





# Optimization, Transesterification and Analytical Study of *Rhus typhina* Non-Edible Seed Oil as Biodiesel Production <sup>+</sup>

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**Abstract:** Production of biodiesel from non-edible oils is one of the effective methods to reduce production costs and alleviate the obstacle of traditional raw material supply. *Rhus typhina L.* (RT) is a promising non-edible plant because it grows fast and has abundant seeds. But previously reported oil content of RT was only 9.7% and 12%. Further research into improving the biodiesel production of RT seed oil is urgently needed. Here we obtained the biodiesel production of RT with a maximum oil content of 22% with a low free fatty acid content of 1.0%. The fatty acid methyl ester (FAMEs) of the RT seed oil was produced by a standard optimized protocol use KOH as a catalyst with the highest yield of 93.4% (w/w). The quality and purity of RT FAMEs, as well as the physio-chemical characterizations of the biodiesel products, were investigated and compared with the international standard of ASTM D6751 and EN 14214. The values of fuel properties are comparable with mineral diesel and environmentally friendly. Overall, the proposed RT seed oil could be a potential source of raw materials for producing high-quality biodiesel after the optimization and transesterification.

**Keywords:** *Rhus typhina* biodiesel; non-edible oil; base-catalyzed transesterification; Physico-chemical properties

## 1. Introduction

The speedy reduction of traditional diesel oil resources, as well as the environmental problems epitomized by global warming, has led to a worldwide demand for renewable energy [1]. In response to the crisis, alternative fuels such as biodiesel, bioethanol, biomass, biogas, and synthetic fuels are being developed worldwide [2]. Among them, biodiesel is paid much attention because it is renewable, with reduced emissions of  $CO_x$ ,  $SO_x$ , and particulate matter into the atmosphere compared to diesel, with a higher flash point, ensuring greater safety in transportation and storage [3]. It is estimated that biodiesel/bioethanol can replace about 10% of diesel consumption in Europe and 5% of total fuel demand in Southeast Asia [3,4]. Generally, biodiesel, also named fatty acid methyl ester (FAME), was derived from triglycerides, which are produced from vegetable oils and animal fats with a variety of lipid parameters [5]. Direct use of triglycerides (crude oil) is severely restricted due to its high viscosity and poor ignition quality [4,6]. Therefore, a variety of treatment methods are developed to overcome the viscosity and combustibility of vegetable oils [4]. The strategies including dilution, micro emulsification, pyrolysis, and transesterification for biodiesel fuel production. Among them, the base-catalyzed transesterification reaction can converts triglycerides to methyl ester in shorter reaction times with high efficiency [4,6,7]. Therefore, this method has been widely used in the production of biodiesel fuel.

Currently, 95% of commercial biodiesel is made through different edible vegetable oil sources such as palm, sunflower, rapeseed, and soybean oil [7,8]. But the industrial expense, especially raw feedstock, is the major obstacle in the moneymaking of edible oil biodiesel [9]. Due to the competition with food raw materials and fuel dispute, the continuous and large-scale production of biodiesel from edible oil is severely challenged [10]. A promising alternative is to shift the focus to the use of non-edible oil resources and/or waste cooking oil to produce biodiesel [11–13]. Many non-edible oil crops have been used for biodiesel production, evaluation, and commercialization such as Jatropha curcas and Karanja [12,14,15], waste tallow [16], *Silybum marianum L*. [17], wild *Brassica Juncea L*. [18], and prominently, algae [19]. To further promote it, there is an urgent need to shift the focus to planting non-edible oil plants on poor land, which are often unsuitable for human crops, cost-effective, and have no impact on biodiesel production in the food market [8].

*R. typhina* (sumac staghorn) is one of the non-edible plant's sources, is a member of family Anacardiaceae. Sumac trees are distributed in the subtropical and temperate regions of the world, especially in Africa and North America. It is native to America that can reach a height of 30–35 feet deciduous shrub to a small tree. The *R. typhina* seed has a good economic potential as feedstock for biodiesel. The reasons are as follows: RT plant growth quickly and produces a huge amount of seeds. Three to four hundreds of *R. typhina* trees can be planted per hectare. Approximately one-hectare area will produce 78,000 kg seeds, the productivity of oil is about 17,160 kg per hectare. Some studies have been carried out on the extraction of *R. typhina* (RT) seed oil. Ruan et al., 2012 [20] reported that based on acetone/water extract 9:1 v/v, the yield of RT seed oil was 9% w/w, and Zhang et al., 2018 [21] improved the seed oil content to 12%. However, the studies warrant further research into improving the biodiesel production of RT seed oil.

Here we produced biodiesel from the RT seed oil (RTSO) and optimized their potential for energy production, such as methanol to oil molar ratio, catalyst concentration, reaction temperature, reaction time, and stirring intensity. The techniques including FTIR (Fourier Transform Infra-Red Spectroscopy), NMR (<sup>1</sup>H and <sup>13</sup>C) (Nuclear Magnetic Resonance Spectroscopy), GC-MS (Gas Chromatography and Mass Spectroscopy) were used to confirm the ester conversion and fatty acid composition. The physic-chemical properties of the FAME were investigated and compared with petrodiesel and standards of ASTM D6751 and EN14214 i.e., density, kinematic viscosity, cloud point, pour point, flash point, fire point, Cetane number, oxidation stability, saponification value, iodine value, acid value, specific gravity, ash content, and cold filter plugging point. Elements analysis by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and elemental analyzer (EA) show that biodiesel is environmentally friendly. Overall, a prospective inedible raw material for biodiesel making was discovered and scrutinized.

## 2. Materials and Methods

#### 2.1. Source Collection and Preparation of Seeds for Oil Extraction

The *R. typhina* seeds were collected from the wild/wasteland in Tianjin Binhai New Area, China. The seeds were separated by hand, washed with distilled water, and then dried in the sunlight first for 48 h and then at 60 °C oven-dried (to remove the moisture) until the seeds reached an unchanged weight. A grinder (XIANTAOPAI XTP-10000A, Zhejiang, China) was used to grind the seeds. The ground seeds were oven-dried at 60 °C for 1 h and 30 min to finish the moisture and then extracted to obtain the oil. Photographs of plants and seeds processing are shown in Figures S1 and S2 (Supplementary Materials).

#### 2.2. Oil Extraction

*R. typhina* seeds were shelled, dried, and pulverized with a grinder (Xiantaopai XTP-10000A, Zhejiang, China). The oil was extracted using soxhlet [22] and mechanical oil extractor (Fangtai Shibayoufang FL-S2017 China and Fangtai Shibayoufang J508, Guangdong, China) (Table S1,

Supplementary Materials). The oil extraction was occurring in a soxhlet instrument at 90 °C for 7 h by various kinds of solvent were used, including petroleum ether, acetone, dichloromethane, and ethyl acetate. The particles and impurities were removed by filter paper (pore size 30–50  $\mu$ m), and the crude RT oil was recovered at 80 °C under reduced pressure by using a rotary evaporator (Tokyo Rikakikai Co. Ltd. N-1210B, Tokyo Japan). The obtained RT oil was stored and dried over anhydrous sodium sulfate before use.

#### 2.3. Biodiesel Production Procedure

By applying 50 g of RT crude oil, 10 mL of methanol at molar ratio 5:1, and 2.3 w/w% of KOH catalyst, the RT seed oil biodiesel was prepared. The transesterification reaction is shown in Figure 1. At 65 °C for 1 h under reflux, the reaction was carried out, and 600 rpm was the agitation rate [23]. By using 99.99% excess of methanol [24], the process was performed, such as methanol to oil ratio was 5:1, KOH ratio was 2.9 w/w%. The reflux condenser was furnished with a reactor to cool down the methanol as it comes out from the reaction process mixture. The reaction mixture was then put in a separating funnel and keep for a one-night stay that the biodiesel, soap, and glycerol can become separate from each other by layers making, the bottom phase is glycerol, and the upper phase is biodiesel. After reaction completion, crude glycerine can separate through gravity, and KOH can be detached with 3-4 time washing with hot distilled water. The complete removal of the catalyst can be check through a phenolphthalein indicator. The leftover unreacted methanol and moisture were finished through vacuum distillation and continue the process till when it confirms that there is no unreacted methanol and moisture in the final product, and the FAMEs weight loss is constant. The crude FAMEs were further washed 3–4 times with heated deionized water, centrifuging and dry with a vacuum dryer to confirm its purity. The phase separation was usually starting very quickly and can be observed in start 10 min, but the biodiesel phase was cloudy, it shows incomplete detachment. The result shows that the cloudy biodiesel layers can become clean and clear, giving them enough time for settling, and complete impartiality needs up to 20 h. In fact, during the resolution process, the transesterification process was still in progress. Hence, to give them a long time for separation is more beneficial, the separation and conversion yields. All analytical reagent grade chemicals were used.



Figure 1. Transesterification reaction.

## 2.4. FTIR Study

The Fourier Transform Infrared (FT-IR) bands spectroscopy were verified by a (Bruker Vertex 70 FT-IR spectrometer, Germany) with a resolution of 1 cm<sup>-1</sup>, scanning 15 times, and using Nujol mull as a dispersive medium in the range of 400–4000 cm<sup>-1</sup>, to originate the obtained biodiesel describe through various functional groups characterization.

#### 2.5. NMR Study

The RT FAMEs NMR spectrum was obtained by (Bruker Avance III400 NMR Spectrometer, Karlsruhe, Germany) at 400 MHz (<sup>1</sup>H-NMR) or 100 MHz (<sup>13</sup>C-NMR). Deuterated chloroform was used as a solvent, and tetramethylsilane was used as the internal standard. The RT biodiesel <sup>1</sup>H NMR

(300 MHz) spectrum was documented with a cycle delay of 1.0 s, and several scans of 8 times, with a pulse duration of 30°. A carbon <sup>13</sup>C NMR (75 MHz) spectrum was recorded with a pulse duration of 30° and a cycle delay of 1.89 s, and a scan of 160 times [25,26].

#### 2.6. GCMS Study

The obtained RT FAMEs result was checked and tested by GCMS (QP2010SE, Shimadzu, Tokyo, Japan). GC-MS conditions are listed in Table 1. Detail procedure is present in Figure S2 (Supplementary Materials).

Parameter.	Descriptions			
	QP2010SE, Shimadzu			
	PEG-20M			
Column	Length: 30 m			
	Internal diameter: 0.32 mm			
	Film thickness: 1 um			
Injector temperature	220 °C			
Detector temperature (EI 250)	210 °C			
Carrier gas	Helium, flow rate = $1.2 \text{ mL min}^{-1}$			
Injection	V = 1 uL			
Split	Flow rate = $40:1$			
-	Initial temperature = $100 \degree C$			
Temperature program	Rate of progression = $10 \degree C \min^{-1}$ .			
	Final temperature = $210 ^{\circ}$ C, 20 min.			

Table 1. Gas chromatograp	h conditions.
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#### 2.7. ICP-OES and EA Study of RT Biodiesel for Elemental Analysis

The presence of metals in the RTSO FAMEs was studied using Inductively Coupled Plasma Spectrometer (Spectro-blue, Kleve, Germany) and Elemental Analyser (Vario EL CUBE, Hanau, Germany). The procedure is presented in Figure S3 (Supplementary Materials).

#### 3. Results and Discussion

*Rhus typhina* plants and their pre-treated seeds are shown in Figure 2. Several varieties of solvent were used to extract oil from the RT seed powder, including petroleum ether, acetone, dichloromethane, and ethyl acetate. Seed collection at the right time, proper pre-treatment of seeds (put in sunlight first for 48 h and then at 60 °C oven-dried for 1.5 h to remove the moisture), use of petroleum ether as the extraction solvent and environmental conditions have a significant role in obtaining the high oil contents. The results are summarised in Table 2. Since the lower percentage of FFAs in the oil is the significant point to process direct transesterification of RT seed oil, this data indicates that petroleum ether is the best solvent for extracting oil from RT seeds because it provides high yields of oil and less FFAs. Besides, petroleum ether is less expensive than other solvents and can be recycled from the process. The oil and FFAs content were related to the polarity of the solvent extracted, in the order of petroleum ether < ethyl acetate < acetone < dichloromethane. Less polar solvents can extract larger amounts of non-polar oils (triglycerides) and less amount highly polar FAA. By soxhlet extraction [22], petroleum ether gives the highest extracted oil content of 22 wt. % (FFAs = 1.0 wt. %), which is significantly higher than the reported seed oil contents (Ruan et al. [20] reported that based on acetone/water extract 9:1 v/v, the yield of RT seed oil was 9.7% w/w, ZHANG et al. [21] reported that based on AOAC method the seed oil content was 12 w/w%). Ethyl acetate gives low oil content of 17.8 wt. % (FFAs = 1.3 wt. %), while more polar solvents like acetone and dichloromethane give somewhat lower oil content of 16–14.2 wt. % (FFAs = 1.5–1.8 wt. %). Based on these extraction results using petroleum ether and the ability to produce RT seeds oil, the RT seed could be an efficient source for biodiesel production as an alternative energy.



(a)

(b)

Figure 2. (a) Optical photographs of RT mature plant and (b) pre-treated seeds.

Solvent	FFAs Content (wt. %)	Oil Content (wt. %)	
Petroleum ether	1.0	22	
Acetone	1.5	16	
Dichloromethane	1.8	14.2	
Ethyl acetate	1.3	17.8	

Table 2. FFAs and oil contents of extracted RT seed oil.

#### 3.1. Optimizations of Reaction Variables on Conversion Yield

We have studied five different parameters through which we have applied different conditions, and each parameter was tested in three conditions to check that what is the most proper and suitable condition for obtaining the optimum result. The five parameters are as follow and discuss one by one, including methanol/oil ratio, catalyst concentration, temperature, stirring intensity, and time. The detail experimental results were presented in Table S2.

## 3.1.1. Effect of Methanol to Oil Molar Ratio on Yield

Methanol to oil molar ratio is one of the main factors affecting the ester conversion during the transesterification process. The transesterification of RT oil was evaluated and investigated at different methanol to oil range. The added amount of methanol in the reaction was varied from 4:1, 5:1, 6:1, and 7:1 (as shown in Figure 3). While temperature ( $65 \,^{\circ}$ C), stirring intensity (700 rpm), and reaction time (60 min) was kept constant. The best proportion of methanol and oil was 6:1, in which the conversion yield was 91.66%. But at proportion 7:1, the conversion percentage was as low as to 70%. It was observed that when the proportion of methanol to oil rises from 4:1–6:1, the product yield was increased. Whereas in an additional increasing proportion of methanol to oil, a reduction in biodiesel production was observed. Excessive methanol can make it difficult to separate glycerol from the biodiesel phase. The higher methanol ratio restricts the separation of glycerol due to high solubility. Thus, in the presence of residual glycerol in the biodiesel layer allows the equilibrium reaction to start the backward reaction and again met with the methyl ester to form a monoglyceride [27]. The results show that excessive use of methanol has no substantial effect on biodiesel production; in fact, the

separation of ester and glycerol is complicated. Therefore, a molar ratio of 6:1 is the optimum ratio of RT methyl ester yield.



Figure 3. The effect of methanol to oil molar ratio on RTOB yield.

3.1.2. Effect of Reaction Temperature on FAMEs Yield

Temperature is a very important factor in the optimization process and has a great impact on product yield. In this work, constant parameters such as KOH concentration (2.9 wt. %), methanol to oil proportion (6:1) reaction time (60 min), and stirring speed (700 rpm) were used. A graph of biodiesel conversion (%) versus temperatures such as 60, 65, and 70 °C is shown in Figure 4. The product yield was increased from 60 °C to 65 °C; it is clear from the reaction process that the temperature had a progressive effect on the transesterification of the RT oil to biodiesel. Though, when the reaction temperature raised from 65 °C to 70 °C, we noticed a slight decrease in the reaction yield, which possibly due to the accelerated saponification reaction at a high temperature. When the transesterification reaction temperature is higher than the boiling point of the alcohol, the methanol cannot evaporate, and a huge number of the bubble will produce, which make fast the reaction and increase the saponification of glycerides [28]. Therefore, 65 °C is the optimum temperature for the reaction.



Figure 4. Effect of temperature on RTOB yield.

3.1.3. Effect of the Catalyst Concentration on FAMEs Yield

The process of variables that can affect transesterification, in addition to saponification and hydrolysis are catalyst concentration. In this reaction, methanol to oil molar ratio (6:1), temperature (65 °C), reaction time (60 min), stirring intensity (700 rpm) was kept constant, respectively. The catalyst (KOH) range of 2.0, 2.4, 2.9, and 3.8 wt. % has applied for the methanol decomposition in the RT seed oil. Figure 5 demonstrates the production of FAMEs at various KOH range. A small amount of catalyst 2.0 and 2.4 wt. % was not enough for the completion of the reaction. The highest conversion percentage rate was achieved (91.66%) at 2.9 wt. % of the catalyst. An additional increase in the catalyst concentration will negatively affect the conversion ratio. When the KOH amount was increased from 2.9 to 3.8 w/w%, the production of the methyl ester decreases, resulting in an increase in the viscosity of the reactants, and a decrease in the yield, a large amount of soap was observed. This observation has been explained by an increase in saponification due to the excess of the basic catalyst rather than the esterification of the triglyceride [29]. By increasing the saponification process reaction, the extra amount of catalyst will improve and help in soap formation so that the FAMEs solubility chances will increase in the glycerol, FAMEs, and glycerol mixture will appear [30].



Figure 5. The effect of catalyst concentration on RTOB yield.

## 3.1.4. Effect of Agitation Speed on FAMEs Yield

Stirring is a key factor in the optimizations because it affects biodiesel production in both ways. In the KOH and methanol mixture, the fat and oil are not soluble, so in the transesterification process, the mixing is very important. The decomposition of methanol was carried out at various agitation speeds, i.e., 500, 600, 700, and 800 rpm. While the methanol to oil molar ratio (6:1), KOH concentration (2.9 wt.%), reaction temperature (65 °C), and reaction time (60 min) was kept constant. The FAMEs production at diverse mixing speed is shown in Figure 6. The reaction was witnessed to be incomplete at 500 rpm, and the mixing rate was not significant for methanol decomposition. The yields of the methyl esters at 600 and 700 rpm were 90% and 92.5%, respectively. As clarified by the results, a direct correlation was elucidated between the agitation rate and the RTOME yield, i.e., as the agitation rate increased, an increase in yield was observed. Therefore, a mixing rate of 700 rpm provides the best conversion rate (92.5%) of RT oil to RTOME. This is consistent with the previous studies [31–33], which concluded that increasing the agitation rate promotes the homogenization of the reactants, resulting in higher methyl ester yields. Once the two phases are mixed, and the reaction is started, stirring is no longer needed. It is clear from the results that a further stirring rate (800 rpm) has no significant effect on RTOMEs yield, but the result was the same as 700 rpm (95.5%).



Figure 6. The effect of stirring intensity on RTOB yield.

The methyl ester transformation percentage rises with the reaction time. Also, the influence of reaction time on methyl ester alteration is shown in Figure 7. The influence of biodiesel yield was studied at different time rates of 40, 60, 80, and 100 min. Though methanol to oil molar ratio (6:1), reaction temperature (65 °C), catalyst concentration (2.9 wt.%), and stirring intensity (700 rpm) was kept constant. The current results presented that biodiesel conversion reached at the optimum rate in 80 min. Experimental results show that biodiesel production increase as the reaction time increases. The reaction time has no significant effect after 80 min, and the methyl ester production starts decreasing, it is indicating that the FAMEs reached the distribution equilibrium. As the duration increases, further, the reaction process will begin to react backward, and the ester yield will certainly begin to decrease by 88% at 100 min. This is consistent with the literature data showing that longer reaction times will result in lower yields due to the reverse reaction of transesterification (hydrolysis), which tends to produce more fatty acid to forming soaps [34,35]. According to the experimental results, the reaction time has an important role in the increase and decrease of biodiesel conversion. The minimum yield was obtained at 40 min, and the optimum yield occurred at 80 min.

<sup>3.1.5.</sup> Influence of Reaction Time on FAMEs Yield



Figure 7. The effect of reaction time on RTOB yield.

## 3.2. Physio-Chemical Characterization of R. typhina Methyl Ester

The physicochemical properties of the *Rhus typhina* seed oil biodiesel (RTSOBD) were evaluated and examined according to ASTM and EN standards and matched well except kinematic viscosity. The kinematic viscosity (6.3 mm<sup>2</sup>/s) is slightly higher than ASTM D6751 (1.9–6.0 mm<sup>2</sup>/s). Kinematic viscosity needs further modification to improve its value under the limits. Accordingly, the kinematic viscosity of the BD produced from the RT seed oil is slightly high than those of conventional biodiesels, and thus must be blended with other less viscosities diesel fuels (biodiesels or petrodiesel fuel) to lessen its properties to the acceptable limits. Also, the results obtained were matched with reported data from the same source of biodiesel mentioned by other researchers and compared with petrodiesel. The results are shown in Table 3.

Studied Parameters	EN 14214	ASTM D6751	Petro-Diesel	RT Experimental Result	ZHANG et al., 2018 [21]	Ruan et al., 2012 [20]
Oil content%	-	-	-	20–22%	12%	9.7%
Density @ 15 °C (g/cm <sup>3</sup> )	0.86-0.90	0.86-0.90	0.81-0.87	0.879	0.879	-
Kinematic viscosity @ 40 °C (mm <sup>2</sup> /S)	3.5–5.0	1.9–6.0	1.3–4.1	6.3	6.87	-
Flash point, (°C)	Min 120.0	Min 130	≥52	168	165	-
Free fatty acid (%)	Max 0.50	<1	-	1.0	-	-
Saponification value (mg KOH/g)	-	-	-	175.6	-	-
Iodine value (g $I_2/100$ mg)	Max. 120	Max. 120	-	85	-	-
Cloud point (°C)	-	-	-15-5	7	-	-
Pour point (°C)	-	-	-2.0	-11	-	-
Fire point (°C)	-	-	-	198	-	-
Oxidation stability (110 °C, h)	Min 6	Min. 3	25.8	18.3	-	-
Ash content (g/100 g)	-	-	-	0.3	-	-
Specific gravity	-	-	-	0.855	-	-
Cold filter plugging point (CFPP, °C)	Max.19	Max.19	-16	14	-	-
Sulphur content ( $w/w\%$ )	< 0.01	< 0.01	-	0.01	-	-
Phosphorous content (mg/kg)	<10	<10	-	4	-	-
Carbon residue ( $w/w\%$ )	-	-	-	0.19	-	-

**Table 3.** Physiochemical characterizations of *R. typhina* seed oil biodiesel.

## 3.3. NMR Spectroscopy

# 3.3.1. <sup>1</sup>H NMR Analysis

The biodiesel yield during the transesterification process was determined by using <sup>1</sup>H NMR techniques, and the progression of its characteristic spectra was depicted. When <sup>1</sup>H NMR was used, the produce methyl ester was used to monitor the product by the protons of the methylene group adjacent to the ester moiety in the TAG and the protons of the alcohol moiety. Though by <sup>1</sup>H NMR spectroscopy technique, the RT seed oil biodiesel was characterized, the spectra of which are shown in Figure 8 and Table S3 (Supplementary Materials). The distinguishing proton methyl ester peaks were detected to be a singlet at 3.663 and triplet of the  $\alpha$ -CH<sub>2</sub> proton at 2.308 ppm correspondingly. The existence of methyl ester in biodiesel was approved by these two distinctive peaks. At 0.895 ppm, the peaks were detected to be terminal methyl proton; at 1.319 ppm, the associated methylene protons of the carbon chain were detected, which shows a strong confirmation. A strong signal was detected for the  $\beta$ -carbonyl methylene proton at 1.623 ppm and olefin hydrogen at 5.342 ppm, respectively. According to the literature review, several studies specified that this diverse standardization curve established on <sup>1</sup>H NMR spectroscopy was used to enumerate the reaction yield throughout biodiesel production by transesterification of a mixture of methanol and fatty acids [36–39]. In this regard, the <sup>1</sup>H NMR spectrum of RT oil biodiesel can be used to quantify the conversion of triglycerides to methyl esters during transesterification, as evidenced by previous studies [40,41]. In this study of <sup>1</sup>H NMR spectra, the divers and distinctive analyses were existing in the *Rhus typhina* seed oil biodiesel methyl ester spectrum. The appropriate indications selected for incorporation are the methoxy group of the methyl ester at 3.66 ppm and the methyl ester group of the  $\alpha$ -carbonyl methylene proton at 2.308 ppm. Thus, <sup>1</sup>H NMR spectroscopy showed a strong conversion of TAG to *Rhus typhina* methyl ester.



Figure 8. <sup>1</sup>H NMR spectrum shows RT FAMEs.

# 3.3.2. <sup>13</sup>C NMR Analysis

Ester carbonyl important peaks (-COO-) 174.24 and (C-O) 51.32 ppm associated with RT biodiesel were depicted by using <sup>13</sup>C NMR spectroscopy. The Rhus typhina biodiesel <sup>13</sup>C NMR spectra are shown in Figure 9, Table S4 (Supplementary Materials). The unsaturated methyl ester peaks were detected at 130.21 and 127.89 ppm, respectively. The other associated peaks at 14.1 ppm and 22.5–34.1 ppm,

correspondingly represent the terminal carbon of the methyl group and the methylene carbon of the long-chain fatty acid ester. The present experimental work spectra were closely matched with the literature work [42] and thus approve our verdicts.



Figure 9. <sup>13</sup>C NMR spectrum of RT FAMEs.

## 3.4. FT-IR Spectroscopy Analysis

To identify the various stretching and bending vibration corresponding functional groups and bands of the pure RT seed oil biodiesel sample, the FTIR spectra mid-infrared regions were used. The FT-IR carbonyl group position is highly sensitive to both molecular structure and substituent effects [43]. The two strong characteristic ester absorption bands which are derived from a carbonyl group are vC=O at 1750–1730 cm<sup>-1</sup> and C-O at 1300–1000 cm<sup>-1</sup>. At 2980–2950, 2950–2850, and 3050–3000 cm<sup>-1</sup>, respectively, the stretching vibrations of CH<sub>3</sub>, CH<sub>2</sub>, and CH appear, and at 1475–1350, 1350–1150, and 723 ( $\rho$ CH<sub>2</sub>) cm<sup>-1</sup> respectively the bending vibrations of these groups appear [44]. As presented in Figure 10 and Table S5 (Supplementary Materials), at 1743 cm<sup>-1</sup>, the Rhus typhina seed oil biodiesel methoxy ester carbonyl group has appeared. The peak  $3464 \text{ cm}^{-1}$  indicated an overtone of the ester function [45]. The C-O stretching vibration exhibited two asymmetric coupling vibrations at 1170 cm due to O-C-C and 1016 cm<sup>-1</sup> due to vC-C(=O)-O. The stretching bands of methylene appeared at 2854 cm<sup>-1</sup>, and methane appeared at 3007, 2925 correspondingly. The bending vibration appeared at 1435, and 1361  $cm^{-1}$  belong to the methyl group, and the bending vibration appeared at 723  $cm^{-1}$ belongs to the methylene group. The peak at 1641 cm<sup>-1</sup> shows that C=C is not saturated in RT seed oil biodiesel. It is worth noting that the chromatography and spectroscopy techniques can be used to assess biodiesel, making observing, and its superiority. GC-MS, IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR was in the FAME-determined features, and different functional group structure is considered to be effective, fast, and easy to use techniques. Therefore, they are used for precise facts elucidation in biodiesel is sensible and dependable.



Figure 10. FTIR spectrum of RTME (FAMEs) functional groups.

## 3.5. Profiling of R. typhina Oil Fatty Acid Methyl Esters Using GC-MS Analysis

For the analysis of biodiesel, the most widely used method is gas chromatography. Generally, it is the perfect method to enumerate the trace components configuration accurately. In the present research work, to evaluate the particular methyl ester conversion of prepared RT seed oil to biodiesel, we have applied the gas chromatography and mass spectroscopy. The data on the GC-MS spectrum was shown in Figure 11. We used the GC spectrum and reported seven major peaks, which is consistent with the literature [46]. By using library matching software (NO. NIST 14), the peak was identified, and every peak matched with a fatty acid methyl ester. The retention time of the identified FAMEs and its position are presented in Table 4. Though by retention time data, the properties of fatty acid methyl ester were prepared and verified by mass spectrometry, and from EI ion source, the mass spectra were obtained [47]. The experimental results were compared and matched with the reported results of the RT seed oil biodiesel.



Figure 11. GC–MS analysis of fatty acid compositions of RT seed oil Biodiesel.

S/No	Fatty Acids/Exp. Results	Retention Time	Number of Carbons and Double Bonds	Chemical Name	Chemical Structure	Weight Percentage (%)	Molecular Weight	ZHANG et al., 2018 [21]	Ruan et al., 2012 [20]
1	Palmitic acid	9.545	C16:0	Hexadecanoic acid, methyl ester	0 	14.0	270	Methyl palmitate C16:0	Palmitic acid C16:0
2	Stearic acid	14.248	C18:0	methyl stearate		3.2	298	Methyl stearate C18:0	Stearic acid C18:0
3	Oleic acid	15.042	C18:1	9-Octadecenoic acid (Z)-, methyl ester		47.2	296	Methyl oleate C18:1	Oleic acid C18:1
4	Linoleic acid	16.797	C18:2	9, 12-Octadecadienoic acid (Z, Z)-, methyl ester		32.2	294	Methyl linoleate C18:2	Linoleic acid C18:2
5	α-Linolenic acid	19.565	C18:3	α-Linolenic acid		1.1	292	-	-
6	Arachidic acid	22.587	C20:0	Eicosanoic acid, methyl ester		0.8	326	-	Arachidic acid C20:0
7	Gondoic acid	23.922	C20:1	CiS- 11- Eicosenoic acid, methyl ester		0.5	324	-	Arachidonic acid C20:1

 Table 4. The detail fatty acid composition of RT seed oil Biodiesel.

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The occurrence of elements within the biodiesel is offensive, as these elements cause many complications such as stimulating biodiesel deprivation, deterioration of engine, operability complications [48]. The essentials whose capacity in biodiesel requires to be controlled are sodium (Na) and potassium (K), which come from the mechanism in biodiesel manufacture. The amount of metal phosphorus (P) is also significant that originate from the raw materials. The elemental concentrations in RT oil biodiesel (RTOBD) were matched with Petro-diesel. It is confirmed from the results that the concentrations of elements were reasonably lower in RT seed oil biodiesel than high-speed diesel (HSD).

Prerequisites (Elements) such as potassium (K), sodium (Na), magnesium (Mg), and calcium (Ca) within biodiesel guide to the injector, stimulate drain, piston and circle wear, locomotive deposit and pass through a filter plug [49]. The recorded concentrations of C, H, N, and O were mentioned in Table 5 and Figure S3 (Supplementary Materials). The high oxygen content results in a low calorific value in the pyrolysis liquid product. The presence of oxygen reduces the ignition delay time, improves the combustibility and burning degree, thereby reducing CO, PM, and other exhaust emissions. Many researchers [50–52] found that high oxygen content in biodiesel can effectively reduce PM emissions from diesel engines. Table 5 shows that the oxygen content of BD100 is 11.12%. The most common biodiesel has an oxygen content of about 10% [53–55]. The high hydrogen contents (13.02%) of biodiesel are attractive for its utilization as fuel [56]. High H to C ratio means higher hydrogen molecules in the fuel. As hydrogen has the highest burning velocity between all fuels, whether gases or liquids. Increasing hydrogen ration in the fuel combination means that the fuel-burning velocity will be better and cleaner. The heating value generally increases as the proportion of H to carbon atoms increases due to the higher heating value of hydrogen than carbon. The HHV is an important property to define the energy content and efficiency of fuels. The HHV of biodiesel (23.73 MJ/kg) was lower than that of diesel (49.65 MJ/kg). The structural oxygen content of fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. We compared with some reported results (Table 5), our experimental results matched them well. The nitrogen content is moderate. Though K, Na, Mg, and Ca Values Table S6 (Supplementary Materials) RTOBD (3.219, 70.29, 32.74, 7.360 µg/g) were low as compared to HSD (213.3, 868.3, 35.6, and 21.4 µg/g). The highest acceptable concentration of Na and K in biodiesel was 5 mg·kg<sup>-1</sup>, while P is 10 mg·kg<sup>-1</sup> [57], Figure 12. The concentration of Na and K was lower in RTOBD, but in HSD, its amount is very high; that's why RT biodiesel will be more capable of utilizing and environmental friendly.

Ultimate Analysis	RT-BD	Pistachio Shell [58]	Peach Stones [59]	Apricot Kernel Shells [60]	Cherry Stones [61]	Mahua Seed [62]
C%	74.89	42.41	45.92	47.33	52.48	61.24
H%	13.02	5.64	6.09	6.37	7.58	8.40
N%	1.97	0.070	0.580	0.370	4.54	4.12
O%	10.12	51.87	47.38	45.93	35.30	25.50
HHV (MJ/kg)	23.73	22.21	24.07	24.29	24.11	25.30

 Table 5.
 RTBD EA (Elemental Analyser) analysis in comparison with other plant seed and shells biodiesel.



Figure 12. Elemental analysis of RTBD ICP-OES.

#### 4. Conclusions

In conclusion, the crude RT seed oil transesterification was done to produce biodiesel with a highest yield of 93.33% by using a base catalyst. We obtained the optimal transesterification conditions and achieved a maximum oil content of 22%. Seven fatty acids were detected in the RT FAMEs production. ICP-OES and element analyzer indicate it could be environment-friendly energy. RT FAMEs were matched and follow well the recognized biodiesel standards of ASTM D6751 and EN 14214. The RT could be a better choice for renewable energy. This crop can be grown on barren wasteland on a large scale for the mass manufacture of biodiesel to fulfil the energy demand and reduce the energy crises.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/1996-1073/12/22/4290/s1, Figure S1: R. typhina plant with fruit, Figure S2: (a) RT crude oil filtration (b) optimization (transesterification) (c) BD washing (d) RT biodiesel. Figure S3: RTBD EA (Elemental analysis) for C, H, O, and N, Table S1: Source collection, oil extraction and transesterification of non-edible R. typhina (Sumac fruit) seed oil as biofuel, Table S2: RT FAMEs detail process of optimization, Table S3: 1H NMR spectroscopic data showing the chemical composition of various methyl esters (Methoxy proton) in RT, biodiesel (FAMEs) sample, Table S4: 13C NMR spectroscopic data showing the chemical shift values corresponding to various structural features in RT (Methoxy carbon) FAMEs, Table S5: FTIR data presenting various functional groups in RT FAMEs, Table S6 Comparison ICP-OES elements concentration (ug/g) of RT-BD with petro-diesel.

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