

Albizzia julibrissin: a non-edible seed oil source for biodiesel production

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Abstract— We aimed to optimize different reaction parameters for oil extraction from *Albizzia julibrissin* (A.J.) seed. The best conditions included the ratio of methanol to oil (6:1M), the reaction time (60 min), the catalyst concentration (0.30wt %), and the temperature (65°C). The A.J. methyl ester (AJME/biodiesel) yield was 98%. Soxhlet extraction method provided the highest A.J. oil content ranging from 19 to 24% followed by 9.9% by mechanical extraction. Gas chromatography provided the basis for classifying fatty acid composition of the oil. The characterization of biodiesel products was carried out by FTIR, ¹H NMR and ¹³C NMR, and GCMS. The fuel characteristics of A.J. were determined according to the ASTM and EN test methods which confirmed it as a suitable alternative to petroleum diesel. In conclusion, *A. julibrissin* seed oil can be considered as a new raw material for biodiesel production.

Index Terms— *Albizzia julibrissin*, Non-edible oil, biofuels, transesterification, FTIR, NMR, GCMS, ICP-OES.

1 INTRODUCTION

The rapid growth in human population and industrialization has greatly augmented the energy needs [1, 2]. The energy safety and emissions of greenhouse gases have aroused global attention and thus paved the way for research and technological development in domains of renewable energy by replacing petroleum fuels with biofuels [3, 4]. In accordance with the American Biodiesel Standard Specification (ASTM 6751), biodiesel is a fuel consisting of monoalkyl esters of long-chain fatty acids obtained from vegetable oils or animal fats. Biodiesel raw materials are divided into three categories: vegetable oil (edible or non-edible oil), animal fat, and edible waste oil. Among liquid biofuels, biodiesel derived from vegetable oil is recognized and has a market share as diesel in the United States and Europe [5]. Like many countries, China does not have sufficient reserves of fossil resources, which means relying on oil imports to meet the transportation sector's demand for gasoline and diesel. The partial supply of biodiesel will help reduce this dependence [6]. Therefore, challenge remains to find an appropriate raw material, its extraction and characterization for biodiesel production.

The synthesis and use of vegetable oil, animal fat, and

second-hand frying oil containing triglycerides have been focused as alternate source of biodiesel production keeping in preview their utility advantages. Generally, the reaction is catalyzed by chemicals involving as enzymes or bronsted acids or bases [7]. The biodiesel has lower exhaust emissions (CO_x, SO_x) and particulate matter and proved to be better biodegradable, and possess inherent lubricity, renewability, higher flash point, and availability from domestic sources [8, 9]. Moreover, higher flashpoint of biodiesel is superior to diesel thereby warranting its profound transportation and storage [10]. However, the availability and manufacturing cost, primarily the raw are the main obstacles for producing and commercializing biodiesel from vegetable oils [11]. In the year 2008, the cost values of both biodiesel and petroleum diesel were noticed closer; raw materials alone accounted for 60–85% of the total cost incurred. There are also legitimate concerns about the likely impact of consuming vegetable oil as fuel on food prices [12]. The International Energy Agency (IEA) estimates that by 2030, the share of biofuels in global road transportation will be about 7%, compared with only 1% in 2004 [13].

The selection of a suitable raw material for biodiesel production involves technical and economic prerequisites. The

production of biodiesel from vegetable oils [14] principally involves the process of converting one form of ester to another type of ester employing a transesterification reaction. This method is accounted to be an ideal for converting vegetable oils into various forms of esters, and its low viscosity is comparable to that of mineral diesel [15]. The base-catalyzed transesterification reaction is judged as faster and can be completed in a few min. Fatty acid methyl ester (FAME) has great potential as a diesel substitute called biodiesel [16]. Although, vegetable oil is a reliable source of biofuels [17, 18], it however, cannot be applied directly in diesel engines due to its chemical structure. Moreover, the extensive production of biodiesel from edible oil may result into unevenness in global food supply and demand. Additionally, deforestation and wildlife destruction are other possible implications of using edible oil as raw materials. Therefore, inedible vegetable oil, as raw material, has sought considerable scientific attention for biodiesel production [19, 20].

In terms of biodiesel production, non-edible oil raw materials have multiple benefits over edible oil. Inedible oils contain toxic ingredients, making them unsuitable for human consumption [21]. Non-edible oils that cannot be used for human nutrition their plants can grow in poor soil, so they should be used more and more. Non-edible oil plants can usually be planted on land that is inappropriate for human crops; are cheaper and have no potential effect on the food market [20]. Therefore, growing non-edible plants for the oil production are not bound to the specific conditions. Therefore, barren and fallow land, road/field boundaries, degraded forests, and irrigation canals could possibly be employed for production of non-edible oil crops. Thus, in low rural areas, the production of biodiesel from non-edible oils can be adopted as a major attribute in economic improvement programs [22]. One of the plants, *Albizia julibrissin* (A.J.), which contains non-edible seeds, can be evaluated for biodiesel production. *A. julibrissin* is a deciduous tree, wide and 12 m (40 ft) high, but usually 3-6 m (10-20 ft), smooth bark, gray. *A. julibrissin* fruit comprises of lentil pods with enlarged seeds. Each pod is 8-18 cm long and 1.5-2.5 cm wide and can be observed from June to February. Each pod usually grows 5-10 elliptical seeds, about 1.25 in length. Some authors assert that mimosa produces many seeds[23]. The mimosa can produce 8,000 seeds per year. The average mimosa seed per pound is 11,000 to 11,500 [24, 25]. Wind, gravity, and water are major contributory factors for dispersal of seeds and pods. *A. julibrissin* is native to Asia and found in Turkey, Azerbaijan, China, Japan, Taiwan, and other temperate regions, Bhutan in Asia, India, Nepal, Pakistan, Myanmar, Japan and other tropical areas [26].

Keeping this scenario in pretext, we selected wild *A. julibrissin* (A.J.), for the first time, as a potential source of biodiesel production. The present study used a variety of analytical techniques, including FT-IR, NMR (¹H and ¹³C) and GC-MS, ICP-OES, and E.A., to determine the compo-

sition of different types of fatty acids after the transesterification reaction, characterize and confirm the reaction. Using KOH as a catalyst, crude oil and methanol are subjected to a transesterification reaction to produce biodiesel from A.J. seeds. The properties of A.J. seed oil biodiesel produced by transesterification are within the range of ASTM and EN standards.

2 MATERIALS AND METHODS

2.1 A. julibrissin Seeds and Chemicals

Common *A. julibrissin* seeds can be procured from the local market. First, the seeds were cleaned manually to remove dust, dirt, and other foreign bodies. They were washed with distilled water, afterwards dried in the sunlight first and later at 50°C in the oven for 48 h, and then crushed them in an electric grinder. All analytical reagent grade chemicals were purchased from local suppliers, and methanol (> 99% purity), sulfuric acid (purity 95%) and KOH were used in the form of particles.

2.2 Sample Preparation

In a heavy-duty pulverizer (China XANTAOPAI XTP-10000A), *A. julibrissin* seeds were gently pulverized to cut their outer shells. The ground seeds were categorized in accordance with the standard series of Taylor sieves (Bertel, ASTM), and the fractions held on the 28 mesh sieve were used for the experiment. The plastic bag was used for packing of the material and it was kept in the refrigerator until the experimental use.

2.3. Oil Extraction and Quantification

A. julibrissin seeds (10 g) were added to the Soxhlet extractor. 400 ml of petroleum ether was used for filling the extractor and heated to reflux at 80°C for 8 h through a water bath. Subsequently, the extract was shifted to a rotary evaporator for removing the extraction solvent under lower pressure and nitrogen flow. After collection, the amount of oil extracted was determined gravimetrically as shown in Table. 1. The following equation was used for the relative oil content for gravimetric analysis:

$$\% \text{ oil contents} = \frac{\text{Weight of oil obtained (g)}}{\text{Weight of sample used (g)}} \times 100$$

The percentage of oil was used to evaluate the oil content in the seed considering the biomass. The oil was stored at 4°C until further analysis.

TABLE 1 FFAs and oil contents of extracted *A. julibrissin* seed oil.

Solvent	FFAs content (wt. %)	Oil content (wt. %)
Petroleum ether	0.9	24
<i>n</i> -hexane	1.0	23.3
Acetone	1.6	18
Dichloromethane	2.3	15.9
Ethyl acetate	1.8	19.5

2.4 Transesterification

The vegetable oil was weighed (100 g) and poured into a 500 ml three-necked flask. The oil was then heated to 60°C with a heater. The methanol and catalyst were weighed and added to the oil reactor. The oil, methanol, and catalyst were mixed with magnetic stirrer. The reaction was performed until reaching the expected reaction time. Subsequently, the reaction was terminated by cooling the reactor to room temperature, and the catalyst was instantly split from the product mixture through a suction bottle. The mixture was put in a separatory funnel and left for overnight to assure and allow phase separation to form three layers. The methyl ester and glycerol phases are entirely separated. The upper, middle and lower layers are methyl ester, glycerin, and catalyst, respectively. The glycerin phase (bottom phase) was removed and left it in a separate container. The trace catalyst contained in the biodiesel was separated by centrifugation, and the surplus methanol present in the biodiesel was distilled at 70°C to obtain biodiesel. Finally, based on the weight of the oil, the methyl ester (biodiesel) was dried by addition of 25% by weight of Na₂SO₄ (Fisher Scientific). The methodology was followed as reported previously [27] with slight modifications. As shown in formula (2), it represents the yield of biodiesel obtained. Fig. 1 illustrates the transesterification reaction.

$$\text{Yield of methyl ester} = \frac{\text{Weight of methyl ester produced (g)}}{\text{Weight of oil taken for reaction (g)}} \times 100$$

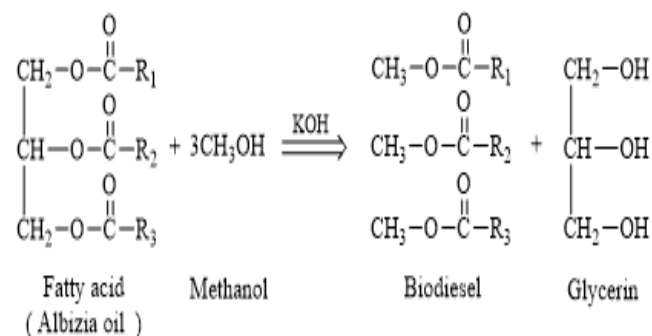


Fig. 1. Transesterification of *A. julibrissin* seed oil.

2.5 Biodiesel Purification

The separated biodiesel volume was more purified by heating (50°C) and washing with demineralized water [28]. About 300 mL of water was sprayed on the upper surface of the sample for washing each sample and then water was separated by gravity settling. After water removal, the biodiesel was heated for 1 h to remove remaining any water or methanol residues from the end product before analysis.

2.6. Physicochemical properties of biodiesel

The standard test methods comprising ASTM D6751, EN 14214, and AOCs were used for evaluating the major physicochemical properties of biodiesel. The density, kinematic viscosity, flashpoint, cold filter blockage temperature, acidity, refractive index, water, oxidative stability, and acid value were accounted for comparison [29-31].

2.7. Analytical Characterization of biodiesel

The fatty acid composition of *A. julibrissin* oil was evaluated by gas chromatography GC-MS (QP2010SE, Shimadzu, Japan) which was equipped with a flame ionization detector (FID) and capillary column PEG-20M (30m x 0.32mm x 1um film thickness). Helium served as the carrier gas, while the temperature of the injector port and detector port was maintained at 270°C and 280°C, respectively. The detailed conditions of GCMS included: the flow rate of helium (1.2 mL/min); the spectral ratio (40:1); the inlet temperature (220°C); the injection volume (1 uL); the oven temperature was maintained at 100°C for 1 minute, and then the speed was increased from 100°C to 210°C; the detector temperature was 210°C and then held at 210°C for 20 min; the ion source temperature was 200°C; the ionization mode used under 70 eV electron impact; the mass range was 35–500 m/z. The identification of FAME was based on comparing its mass fragmentation spectrum with the mass fragmentation spectrum stored in the mass spectrometry library NIST14 provided by the GC-MS system software and further confirmed its identity by comparing the data with known standards.

NMR (¹H and ¹³C) analysis of biodiesel was conducted by a Bruker Avance III 400NMR Spectrometer (Germany). The spectra for ¹H and ¹³C were acquired at 400 MHz in 12.58 min, respectively. The pulse duration, recycle delay, and scans for ¹H spectrum were 30°, 1.0 sec and 8, respectively; whereas same parameters for ¹³C spectrum were 30°, 1.89 sec and 160, respectively. Deuterated chloroform (CDCl₃) was used as a solvent.

The infrared spectrum of *A. julibrissin* biodiesel was measured using an FTIR spectrophotometer, and the spectrum was recorded on Bruker vertex 70 FT-IR spectrometer (Germany). The measurement of FTIR spectrum was conducted within the range of 400-4000 cm⁻¹ at 4 cm⁻¹ resolution, and MestreNova software was used to analyze the spectrum.

2.8 Elemental Analysis

The existence of metals in AJSO FAME was analyzed by ICP-

OES spectrometer (German Spectro-blue) and elemental analyzer (German Vario EL CUBE). The steps are described in S3 (Support Information).

3. RESULTS AND DISCUSSION

The quality of biodiesel can be evaluated by physical and chemical methods, such as viscosity, density, C.N., flashpoint, saponification value, and iodine value. Advanced analytical techniques, including G.C., NMR, and FTIR, have also been widely used to assess the quality of biodiesel. *A. julibrissin* plant with flowers and seeds is shown (Fig. 2).

To determine the effect of catalyst types on the production yield of *A. julibrissin* oil methyl esters (AJOMEs). Six different experiments using KOH, NaOH, CH₃ONa, CH₃OK, CaO, and ZrO₂ at concentration of 2.0-4.0% (w/w) were tried. In all experiments, variables such as methanol/oil molar ratio (6:1), agitation intensity (700 rpm), and reaction temperature (65 °C) were kept constant. The optimum yield of AJOMEs was obtained with KOH catalyst (Table 2) and Fig. S1 (Supplementary Material).



Fig. 2. *A. julibrissin* plant photographs.

Table 2 Catalysts effect on FAMEs conversion yield.

Catalyst	Catalyst Conc.	FAMEs %	Glycerin %	Soap %
KOH	0.20	81	14	5
	0.25	86	9	5
	0.30	94	5	1
	0.35	91	6.5	2.5
NaOH	0.25	83	13	4
	0.30	93.5	4.5	2
	0.35	93	5	2
CaO	0.25	87	9	4
	0.30	92	5	3
	0.35	91.5	7	1.5
CH ₃ ONa	0.25	88	8	4
	0.30	91.5	6.5	2
	0.35	90	7	3
CH ₃ OK	0.25	81	13	6
	0.30	91	7	2
	0.35	88	6	6
ZrO ₂	0.25	85	10	5
	0.30	90	6	4
	0.35	88	7	5

3.1. The oil content of the *A. julibrissin*

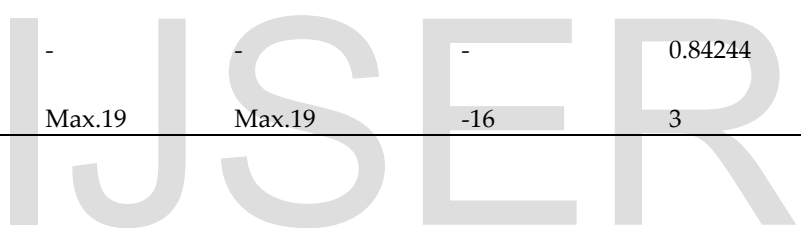
The mechanical extraction of oil from the *A. julibrissin* seeds gave a 9.9 w/w% yield. The Soxhlet extractor with petroleum ether gave a yield of 19-24% (Table 1). This highlights that solvent/chemical extraction methods are used to obtain maximum oil yield. Although oil content is a vital factor to identify oil-rich species for industrial usage, other significant parameters to consider are the reproductive cycle, seed biomass and productivity, seed pre-treatment, and extraction using suitable solvents. The economic significant of raw material relies on the certain prerequisites including the short reproductive cycle, production of large number of seeds, oil-rich seeds with medium biomass which have been sustained by *A. julibrissin*.

3.2. Fuel Properties of *A. Julibrissin* Biodiesel

To assess the quality of biodiesel produced from *A. julibrissin* seed oil, its physical and chemical properties were evaluated and compared with ASTM, EN, and petroleum diesel standards (Table 3).

Table 3 Physiochemical characterizations of AJOMEs and their comparison with standards (ASTM, EN) and petrodiesel.

Studied parameters	EN 14214	ASTM D6751	Petro-diesel	Experimental result
Density @ 15 °C (g/cm ³)	0.86–0.90	0.86–0.90	0.8091	0.84244
Kinematic viscosity@ 40 °C (mm ² /S)	3.5–5.0	1.9–6.0	1.3–4.1	3.75
Flashpoint (°C)	Min. 120.0	Min. 130	60–80	160
Fire point (°C)	-	-	-	190
Acid value (mg KOH/g)	Max. 0.50	Max. 0.5	-	1.2
Saponification value (mg KOH/g)	-	-	-	180.4
Iodine value (g I ₂ /100 mg)	Max. 120	Max. 120	-	118.5
Cloud point (°C)	-3 to 12	-3 to 12	-15 to 5	9
Pour point (°C)	-15 to 16	-5 to 5	-2.0	-12
Cetane number	Min. 51	Min. 47	49.7	58
Oxidation stability (110 °C, h)	Min. 6	Min. 3	25.8	4.71
Ash content	-	-	-	0.003
Specific gravity	-	-	-	0.84244
Cold filter plug point (°C)	Max.19	Max.19	-16	3



3.3 Optimization of *A. julibrissin* FAMES

We investigated different parameters of the transesterification process to obtain maximum biodiesel yield, such as methanol/oil molar ratio, catalyst concentration, agitation intensity, reaction time, and reaction temperature. The detailed optimization process is shown in Fig. 3-7, and Table S2 (Supporting Materials).

3.3.1 Effect of Methanol to Oil Molar Ratio

Molar ratio of alcohol to triglyceride is a vital factor which affects the ester yield. Methanol addition to crude oil causes large branched-chain molecules of vegetable oil to splinter into smaller linear methyl ester oils [32]. A considerable quantity of methanol is required for optimizing the reaction conditions to complete the reaction in addition to base catalysts including potassium hydroxide, sodium hydroxide, potassium methoxide, and sodium methoxide. The relationship between the catalyst to methanol/oil molar ratio and the ester yield is depicted in Fig. 3. Our findings specify the critical influence on the transesterification reaction procedure. We found that with 6:1 molar ratio of methanol to oil, the maximum yield of AJOMEs (95%) was obtained using a catalyst (0.30 g) KOH. Excess methanol (7:1) with caustic or methoxide catalyst contribute as an emulsifier and can further amplify the glycerol solubility during ester phase, renders separation more complex [33-35]. At the molar ratio of 7:1, we obtained the maximum biodiesel yield (86%). Our results further demonstrate that extra use of methanol had no significant effect on the biodiesel yield. The separation of ester and glycerin is very intricate step (Fig. 3). Similarly, low free fatty acids frequently use a 6:1 molar ratio to attain maximal methyl ester yields up to 98% (w/w) from vegetable oil fuels [36]. To get maximum conversion, it is recommended that the molar ratio of base-catalyzed transesterification be 6:1 [37]. The molar ratio does not affect the acid, peroxide, saponification, and iodine value of the methyl ester [38]. The molar ratio depends on the type of catalyst used. The application range of the molar ratio of methanol to oil is 4:1, 5:1, 6:1, and 7:1 [39]. Nevertheless, potassium hydroxide as a basic catalyst has been reported in other studies due to its cost effectiveness and rapid production [40, 41]. However, excessive application of alcohol can offer operational problems related to downstream processes and make product recovery difficult.

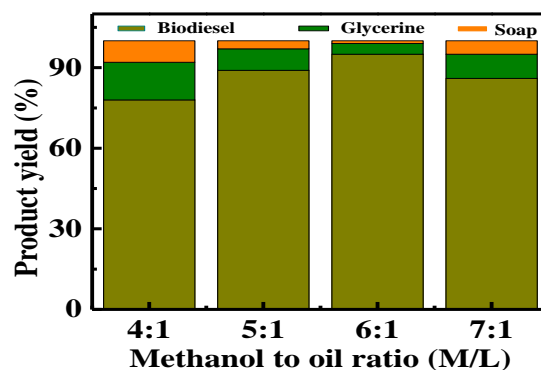


Fig. 3. Effect of molar ratio on biodiesel yield.

3.3.2 Effect of reaction temperature

The effect of reaction temperature and catalyst concentration on the ester yield of *A. julibrissin* is illustrated in Fig. 4. The highest ester yield (88%) was attained at 65°C using KOH catalyst (0.30g). Lower temperatures reduced the ester yield of the transesterification reaction. In addition, before alkaline hydrolysis, the reaction temperature in the alkaline catalyst was higher than 65°C, forming soap and glycerides. The reaction temperature has a profound effect on the biodiesel processing and output. A higher reaction temperature is generally favoured because it can minimize the viscosity of the oil and accomplish faster reaction rate in a shorter span of time. However, when the reaction temperature rises above the optimal level, biodiesel products will be reduced due to the higher reaction temperature and these will further accelerate the saponification of triglycerides [40, 42]. In order to check leakage owing to vaporization, the reaction temperature is kept lower as compared to the boiling point of the alcohol. The optimal temperature range is 60 to 75°C; depending on the oil used, higher temperatures and prolong time will burn alcohol and decrease the yield of methyl ester [40, 43, 44].

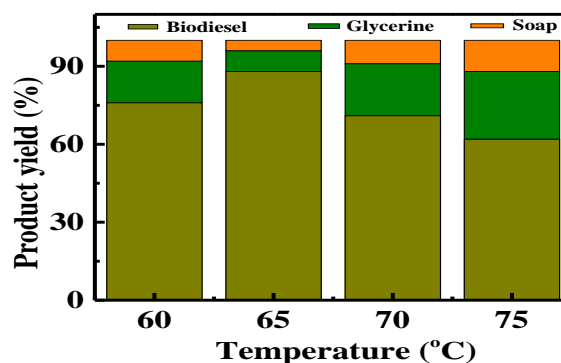


Fig. 4. Effect of reaction temperature on biodiesel

yield.

3.3.3 Effect of Reaction Time on Biodiesel Yield

In this study, a catalyst (KOH) with an acid value of less than 2 mg KOH/g was used for the primary catalyzed transesterification reaction. After that, the transesterification process of AJSO was carried out in various time periods of 40 to 100 min. The reaction time and catalyst type ester yield products are illustrated in Fig. 5. The methyl ester yield was observed in a steady phase within 80 min of reaction time. KOH turned out as the superior catalyst and the yield of AJSO reached 98% of the ester yield; no positive impact on FAMEs yield was observed by increasing the reaction time. To evaluate the effect on the reaction temperature, methanol decomposition of vegetable oils was carried out at an alcohol boiling point of about 60-65°C [44-46]. Studies have shown that the conversion of fatty acid esters augments with longer reaction time. The reaction gets slower due to the mixing and dispersal of alcohol in the oil. In a short time, the reaction occurs faster. Generally, the yield reaches a highest value within a reaction time of less than 80 min and remains relatively constant as the reaction time further increases [47, 48]. Moreover, due to the reverse reaction of the transesterification reaction, excessive reaction time will result into a decrease in the ester yield, leading to the loss of the ester and formation of more fatty acid soaps [41, 49].

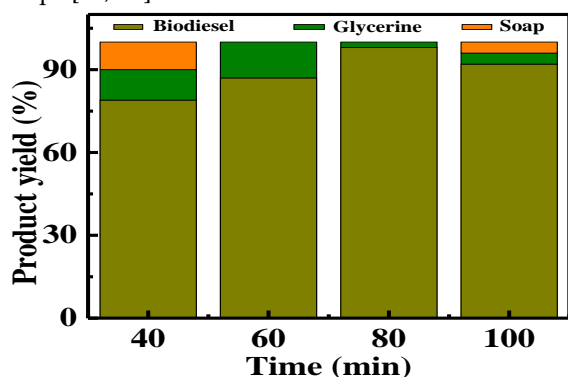


Fig. 5. Effect of reaction time on biodiesel yield.

3.3.4 Effect of the Catalyst Concentration

The study used a catalyst concentration ranging from 0.20, 0.25, 0.30, and 0.35g, respectively. We observed the effect of the quantity of catalyst in the transesterification procedure, with a molar ratio of 6:1, at 65°C, 80 min, and constant 700 rpm. By 0.30g weight of catalyst (KOH), the ester

yield exceeded 93 %. Fig. 6 shows the relationship between the different amounts and the catalyst concentration on the ester yield. The results show that the KOH catalyst has a higher ester yield for higher free fatty acid oils and unsaturated chains. The pre-treatment and esterification processes are carried out to decrease the sodium soap formed and amplify the ester yield because almost no emulsifier is formed when the upper methyl ester phase is washed with KOH catalyst. By using (0.30g) KOH catalyst and the best product (93%), the highest yield of ester biodiesel was produced. The results highlight the contribution of the catalyst to produce an improved ester yield in the production of ester yield by KOH. The results further indicate that with the increase in catalyst concentration, the yield does not increase linearly.

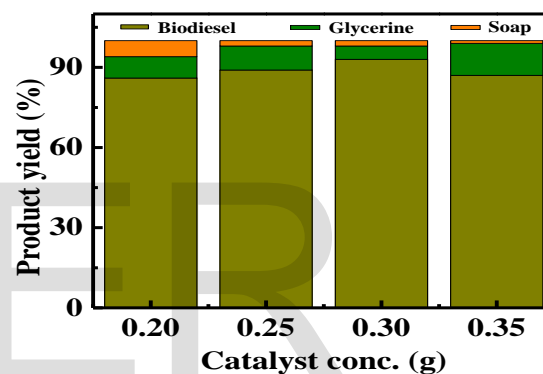


Fig. 6. Effect of catalyst concentration on biodiesel yield.

3.3.5. Effect of stirring intensity on biodiesel yield

During the transesterification reaction; the stirring intensity had affected the output of AJSOB, as shown in Fig. 7. We determined the direct correlation between agitation rate and AJSOB production because any controlled elevation in agitation rate may increase biodiesel production. We noticed that a stirring intensity of 700 rpm is the best range for a higher conversion rate (95%) of *A. julibrissin* oil to FAMEs. This is consistent with previous reports [50, 51]. The authors concluded that increasing the stirring speed will promote the homogenization of the reactants, thereby increasing the yield of the ester. Stirring and mixing are essential for the transesterification reaction because the grease is not miscible with potassium hydroxide in methanol. Due to the slow diffusion difference between the phase results, the reaction can be controlled by diffusion. Stirring was rendered after mixing of two phases

and initiation of the reaction. Ma, Clements, and Hanna (1998) reported the effect of mixing on the transesterification of tallow [52]. In case of no mixing, no reaction was observed. When NaOH-MeOH was added to the melted beef tallow in the reactor, the stirring speed was insignificant. This indicates that the stirring speed exceeds the mixing threshold requirement. In the current work of *A. julibrissin* (Fig. 7), four different stirring rates have been studied, such as 500, 600, and 700, and 800 rpm. The highest output was obtained at 700 rpm, and the lowest result was obtained at 500 rpm. Therefore, stirring has a direct effect on the yield of FAME.

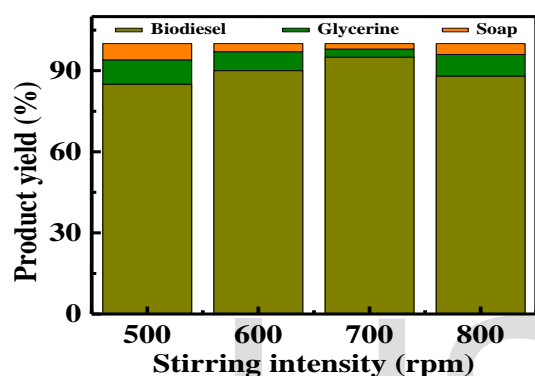


Fig. 7. Effect of stirring intensity on biodiesel yield.

3.4. FTIR spectroscopy analysis of biodiesel

FTIR of AJMEs is given in Table S3 (supporting information) and Fig. 8. This spectrum represented the strong absorption peaks at 2854 cm^{-1} and 2926 cm^{-1} which are associated with the existence of C-H stretching vibration of the alkane group. Due to the C-H bending vibration, strong absorption at 1463 cm^{-1} were expressed. The single bonds characterize the saturated functional groups. The strong absorption peak at 1743 cm^{-1} is attributed to the C=O stretching frequency (called ester), which is composed of unsaturated functional groups. In addition, due to the C-O stretching vibration of the ester, strong bands were expressed at 1015 cm^{-1} , 1120 cm^{-1} , 1196 cm^{-1} , and 1245 cm^{-1} , respectively.

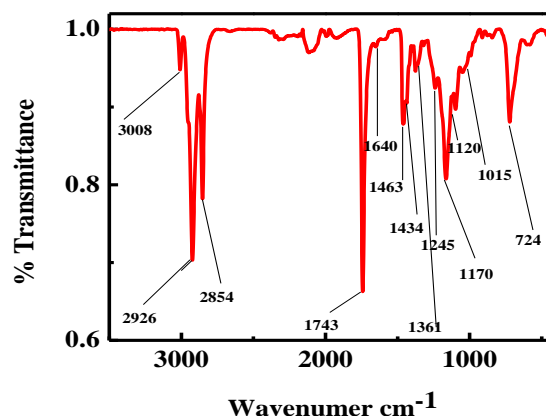


Fig. 8. FTIR analysis of AJOMEs.

3.5. NMR spectroscopy analysis of biodiesel

3.5.1. ^1H NMR spectrum

The ^1H NMR spectrum of biodiesel is illustrated in Fig. 9 and Table S4 (Supplementary Information). In ^1H NMR spectroscopy, signals between 0.88 and 0.90 ppm (m) were allocated to terminal methyl protons ($\text{C}-\text{CH}_3$), and signals between 1.25 and 1.31 ppm (m) were attributed to methylene group from aliphatic chain ($-(\text{CH}_2)_n-$), and the signal at 1.58-1.65 ppm (m) indicates the proton of β -methylene ester ($\text{CH}_2-\text{C}-\text{CO}_2\text{Me}$) connected to the nearby allylic group ($-\text{CH}_2-\text{C}=\text{C}-$) occurs at 2.00-2.07 ppm (m), and the signal in between 2.27 and 2.31 ppm (t) due to the presence of methylene protons ($-\text{CH}_2-\text{COOMe}$) near the carbonyl group. The methylene proton allylic groups ($-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$) appear at 2.75-2.78 ppm (t) and 3.65 ppm (s). The single peak of this peak represents the CH_3 group ($\text{CH}_3\text{COO}-\text{CH}$) connected to the ester bond. The proton from the glycerol moiety ($-\text{CH}=\text{CH}-$) appears at 5.29-5.41 ppm (m), and the characteristic singlet signal appears at 7.28 ppm (s), indicating the peak of the CDCl_3 solvent [53].

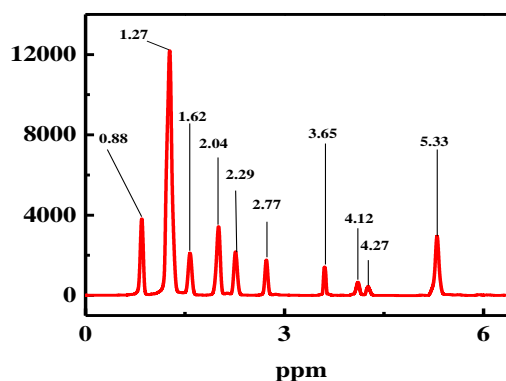


Fig.9. ^1H NMR analysis of AJOMEs.

3.5.2 ^{13}C NMR Spectrum

In the present study, Fig. 10 and Table S5 (Supplementary Information) depict the ^{13}C NMR spectrum of biodiesel obtained from *A. julibrissin*. The signal at 174.25 ppm indicates the presence of ester carbonyl carbon (-COO-), and the peak between 127.98 and 130.23 ppm indicates the occurrence of unsaturated bonds in the methyl ester. The peak at 51.32 ppm indicates the occurrence of ester (C-O) methoxy carbon. The representation of a peak between 29.02 and 29.07 ppm is due to the long carbon chain methylene carbons of the fatty acid methyl ester, while the peak exists at 14.1 ppm indicates the terminal carbon of methyl group [53].

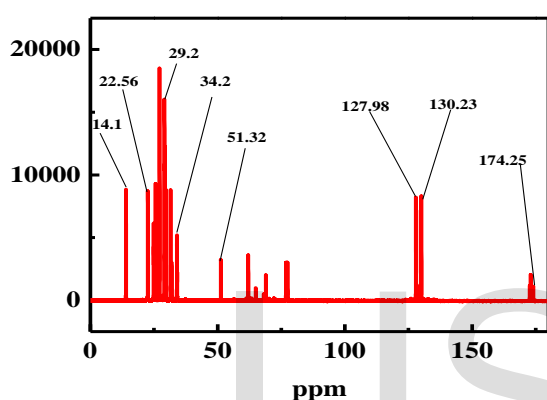


Fig.10. ^{13}C NMR analysis of AJOMEs.

3.6. Fatty acid composition analysis by GCMS

Generally, triglycerides contain three key categories of fatty acids comprising saturated, monounsaturated, and polyunsaturated. The composition of fatty acids has a considerable affect on the quality of biodiesel. As the fats and oils contain higher amount of saturated fat compounds therefore the biodiesel fuel from these materials expresses low-temperature fluidity [54]; on the hand, highly unsaturated compounds possess acceptable cold fluidity but are more prone to oxidation[55]. Table 4 shows the fatty acid profile of AJSO. Fig. 11 depicts the combined GC-MS chromatogram, where the x-axis and y-axis represent retention time and relative abundance, respectively. To determine the composition, the sample was injected into a gas chromatograph, and the molecules in the sample were separated through a chromatographic column. After the eluting of molecules from the GC column, they were carried into the MS and ionized by electron impact. Using AMDIS software, we compared the spectra of unknown compounds with the spectra of known compounds stored in the NIST

2014 library. The main fatty acids present in AJSOB were palmitic acid (10.59%), stearic acid (2.12%), oleic acid (12.03%), and linoleic acid (55.28%). As the *A. julibrissin* biodiesel (AJBD) contains the huge amount of unsaturated compounds, it may have acceptable cold flow characteristics and be more easily oxidized.

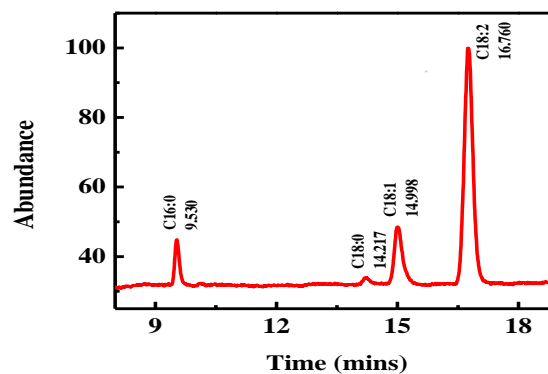
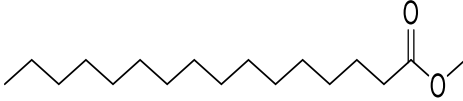
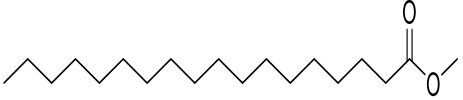




Fig.11. GCMS analysis of AJOMEs.

Table 4 GCMS analysis (fatty acid compositions) of AJOMEs.

S/ No	Fatty acids	Reten- tion time	Number of carbons and double bonds	Fatty acid (weight per- centage)	Chemical name	Chemical structure	Molec- ular weight
1	Palmitic acid	9.545	C16:0	10.59812	Hexadecanoic acid, methyl ester		270
2	Stearic acid	14.248	C18:0	2.12	Octadecanoic acid		298
3	Oleic acid	15.042	C18:1	12.0304	9-Octadecenoic acid (Z) -, methyl Ester		296
4	Linoleic acid	16.797	C18:2	55.28952	9, 12- Octadecadienoic acid (Z, Z)-, methyl ester		294

3.7. Elemental analysis

The existence of metal elements in biodiesel is nasty because these elements can lead to many impediments, for instance stimulation of biodiesel deprivation, engine degradation, operable difficulties, and environmental impurities [56]. K, Na, Mg, Ca, and other elements in biodiesel will be directed to the injector, stimulating drainage, piston and piston ring wear, locomotive deposits, and passing through the filter plug [57]. As shown in Fig. 12 and Table S6 (Support Information), the element concentration in AJOB matches the element concentration of petroleum diesel. The results confirm that the element concentration in A.J. seed oil biodiesel is reasonably lower than that of high-speed diesel (HSD). The concentration of Na and K in AJOB is deficient, so the biodiesel will be usable and environmentally friendly.

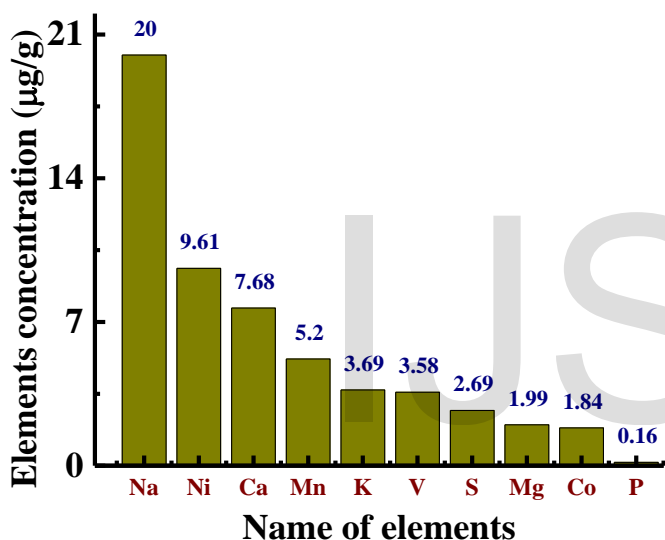


Fig. 12. AJMEs ICP-OES analysis.

The observed concentrations of C, H, N, and O are given in Table 5 and Fig. S2 (Supporting Information). The oxygen content in biodiesel is very high; the reason for the high oxygen content and lower calorific value of pyrolysis liquid products than fossil fuels. The existence of oxygen can lessen the ignition delay time, improve the combustion environment, and make the fuel burn completely, thereby reducing the emissions of C.O., PM, and other exhaust gases. In this study, the oxygen content of BD100 was 9.86% (Table 5). Similarly, the oxygen content in the most common biodiesel has been reported about 10%[58, 59]. The high hydrogen content (11.25%) in biodiesel is attractive as a fuel[60]. High H/C means that the hydrogen molecules in the fuel are higher. Since hydrogen has the superior burning rate among all fuels, it will corrode gases or liquids. The elevated hydrogen ratio contained in the fuel mixture depicts fast and clean burning of the fuel. Because hydrogen has a higher heating value than carbon, the heating value

generally elevates with the higher the ratio of H to carbon atoms.

4. CONCLUSIONS

The study investigated the potential of non-edible and wild *A. julibrissin* seed oil as a new source of biodiesel production and characterization. Our results indicate that wild *A. julibrissin* oil can potentially be used as a raw material for biodiesel production, mainly due to its high oil content and biodiesel recovery rate. The basic catalyzed transesterification reaction was found as a promising research area for the largest biodiesel production. For high-yield biodiesel, the optimal combination of various parameters was a molar ratio of methanol to the oil of 6:1, a potassium hydroxide catalyst of 0.30%, a reaction temperature of 65°C, and a reaction time of 60 min. The biodiesel obtained is considered clean fuel because of its enormously low sulfur content and high cetane number (58), which can improve ignition quality. The fuel characteristics of wild AJ petroleum biodiesel (AJOB) are within the specifications of ASTM and EN. The study recommends that if the engine performance test results are satisfactory, AJOB can be used as a potential fuel.

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AUTHORS' CONTRIBUTIONS

I.U.K. carried out the experiment and wrote the first draft of the manuscript. J.C. and Z.Y. supervised the research and revised the manuscript. Chen Hang helped in seed collection and revised the manuscript. SAHS edited, formatted the manuscript and worked on bibliography.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ETHICAL STATEMENT

This is to certify that study has been undertaken by keeping in preview and adherence to research ethics.

SUPPORTING DATA

The supporting data is provided.

Table 5 *A. julibrissin* FAMES EA (element analyzer) study and their comparison with vegetable seed oil, kernel, and shells.

Ultimate analysis	AJ-BD/ Experimental results	pistachio shell[61]	Peach Stones[62]	Apricot kernel shells[63]	Cherry Stones[64]	Mahua Seed[65]
C%	76.86	42.41	45.92	47.33	52.48	61.24
H%	11.25	5.64	6.09	6.37	7.58	8.40
N%	2.03	0.070	0.580	0.370	4.54	4.12
O%	9.86	51.87	47.38	45.93	35.30	25.50
HHV (MJ/kg)	23.39	22.21	24.07	24.29	24.11	25.30

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