. A production procedure was selected based on its specific characteristics and fatty acid content. Oleic acid emerged as the predominant unsaturated fatty acid, constituting 64.64% of the total, followed by linoleic acid at 17.76%. Palmitic acid exhibited the highest concentration among saturated fatty acids. The Manilkara Zapota oil was found to have a total unsaturated fatty acid content of 84.23% and a saturated fatty acid content of 15.77% (Table 2).

Table 2. Sensory evaluation of the Zapota wine (n=32)

Sl. No	Attributes	Zapota Wine
1	Taste	8.2
2	After Taste	4.4
3	Aroma	5.7
4	Colour / Appearance	6.5
5	Flavour	8.3

Table 3 displays the main characteristics of Manilkara Zapota oil that were ascertained using ASTM standards, including density, viscosity, acid value, peroxide value, heating value, pour point, flash point, pH, and cetane number. The evaluation of Manilkara Zapota oil's eligibility as a feedstock for the production of biodiesel and its prospective performance as a biofuel is contingent upon these features.

3.2. Effect of Bio-Ethanol concentration

According to the findings, it seems that over time, the ethanol concentration initially increases before declining due to its early conversion into the intended products. Similarly, in the secondary conversion phase, the concentration of other components experiences a sudden rise while the percentage of ethanol decreases. These oscillating graphs depict the rate at which the substrate reacts in the presence of yeast to produce the intended product, ethanol.

Table 3. Properties of Manilkara Zapota Oil

Sl. No	Properties	Values
1	Boiling Point	162^{o}C
2	Specific Gravity	0.904
3	Kinematic Viscosity	64.75Cst.
4	Density at 15^{o}C	0.876Kg/m^{3}
5	Acid value	6.55 mg KOH/gm
6	pH	3.26
7	Percentage of oil content	24 to 32%
8	Free Fatty Acid	3.25 % of mass

A significant quantity of substrate is necessary in the initial phases of fermentation to initiate the reaction. However, the substrate concentration stabilizes over time. This occurs because a large amount of substrate (sugar) can participate in the reaction early on, given the abundance of accessible enzyme molecules with vacant active sites. Eventually, the substrate concentration reaches a steady state.

The results indicate that MZME, likely an enzyme or microbe used in the fermentation process, meets all EN14214 biodiesel standards in terms of characteristics. As illustrated in Table 4, MZME thus has the capacity to serve as a substitute for petro diesel. This suggests that the biofuel produced meets the necessary quality requirements for use as an alternative to diesel.

Table 4. Biodiesel Properties as per the EN14214 Biodiesel Standards

Sl. No	Property of Biodiesel	Values
1	Flash Point	173^{o}C
2	Pour Point	-6^{o}C
3	Ash content	0.58 % mass
4	Kinematic viscosity	4.48Mm^{2}/s
5	Acid value	0.156 Mg KOH/g
6	Cetane Number	51.5
7	Glycerol	0.168 %m/m
8	Carbon residue	0.158 %mass
9	Calorific value	37.124 Mj/kg

3.3. Signal-to-noise ratio (S/N ratio)

The S/N ratio is employed to estimate the deviation of performance variables from the intended outcome. To calibrate the disparity between the intended and experimental results, a loss function is recommended for use. The logarithmic functions of the estimated outcomes, as presented in Table 5, represent S/N ratios, which can be broadly classified into three types: smaller values are

better for minimization, larger values are better for maximization, and normal values are better for normalization. In this context, larger values were considered more favorable as they align with the desired optimum efficiency of the synthesized biodiesel. Figure 5 represents the mean S/N ratios of different performance variables at different phases. In this concept, mean S/N ratio aspect phase 1 as the optimum value in alcohol to oil ratio.

Table 5. Mean S/N ratios at different phases

Performance Variables	Phase 1	Phase 2	Phase 3
NaOH catalyst (wt%)	38.72	38.96	38.84
Experimental duration (Min)	38.82	38.80	38.92
Alcohol to oil ratio	39.46	38.85	38.27
Reaction Temperature (°C)	38.86	38.62	39.04

To measure the Signal-to-Noise Ratio (SNR) for each experiment, each of the nine set trials is conducted three times in order to discover the ideal combination of performance variables. By taking the S/N ratio into account, the optimal circumstances for each performance characteristic can be found, and the conversion of synthesized biodiesel may be completed with optimum efficiency. It is advised to use statistical Analysis of Variance (ANOVA) of the response to accomplish this goal. ANOVA is a popular method for looking at data correlations and is used to evaluate each performance variable's performance in detail. Finding the performance variable that has the biggest impact on the efficiency of the maximum conversion of synthesized MZME is the main goal of employing ANOVA.

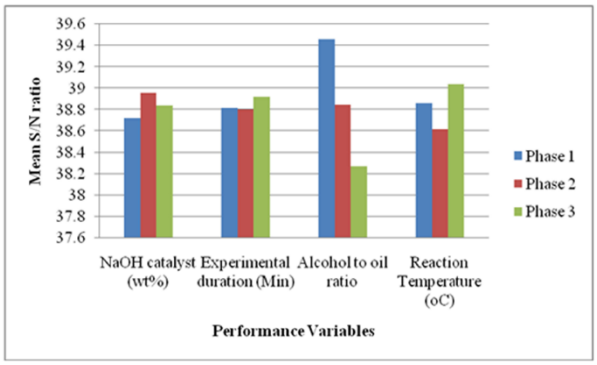

Figure 5. Mean S/N ratios of different performance variables

3.4. Estimation of the optimal performance condition

The efficiency of the synthesized Manilkara Zapota Methyl Ester (MZME) was determined through multiple sets of designed experiments, and the corresponding S/N ratios as well as the mean S/N ratio were compiled in Table 6.

Table 6. Efficiency of synthesized MZME and S/N ratio

Exp. No.	A	B	C	D	1st Trial	2nd Trial	3rd Trial	Mean efficiency	S/N ratio
1	6:1	0.5	120	40	94.89	93.55	93.76	94.07	39.46
2	6:1	1.0	150	50	88.14	92.78	94.86	91.93	39.26
3	6:1	1.5	180	60	94.41	93.14	93.42	93.66	39.57
4	9:1	0.5	120	40	87.92	91.14	91.12	90.06	39.11
5	9:1	1.0	150	50	88.41	85.42	81.28	85.04	38.58
6	9:1	1.5	180	60	82.86	90.02	90.41	87.76	38.85
7	12:1	0.5	120	40	78.38	85.44	82.17	82.00	38.27
8	12:1	1.0	150	50	76.80	78.16	78.13	77.70	37.90
9	12:1	1.5	180	60	88.82	85.31	84.87	86.33	38.62
Overall mean S/N ratio									38.85

3.5. Analysis of variance (ANOVA)

Based on their relative influence on the efficiency of synthesized MZME, the performance variables that significantly affect the reaction are identified and evaluated, as per the ANOVA (Vellaiyan and Amirthagadeswaran 2016). Table 7 displays the relative degrees of influence. Remarkably, the alcohol-to-oil ratio is found to be the most significant element, accounting for 84.34% of MZME's efficiency. About 11.46% and 3.25% of the total contribution come from the reaction temperature and catalyst weight, respectively. However, it is discovered that the experimental time, which has a 0.086% contribution to the process, has the least impact. The results obtained are contrasted with those of related studies (Singh *et al.* 2018, Muqeem et al. 2020).

3.6. Thermogravimetric analysis

Figure 6 displays the biomass's thermal profile for Manilkara Zapota Seeds, which was plotted against temperature or time vs weight loss. Manilkara Zapota Seeds biomass displayed multistage breakdown behavior in its thermal profile. Researchers Mishra *et al.* (2020) and Ceylan *et al.* (2014) have also reported on the similar thermal breakdown behavior of biomass (Mishra and Mohanty 2020, Ceylan and Topçu 2014). The first step, referred to as the drying stage or dehydration stage, was carried out at temperatures below 150°C in order to eliminate moisture and light volatile materials, or lower molecular weight molecules. The second stage, referred to as the active pyrolytic stage where maximum degradation occurred, ranged in temperature from 150°C to 500°C. Hemicellulose and cellulose broke down at this point, releasing the most heated volatiles.

During the second stage, a constant heat is applied to expedite the transformation of higher molecular weight chemicals into lower molecular weight compounds. Research has identified two primary pathways through which cellulose undergoes heat degradation. The first

pathway, occurring at a lower temperature (around 300°C), involves breaking stronger bonds into smaller ones, resulting in the production of CO_2 and CO gases. The second method entails the rapid fragmentation of cellulose into hot volatiles, which, at higher temperatures, condense into a liquid. Additionally, due to its heightened thermal resilience, lignin undergoes decomposition in the third step, typically at temperatures exceeding 500°C. Furthermore, the increased lignin content in biomass contributes to the enhanced production of biochar. The breakdown of lignin necessitated a higher temperature, attributed to its structural composition and the presence of hydroxyl phenolic functional groups. Moreover, it was noted that during thermal depolymerization, lignin generated an increased quantity of aromatic compounds characterized by short chains of organic molecules, along with the release of gaseous emissions such as CO and CH_4. Additionally, lignin played a crucial role in the thermochemical process, contributing to the production of various valuable compounds (Agrawal *et al.* 2014).

Table 7. Relative degree of influence

Performance Variable	% Concentration	Rank
Alcohol to oil ratio	84.34	1
Reaction Temperature	11.46	2
NaOH Catalyst	3.25	3
Experiment Duration	0.086	4

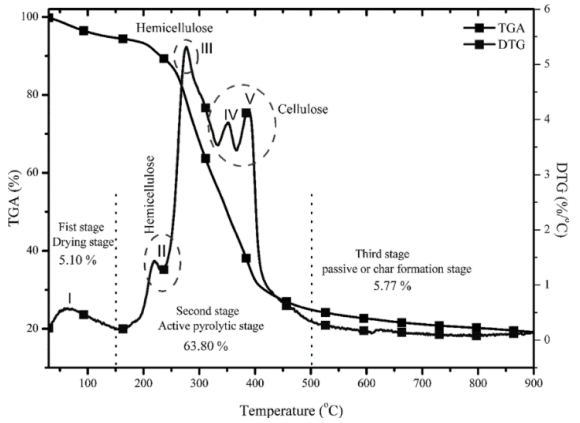

Figure 6. Thermal stability analysis of ManilkaraZapota Seeds biomass at 10°C min^{-1}.

4. Conclusions

The study observed that Manilkara Zapota fruit has better fuel-relevant properties for the production of bioethanol compared to other fruit wastes. Zapota fruit contains a higher percentage of sugar content, particularly in its pre-mature stage, making it a suitable source for bioethanol production. A functional wine was successfully produced from zapota fruit pulp and evaluated for its biochemical and sensory characteristics. This antioxidant rich wine has an alcohol content of 8.23% per volume. In South Asian countries like India, where zapota fruits are seasonally available during May through June and have a short shelf life of 8-10 days, utilizing these fruits for alcohol production helps preserve their value by creating value-added products like wine. This ensures that consumers can enjoy zapota based products throughout the year. This study also suggests that recycled agricultural waste and management processes can be employed to produce bioethanol from vegetable and fruit waste.Optimal bioethanol yield was achieved under specific conditions, including a pH of 4, a temperature of 32°C, and the use of 3g/L of yeast.

In this current investigation, synthesized biodiesel procured from Manilkara Zapota seed oil was analyzed. The synthesis, characterization, optimization of performance variables influencing the two-step transesterification process of MZME was described as follows, i.e., reaction temperature, alcohol-to-oil ratio, experimental duration and catalyst wt. % were the four influencing performance variables preferred for the Taguchi orthogonal array. The optimal conditions for the efficiency of maximum conversion of synthesized biodiesel from Manilkara Zapota Seed Oil are 40°C reaction temperature, 6:1 alcohol-to-oil ratio, 90 min experimental duration and 0.5 wt.% catalyst. The corresponding efficiency is 94.89%. & The relative degree of influence of each performance variable for the synthesized MZME is found as reaction temperature: 11.46%, alcohol-to-oil ratio: 84.34%; experimental duration: 0.086% and catalyst weight 3.25% & The Manilkara Zapota Methyl Ester (MZME) properties were matched and fulfilled with ASTM D 6751 and EN14214 standards. Finally, Manilkara Zapota Methyl Ester could be a better substitute for existing fossil fuels in an unmodified diesel engine.

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