energies

MDPI

Article

Biodiesel from Mandarin Seed Oil: A Surprising Source of Alternative Fuel

A. K. Azad

School of Engineering and Technology, Central Queensland University, Melbourne VIC 3000, Australia; azad.cqu@gmail.com or a.k.azad@cqu.edu.au; Tel.: +61-469-235-722

Received: 1 October 2017; Accepted: 20 October 2017; Published: 26 October 2017

Abstract: Mandarin (Citrus reticulata) is one of the most popular fruits in tropical and sub-tropical countries around the world. It contains about 22–34 seeds per fruit. This study investigated the potential of non-edible mandarin seed oil as an alternative fuel in Australia. The seeds were prepared after drying in the oven for 20 h to attain an optimum moisture content of around 13.22%. The crude oil was extracted from the crushed seed using 98% *n*-hexane solution. The biodiesel conversion reaction (transesterification) was designed according to the acid value (mg KOH/g) of the crude oil. The study also critically examined the effect of various reaction parameters (such as effect of methanol: oil molar ratio, % of catalyst concentration, etc.) on the biodiesel conversion yield. After successful conversion of the bio-oil into biodiesel, the physio-chemical fuel properties of the virgin biodiesel were measured according to relevant ASTM standards and compared with ultra-low sulphur diesel (ULSD) and standard biodiesel ASTM D6751. The fatty acid methyl esters (FAMEs) were analysed by gas chromatography (GC) using the EN 14103 standard. The behaviour of the biodiesel (variation of density and kinematic viscosity) at various temperatures (10–40 °C) was obtained and compared with that of diesel fuel. Finally, mass and energy balances were conducted for both the oil extraction and biodiesel conversion processes to analyse the total process losses of the system. The study found 49.23 wt % oil yield from mandarin seed and 96.82% conversion efficiency for converting oil to biodiesel using the designated transesterification reaction. The GC test identified eleven FAMEs. The biodiesel mainly contains palmitic acid (C16:0) 26.80 vol %, stearic acid (C18:0) 4.93 vol %, oleic acid (C18:1) 21.43 vol % (including cis. and trans.), linoleic acid (C18:2) 4.07 vol %, and less than one percent each of other fatty acids. It is an important source of energy because it has a higher heating value of 41.446 MJ/kg which is close to ULSD (45.665 MJ/kg). In mass and energy balances, 49.23% mass was recovered as crude bio-oil and 84.48% energy was recovered as biodiesel from the total biomass.

Keywords: mandarin seed oil; biodiesel; transesterification; fatty acid methyl esters; mass and energy balance

1. Introduction

Energy demand is increasing day-by-day. The total world energy requirement is met 84% by non-renewable energy and 16% by renewable energy resources [1,2]. In the non-renewable energy contribution, 80% comes from fossil fuels (such as coal, oil, natural gas, etc.) and 4% from nuclear energy. The large percentage of fossil fuel usage also leads to an increase in environmental pollution. For the renewable energy supply, 6% comes from clean energy (zero emission energy such as solar, wind, hydro, wave, etc.) and 10% from bioenergy (i.e., biomass and biodiesel) [3,4]. Nowadays, greenhouse gas emissions are one of the major concerns throughout the globe because of the increasing evidence of the adverse effects of global warming. In addition, developed countries, as well as large developing countries, are consuming more energy to accelerate their economic growth which leads to

increases in greenhouse gas emission [5,6] as well as diminishing reserves and increased prices for fossil fuels. It is therefore critical that this increasing energy demand should be met by cost effective, low emission renewable energy sources which are currently being investigated throughout the world. Energy recovery from waste and non-edible oil seeds is the main focus of this study. More specifically, the energy recovery from mandarin juice factory waste is discussed and presented in this article.

Energy extraction from waste offers some visible benefits such as easy management of waste, energy savings and the generation of income. For instance, Aussie Mandarins is one of the mandarin suppliers in Australia who are currently using more than 50,000 hectares of land for plantations of about 2.5 million mandarin trees. They produce about 107 thousand tonnes of mandarin fruit per year [7] and export 28% of their total production, market another 15–20% for local consumption as fruit and more than 50% is used for juice production. In 2009, they produced about 16.69 thousand tonnes of green mandarin waste which contains about 1.5–2.0 thousand tonnes of seeds. It is reported in the literature that annual estimated production of mandarin fruit throughout the world is 105 million metric tonnes (MMT), with Brazil being the largest producer (about 19.2 MMT) [8,9]. Rashid et al. [8] reported that 0.072 MMT of total mandarin seed is produced per year globally. This seed, which contains non-edible oil, is usually waste residue of the fruit. It could be one of the prospective sources of alternative fuel (biodiesel) and has therefore been investigated in this study. Biodiesel is biodegradable, non-toxic, non-corrosive, safer (higher flash point), free of sulphur content, produces low emission of greenhouse gases and has good lubrication properties. These fuels can be used in transport (bus, truck, sea transport) and heavy mining equipment and diesel power generators.

Australian mandarin mainly grows in Queensland (about 60.8%), South Australia (about 31.6%) and Western Australia (about 5.3%) [10]. It is available from June to November, September is the picking season for mandarin production. Mandarin has some common English names such as Clementine, Satsuma, Tangarine, Kinnow, etc., as listed in Table 1. Around the world, it is distributed in Australia, Japan, China, India, Philippine and South-East Asia, etc. The taxonomical classification, common English names, world distribution and distribution map in Australia are also presented in Table 1. It is one of the main natural sources of vitamin C. One fruit contains about 187 kJ food energy. There are several types of plants belonging to the *Rutaceae* family such as *Citrus reticulate*, *Citrus sinensis*, *Citrus paradise*, *Citrus limon* etc. grown in Australia.

Table 1. Taxonomical classification, common names and distribution of Mandarin in Australia.

Taxonomical Classification		Common English Name	World Distribution
Kingdom	*Plantae*	Mandarin	Australia
Phylum	*Charophyta*	Clementine	Japan
Class	*Equisetopsida*	Tangarine	China
Subclass	*Magnoliidae*	Tangerine	India
Superorder	*Rosanae*	Satsuma	Philippine
Order	*Sapindales*	Kinnow	South-east Asia
Family	*Rutaceae*		California
Genus	*Citrus*		USA
Species	*Citrus reticulata*		Brazil

Distribution map in Australia [11].

Biodiesels are renewable eco-fuels mainly produced from biological resources such as vegetable oil (from jatropha [12], karanja [13], beauty leaf [14], soybean [15] etc.), animal fats (from lard, tallow, etc.), agricultural and factory waste (from waste oil, grease, etc.). Based on the type of feedstocks, biodiesel is classified as first generation, second generation and third generation. First generation biodiesels are generally derived from edible food crops and vegetable oils [16,17] including rice, wheat, barley, potato wastes and sugar beets etc., and edible vegetable oils including soybean oil [18–33], sunflower oil [20,21,27–29,31,34,35], corn oil [20,21,27], olive oil [31,36], palm oil [27,31,34,37], coconut oil [31], rapeseed oil [38], mustard oil [39,40]. Second generation biodiesels are produced from a wide array of feedstocks, ranging from lignocellulosic feedstocks to municipal solid waste and animal fat [16,41].

These non-edible feedstocks include wood and wood waste, animal fats [29,30], non-food crops [42], waste cooking oil [43,44] etc. and non-edible oils such as *Jatropha curcas* [34,45–50], lesquerella oil, cotton seed [21,28,31,32,51], *Pongamia glabra* [34,52], beauty leaf [53,54], karanja [55], castor oil [32,51,56–61], *Salvadora oleoides* and linseed oil [28], forestry residues, switchgrass [20], wood [20] and biomass sources [62–65]. Third generation biodiesels are produced from micro-algal biomass which has a very distinctive growth yield compared to classical lignocellulosic biomass [16,66].

Recent research has concentrated on the study of a wide variety of feedstocks for biodiesel [2]. For example, Kamal et al. [9] studied oil extraction from citrus seed and determined its chemical composition. Anwar et al. [67] investigated physio-chemical properties of citrus seeds and oils, and also analysed the fatty acid composition of the oil. Rashid et al. [8] obtained biodiesel from citrus seed oil and analysed the fatty acid composition of the fuel. The literature has reported that mandarin oil is one of the main sources of palmitic acid, stearic acid, oleic acid and linolenic acid. It also contains lesser amounts of other fatty acids. Each fatty acid has a specific influence on overall fuel properties. Biodiesel is an alternative fuel which can be used by blending up to 20% with diesel without requiring any modification of diesel engines. Biodiesel production from seeds follows process steps of seed preparation, oil extraction, pre-treatment, and oil to biodiesel conversion. Figure 1 graphically represents a summary of the biodiesel production process from mandarin seed.

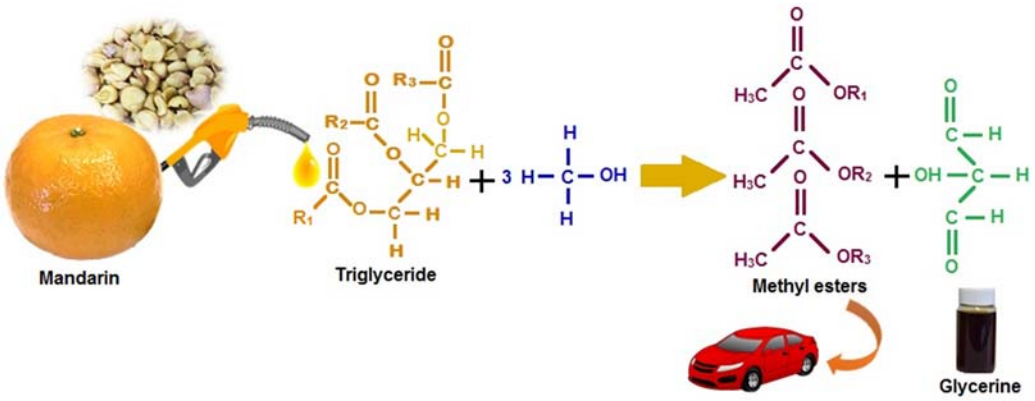

Figure 1. Summary of biodiesel production from mandarin oil.

In this study, the mandarin seed was prepared by controlling moisture to facilitate the *n*-hexane oil extraction process. The extracted oil was converted to biodiesel by an alkali catalyst transesterification reaction. The effects of reaction variables on conversion yield were carefully analysed. The glycerine was removed in three different stages. Excess or unreacted methanol and catalyst were removed by heating and washing, respectively. The fatty acid composition (FAC) was measured by gas chromatography (GC) using the AOCS Ce 1a-13 standard. Important fuel properties were tested using relevant ASTM and EN standards. The behaviour of the fuel was analysed for varying ambient temperatures from 10 to 40 °C. Finally, mass and energy balances were conducted for both the oil extraction and the biodiesel conversion from mandarin seed oil.

2. Materials and Methods

2.1. Oil Extraction

2.1.1. Seed Collection and Kernel Extraction

The mandarin seeds were collected from a mandarin farm in Queensland, Australia. Ten random samples of the fruit were selected to determine the contents. The summary of observations is presented in Table 2, showing that the average weight per fruit is 238 g containing about 155 g of juice, 22 to 34 seeds (average weight 5.6 g) and an average 83.6 g of the rind. The study recorded about 35.5% green

waste per fruit which contains about 6.83% of seeds. The kernels were extracted from the mandarin seed and the moisture was removed by heating in an oven prior to oil extraction. The kernels were crushed using a food grinder for to facilitate removing the moisture and uniform drying. Figure 2 summarises the necessary steps for oil extraction from mandarin seed.

Figure 2. Oil extraction from mandarin seed by *n*-hexane method.

Table 2. Summary of observations on random samples of Australian mandarin fruit.

Sample Number	Gross Weight per Fruit (g)	Liquid Juice per Fruit (g)	Rind Per Fruit (g)	Number of Seeds per Fruit	Average Seed Weight (g)	% of Seed from Total Waste
1	232.11	150.40	84.07	26	4.94	5.88
2	269.39	169.39	104.34	34	7.27	6.97
3	248.63	132.59	116.04	36	5.20	4.48
4	276.87	189.70	87.16	22	5.43	6.23
5	239.78	167.42	72.36	34	6.84	9.45
6	241.30	145.53	95.81	28	6.47	6.75
7	217.94	156.61	57.20	27	4.13	7.22
8	220.28	147.55	69.34	23	3.39	4.89
9	222.74	146.74	76.00	28	6.19	8.14
10	214.37	134.55	73.70	31	6.12	8.30

2.1.2. Moisture Control and Kernel Drying

Kernel drying is an important pre-treatment step for oil extraction. The moisture content directly influences the oil yield. Bhuiya et al. and Jahirul et al. [14,68] studied the effect of moisture content on oil seeds such as jatropha, beauty-leaf, karanja etc., and found maximum oil yield at an optimum moisture content of 15% for mechanical and chemical extraction. In this study, crushed kernel moisture was carefully maintained at 60 °C by use of a microprocessor temperature controlled incubator (Figure 2). The drying process was closely monitored and the weight loss recorded (using a digital balance with 0.001 g tolerance) every 2 h. In this study, the kernel drying curve was obtained by plotting weight as a function of time to find the optimum moisture control point as shown in Figure 3.

The trend of the kernel drying curve follows the second order polynomial equation of $y = 0.3862x^2 - 12.229x + 745.13$ where the value of goodness-of-fitting was $R^2 = 0.991$. The curve shows that, after 16 h of drying, the ongoing kernel weight loss was negligible, and the curve becomes a straight line. The study found that the optimum moisture content is about 13.22%. A full 20 h drying process was observed and analysed for uniform drying of the kernels before oil extraction. Finally, dried kernels were crushed into smaller size (less than 0.5 mm) for extracting oil by the *n*-hexane method.

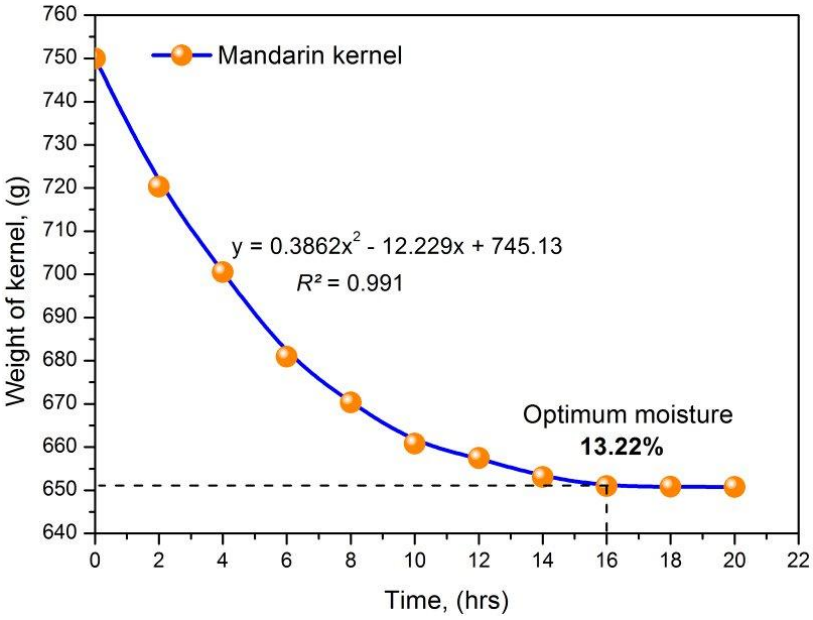

Figure 3. Kernel drying curve for mandarin.

2.1.3. Oil Extraction (*n*-Hexane Method)

Figure 2 shows the process of oil extraction technique by the *n*-hexane method. It is one of the most efficient methods to extract oil from the kernel. As discussed above, the dried kernels were crushed to maximise particle contact surface area. Then the total sample material was divided into small lots of 65 g each for oil extraction. A total of 16 conical flasks were used for mixing of the kernel with a 98% *n*-hexane solution at a 2:1 ratio of solution to kernel for the initial extraction. Each flask was sealed and initially manually shaken for proper mixing of crushed kernel with the solution. The mixture was then shaken in an orbital shaker machine at 300 rpm for 18 to 20 h. After shaking, the oil-chemical mixture was kept for 5–10 h to allow the solids from the liquid to settle. A summary of the oil extraction process parameters and the extracted oil amounts and the overall percentage is presented in Table 3. The extraction process was repeated five times on each 65 g lot of kernel material, however, the *n*-hexane: kernel ratio was changed to 1:1 after the first extraction. The shaking frequency was also reduced to 270 rpm in the second extraction and 250 rpm in subsequent extractions. From the Table, it can be noted that shaking time was also gradually reduced from 18 h to 11 h because of the reduction of total mass in the mixture. Settling time was also recorded for this experiment. The separated oil-chemical mixture was kept in the fume hood to remove unreacted *n*-hexane. It is to be noted that unreacted *n*-hexane can be recovered and recycled for large scale production. After removing *n*-hexane, the virgin oil was collected and stored at room temperature. After the fifth extraction, the amount of extracted oil was found to be negligible (less than 1%). The authors believe that further extraction was not needed. The study found an overall 49.23% oil yield from the mandarin seed. It is important to check the acid value of the oil before proceeding to the next step [69]. The acid value of the crude oil was found to be less than 1 which indicates that no pre-treatment is needed for biodiesel conversion.

Table 3. Summary of mandarin oil extraction by *n*-hexane (for 1000 g of sample).

Extraction Number	*n*-Hexane to Kernel Ratio	Shaking Frequency (rpm)	Shaking Time (h)	Settling Time (h)	Total Extracted Oil (g)	Overall Oil Yield
Extraction 1	2:1	300	18	10	301.84	
Extraction 2	1:1	270	15	11	114.46	
Extraction 3	1:1	250	13	6	48.46	49.23%
Extraction 4	1:1	250	12	3	20.61	
Extraction 5	1:1	250	11	6	6.92	

2.2. Biodiesel Conversion

2.2.1. Reaction Design

The biodiesel conversion requires a specific reaction designed for processing each particular oil. This is the most sensitive step in the fuel processing technique. There are several techniques available for biodiesel conversion. Transesterification is one of the most efficient techniques to convert triglycerides into methyl esters and remove glycerine from the bio-oil [70]. The conversion occurs in the presence of an alkali or acid catalytic with methanol and crude bio-oil by maintaining a standard reaction environment to satisfy the ASTM D6751 biodiesel standard [71–73]. There are two methods of transesterification reaction, namely catalytic and non-catalytic transesterification [74–88]. The catalytic method enhances the solubility of methanol into the bio-oil, thus increasing the reaction rate. The catalytic transesterification method involves use of an acid catalyst, a base catalyst or an enzyme catalyst [89–93]. The alkaline catalysts include NaOH, $NaOCH_3$, $KOCH_3$, KOH, NaMeO and K_2CO_3 [26,75,94–100]. Acid catalysts include sulphuric acid, hydrochloric acid, ferric sulphate, phosphoric acid and organic sulfonic acid [101–103]. Non-catalytic transesterification includes supercritical, alcohol and BIOX co-solvent techniques [104–108]. Figure 1 shows the designated transesterification reaction for the mandarin biodiesel conversion. There are four main variables, namely methanol to oil molar ratio, catalyst concentration, reaction time and reaction temperature which have a direct or indirect influence on the transesterification reaction. The effect of reaction variables on conversion yield was analysed and the conversion rate or yield of methyl esters was calculated using Equation (1) [70,109,110]:

$$\text{Conversion yield, } Y = \frac{grams\ of\ produced\ methyl\ esters}{grams\ of\ oil\ used\ in\ reaction} \times 100\% \quad (1)$$

2.2.2. Conversion Procedure

The biodiesel conversion requires some specific steps (namely chemical reaction, glycerine separation, unreacted methanol removing, washing and drying) to follow standard procedure. Figure 4 shows the main steps followed for biodiesel conversion in this study. In the first step, the experimental setup was prepared with a 1000 mL capacity three-necked round-bottomed glass reactor equipped with a Liebig condenser, 250 mm effective length and 380 mm overall length), thermometer (range 0–150 °C) and flat bottom water bath (capacity 2.5 L) with magnetic stirrer and heater under an automatically controlled chemical fume hood located in the Chemical and Biomedical Engineering laboratory. The conversion process was conducted in multiple batches (750 mL in each batch) to avoid any risk of saponification (the process that produces soap). The oil was preheated to 60 °C before adding the catalyst. The potassium methoxide ($KOCH_3$) solution was prepared separately by adding 1 wt % KOH pellets into methanol (6:1 molar ratio of methanol to oil). The mixture was stirred on a hot plate until all the crystals completely dissolved into the methanol. Then the $KOCH_3$ solution was slowly added into the preheated mandarin oil. The water was circulated before adding the chemicals and the reactor was closed thereafter. The reaction temperature was maintained at 60 °C and stirred continuously at 750 rpm for 60 min reaction time. After completion of the reaction, the mixture was put into a separating funnel and cooled at room temperature under the fume hood system. In step 2, the

glycerine was separated in three different steps from the converted biodiesel. For primary separation, 6–8 h separation time was allowed at room temperature and glycerine was removed from the bottom of the separating funnel. In secondary layer separation, three equal layers (lower, middle and upper) were separated from existing biodiesel in small separating funnels. After 18 h, secondary glycerine (being lighter) was separated from the biodiesel. In tertiary separation, the biodiesel was chilled at 7 °C and centrifuged at 5500 rpm for 20 min using a combined chilling and centrifuge machine. The remaining glycerine was totally removed in tertiary separation. In step 3, the unreacted methanol was removed by heating at 80 °C for 1 h. The remaining catalyst was also removed by washing with warm demineralised water several times in the separating funnel in step 4. The biodiesel generates waste water at this stage. In step 5, the biodiesel was dried at 110 °C for 45–60 min to remove moisture and residual water particles. After cooling at room temperature, the final product was obtained and stored in a closed container to avoid oxidation of the mandarin biodiesel. The properties of the biodiesel were tested and are discussed in the following section.

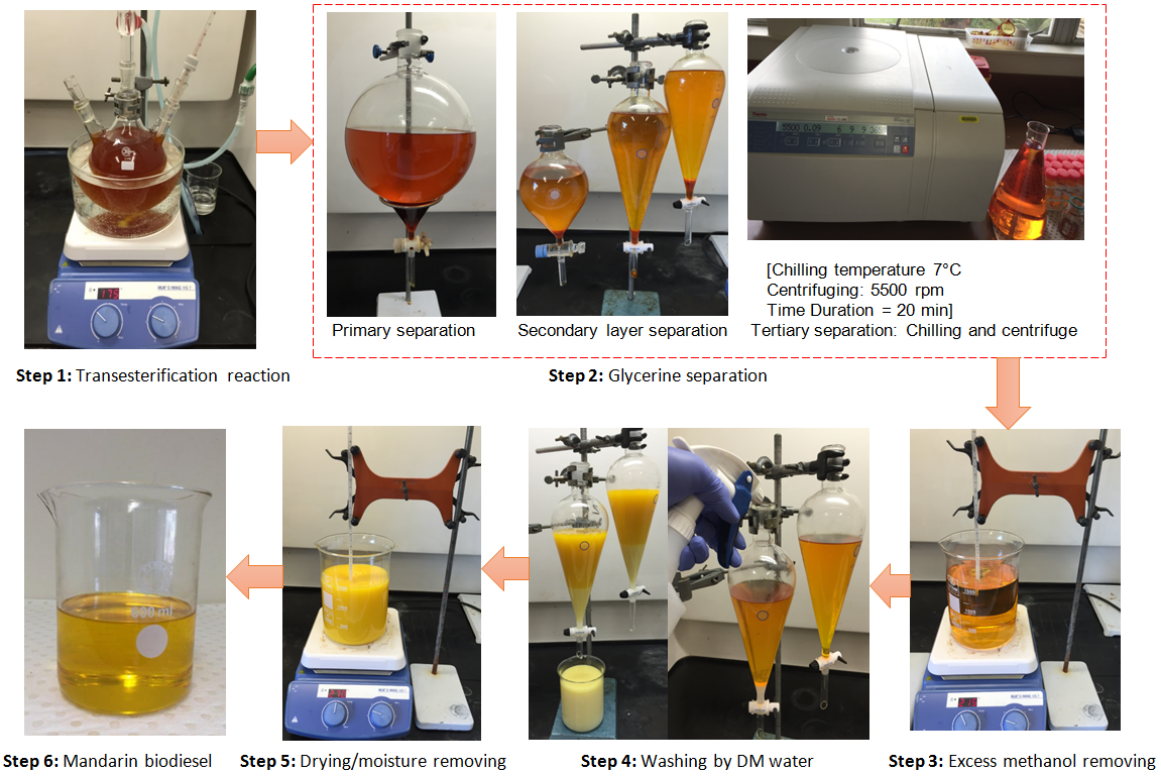

Figure 4. Mandarin biodiesel conversion by transesterification reaction.

2.3. Fuel Properties

The fatty acid composition and physio-chemical fuel properties of the biodiesel were measured using appropriate ASTM and EN standards. The fatty acid compositions were analysed by gas chromatography (GC) using European standard EN 14103. The following fuel properties were determined, namely density at 15 °C (ASTM D1298), viscosity at 40 °C (ASTM D445), calorific value (ASTM D240), flash point (ASTM D93), pour point (ASTM D97), cloud point (ASTM D5773), acid value (ASTM D664), auto-ignition temperature (ASTM D319), carbon residue (ASTM D4530), cold filter plugging point (ASTM D6371) oxidation stability (ASTM D2274) and pH value (ASTM D7946. Some of the properties of the fuel were calculated based on the fatty acid composition of the biodiesel (Table 4). The calculated fuel properties are saponification number (SN), iodine value (IV), cetane number (CN), long-chain fatty acid factor (LCSF) and degree of unsaturation (DU) [111,112]. The numerical calculations were done using Equations (2)–(6), respectively [113]. The measured and calculated fuel

properties were compared with the ULSD fuel and standard biodiesel values. There are few properties which can indicate the physical behaviour of the fuel. In this study, only two properties (density and kinematic viscosity) were considered to analyse the physical behaviour of the fuel at various temperatures (from 10 to 40 °C) for different weather conditions:

$$\text{Saponification number, } SN = \sum\left(\frac{560 \times A_i}{MW_i}\right) \quad (2)$$

$$\text{Iodine value, } IV = \sum\left(\frac{254 \times D \times A_i}{MW_i}\right) \quad (3)$$

$$\text{Cetane number, } CN = 46.3 + \left(\frac{5458}{SN}\right) - (0.225 \times IV) \quad (4)$$

$$\text{LCSF} = (0.1 \times C_{16}) + (0.5 \times C_{18}) + (1 \times C_{20}) + (1.5 \times C_{22}) + (2 \times C_{24}) \quad (5)$$

$$\text{Degree of unsaturation, } DU = MUFA + (2 \times PUFA) \quad (6)$$

where, A_i indicates the percentage of each fatty acid component, MW_i is the molecular mass of each component (Table 4) and D is the number of double bonds present for each component. *MUFA* denotes monounsaturated fatty acid and PUFA refers to polyunsaturated fatty acids. C_{16}, C_{18}, C_{20}, C_{22}, C_{24} stand for palmitoleic acid, stearic acid, arachidic acid, behenic acid and lignoceric acid, respectively.

Table 4. Fatty acid composition of mandarin biodiesel (under EN 14103 standard).

Fatty Acid Name	Structure	Chemical Name	Formula	Molecular Mass (g/mol)	Relative Content (%vol.)
Palmitic acid	C16:0	Hexadecanoic acid	$C_{16}H_{32}O_2$	256.42	26.80
Palmitoleic acid	C16:1	(9Z)-Hexadec-9-enoic acid	$C_{16}H_{30}O_2$	254.41	0.42
Margaric acid	C17:0	Hexadecanoic acid	$C_{17}H_{34}O_2$	270.45	0.34
Stearic acid	C18:0	Octadecanoic acid	$C_{18}H_{36}O_2$	284.48	4.93
Oleic acid	C18:1	(9Z)-Octadecenoic acid	$C_{18}H_{34}O_2$	282.47	1.53
Oleic acid	C18:1	*trans*-Octadecenoic acid	$C_{18}H_{34}O_2$	282.47	19.90
Linoleic acid	C18:2	cis-9,12-Octadecadienoic acid	$C_{18}H_{32}O_2$	280.44	41.61
Linolenic acid	C18:3	Methyl linolenate	$C_{18}H_{30}O_2$	278.43	4.07
Arachidic acid	C20:0	Eicosanoic acid	$C_{20}H_{40}O_2$	312.53	0.40
Eicosenoic acid	C20:1	(9Z)-9-Icosenoic acid	$C_{20}H_{38}O_2$	310.52	0.01
Behenic acid	C22:0	1-Docosanoic acid	$C_{22}H_{44}O_2$	340.58	0.01
Total saturated fatty acid		-	-	-	32.47
Total monosaturated fatty acid		-	-	-	21.85
Total polyunsaturated fatty acid		-	-	-	46.68
Total trans fatty acid		-	-	-	19.90
Degree of unsaturation		-	-	-	113.22
Ester content		-	-	-	99.19

2.4. Calculation of Mass and Energy Balances

The analyses of mass and energy balances were conducted on mandarin oil extraction, biodiesel conversion and the total process based on input feedstock and output products. This analysis helps to better understand the total production loss and to optimise the entire process. Mass balance was calculated numerically based on input mass of the feedstock and output mass of the bio-oil, cake materials or waste and process loss. On the other hand, the energy distribution was calculated based on input energy to the system (the product of mass of feedstock and its gross heating value) and output energy from the system. Total output energy is the summation of the individual energies of the products, by-products and waste. The mass and energy balances were calculated using the following equations [114]:

Mass balance:

$$\% \text{ of mass recovery, } M_{recovery} = \frac{W_{output}}{W_{input}} \times 100\% \quad (7)$$

$$\% \text{ of mass loss} = 100\% - \sum M_{recovery} \quad (8)$$

Energy balance:

$$\% \text{ of energy recovery, } E_{recovery} = \frac{W_{outtput} \times HV_{output}}{W_{input} \times HV_{input}} \times 100\% \quad (9)$$

$$\% \text{ of mass loss} = 100\% - \sum E_{recovery} \quad (10)$$

where W_{input} is the mass (kg) of input feedstock, W_{output} denotes total mass (kg) of output products (i.e., oil, biodiesel, glycerine, etc.), $\sum M_{recovery}$ is the summation of mass recovery from all output products, HV_{output} is the heating value (MJ/kg) of the product and by-product, HV_{input} represents the heating value (MJ/kg) of the bio-oil and $\sum E_{recovery}$ is the summation of energy recovery from all output products.

3. Results and Discussion

3.1. Effect of Reaction Variables on Conversion Yield

3.1.1. Effect of Catalyst Concentration

The study evaluated the effect of variables on the conversion rate (i.e., yield of methyl esters). The experiment was conducted on a small quantity of bio-oil (100 mL each batch) to optimise different parameters. The catalyst selection is an important task for biodiesel conversion because the catalyst enhances the conversion yield of the reaction. The study experimented on the two alkali catalysts KOH and NaOH to analyse the effect of catalyst concentration and to select the most efficient catalyst. This parameter was optimised by varying the catalyst concentration from 0.25 to 1.5 wt % where other parameters (i.e., temperature 60 °C, time 60 min and 6:1 methanol oil ratio) were kept constant. The conversion yield was calculated using Equation (1) and the results are presented in Figure 5. The experimental results indicate that both catalysts show a similar trend but different conversion yields. The KOH and NaOH catalysts follow the second-order polynomial equation $y = -61.606x^2 + 153.84x + 0.882$ where the value of $R^2 = 0.9776$ and $y = -61.80x^2 + 153.59x - 3.11$ where the value of $R^2 = 0.9540$, respectively (maximum value of $R^2 = 1.0$). Both catalysts show a maximum conversion yield at 1 wt % for the same reaction conditions. In this experiment, the KOH catalyst achieved a higher conversion yield (about 96.58%) with respect to the NaOH catalyst. KOH catalyst was therefore selected for the entire experiment to optimise other parameters.

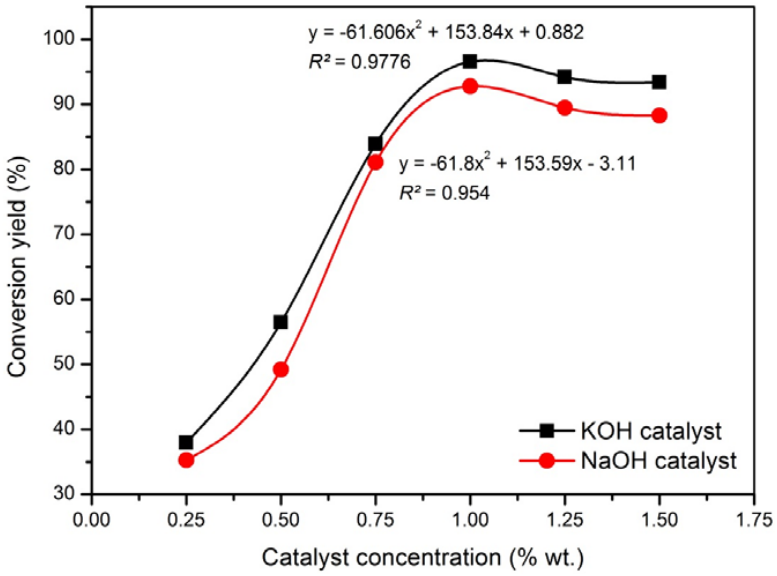

Figure 5. Effect of catalyst concentration on mandarin biodiesel conversion yield at 60 °C reaction temperature, 6:1 methanol–oil ratio and 60 min reaction time.

3.1.2. Effect of Methanol-Oil Ratio

Methanol is the main reactant for biodiesel conversion. It is very important to analyse the methanol oil ratio to achieve the optimum conversion efficiency of the transesterification reaction. The effect of the methanol–oil ratio was studied by varying the range from 4:1 to 8:1 where 1 wt % KOH catalyst was used at 60 °C reaction temperature for 1 h reaction time. The reaction mixture was continuously stirred at 750 rpm by a combined magnetic stirrer and heater. There were eight experiments that were conducted for methanol to oil ratios of 4:1, 4.5:1, 5:1, 5.5:1, 6:1, 6.5:1, 7:1 and 8:1 and the outcome is presented in Figure 6. The trend of the curve follows the second-order polynomial equation $y = -2.3205x^2 + 25.321x + 23.685$ where the value of $R^2 = 0.9493$. The results show that an increase in methanol oil ratio leads to an increase in the conversion yield till 6:1 where the conversion yield reaches its peak (conversion yield is 96.55%) and then gradually decreases. This happened due to the bi-directional characteristics of the transesterification reaction.

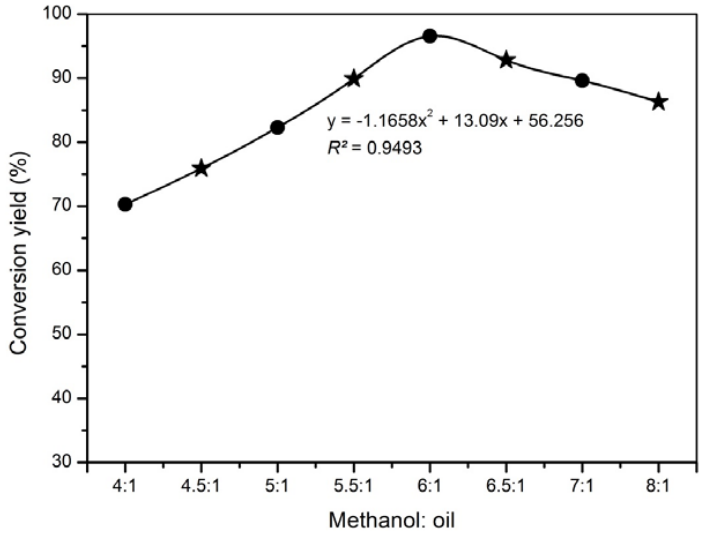

Figure 6. Effect of methanol–oil ratio on conversion yield for 1% KOH catalyst at 60 °C reaction temperature for 60 min reaction time.

3.1.3. Effect of Reaction Temperature

The reaction temperature is one of the important parameters for catalysts to achieve efficient conversion. In this study, the effect of reaction temperature on conversion yield was studied by varying the temperature range from 30 to 70 °C. Figure 7 shows the conversion results when other variables such as catalyst concentration (1 wt % KOH), methanol to oil ratio (6:1), reaction time (60 min) and stirred speed (750 rpm) were kept constant for this investigation. The study experimented with 30, 40, 50, 55, 60, 65 and 70 °C reaction temperatures to investigate the effect on conversion yield. The trend of the curve follows the second-order polynomial equation $y = -0.0477x^2 + 6.5532x - 129.77$ where the value of $R^2 = 0.9743$. Figure 7 shows that conversion yield increases with increase of reaction temperature. The maximum conversion yield (96.56%) was recorded at 60 °C temperature. The yield at 60–65 °C is almost the same, but decreases at 70 °C due to the evaporation temperature of the methanol. The study indicates that 60 °C temperature is the optimum reaction temperature for mandarin biodiesel conversion.

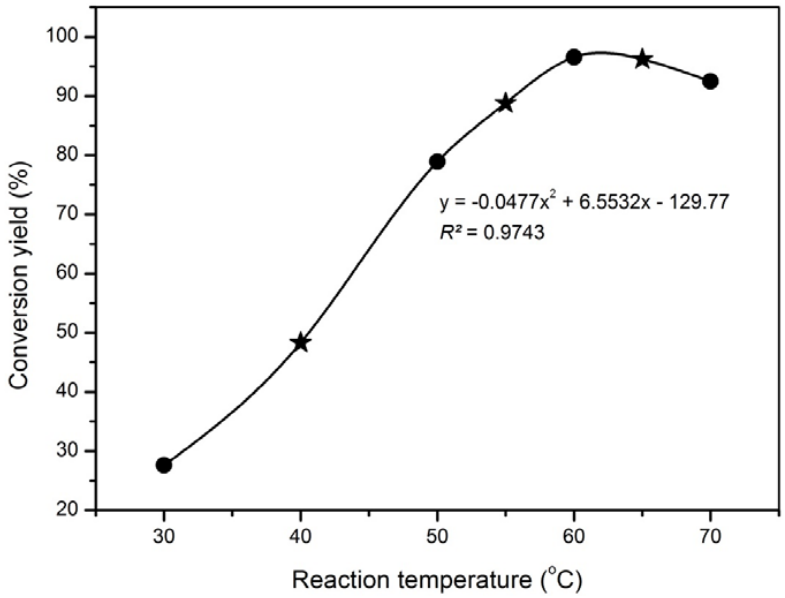

Figure 7. Effect of reaction temperature on biodiesel conversion yield at 1 wt % KOH catalyst concentration, continuous 750 rpm stirring speed for 60 min reaction time.

3.1.4. Effect of Reaction Time

The study investigated the effect of reaction time on biodiesel conversion yield by varying the time range from 30 to 100 min when other reaction variables were kept constant. Figure 8 shows the experimental results for 30, 40, 60, 65, 70, 80, 90 and 100 min reaction time and corresponding conversion yield. The curve follows the second-order polynomial equation $y = -0.0096x^2 + 1.5375x + 35.67$ where the value of $R^2 = 0.9610$. The trend of the curve shows that the increase of reaction time leads to an increase in conversion yield until 60 min reaction time. Above that, the conversion yield slightly decreases and becomes constant. Therefore, the maximum conversion yield was found for 60 min reaction time and this is considered as the optimum reaction time for biodiesel conversion from mandarin biodiesel.

The mandarin oil was converted to biodiesel at an optimised reaction condition (1 wt % KOH catalyst concentration, 6:1 methanol to oil ratio at 60 °C reaction temperature for one hour reaction time). The conversion was conducted using 750 mL lots to avoid the risk of saponification. After biodiesel conversion, the fatty acid methyl ester composition of mandarin biodiesel was analysed and is briefly discussed below.

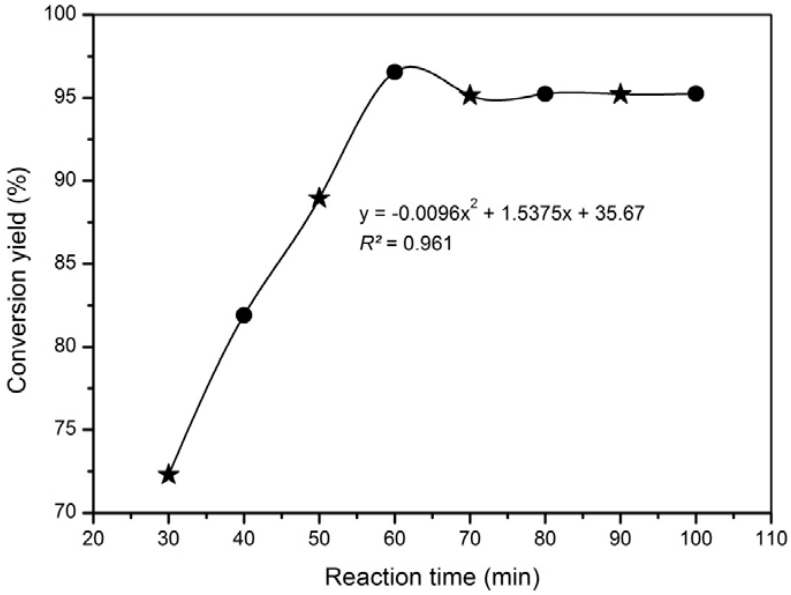

Figure 8. Effect of reaction time on conversion yield at 1 wt % KOH, 6:1 methanol–oil ratio, continuous 750 rpm stirring speed at 60 °C reaction temperature.

3.2. Fatty Acid Methyl Esters (FAMEs)

The analysis of fatty acid methyl esters (FAMEs) was undertaken using a GC-2010 Plus gas chromatograph (Shimadzu, Japan) equipped with 0.25 × 25 m inner diameter and 0.25 μm film thickness capillary columns. The test was conducted using AOCS Ce 1a-13 standard and a summary of the results is presented in Table 4. The mandarin biodiesel sample was separated in a capillary gas-liquid chromatography column having a highly polar stationary phase, and analysed according to carbon chain length, the degree of unsaturation, plus the geometry and position of the double bonds present in the biodiesel. The profile of the FAMEs in the proton nuclear magnetic response (H-NMR) spectrum for the 60 min period is presented in Figure 9.

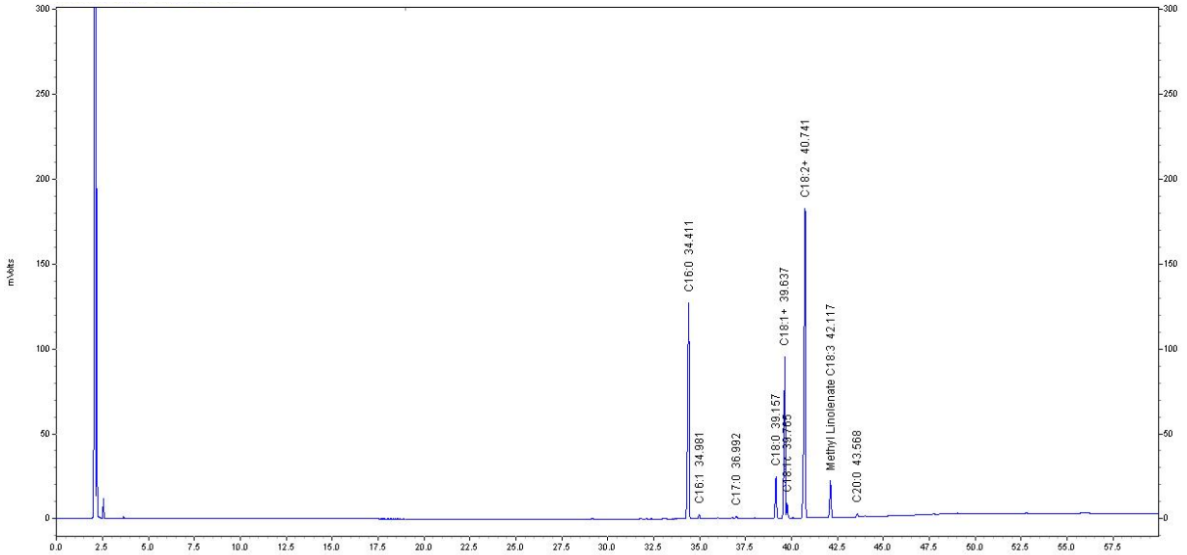

Figure 9. Fatty Acid Profile of the mandarin methyl esters.

There are 11 fatty acids that were identified in the mandarin biodiesel. They are 26.80 vol % C16:0 (palmitic acid), 0.42 vol % C16:1 (palmitoleic acid), 0.34 vol % C17:0 (margaric acid), 4.93 vol % C18:0

(stearic acid), 1.53 vol % C18:1 (cis-oleic acid), 19.90 vol % C18:1 (*trans*-oleic acid), 41.61 vol % C18:2 (linoleic acid), 4.07 vol % C18:3 (linolenic acid), 0.40 vol % C20:0 (arachidic acid), 0.01 vol % C20:1 (eicosenoic acid), and 0.01 vol % C22:0 (behenic acid). The study also found 32.47% total saturated fatty acid, 21.85% total monosaturated fatty acid, 46.68% total polyunsaturated fatty acid and 19.90% trans fatty acid in the mandarin biodiesel. The degree of unsaturation of 113.22% was calculated using Equation (6) and 100% ester content was recorded in the converted mandarin biodiesel. The physio-chemical fuel properties were measured and are discussed in the next section.

3.3. Physio-Chemical Fuel Properties of the Biodiesel

The physio-chemical fuel properties of the biodiesel were measured under corresponding ASTM standards. The measured values were compared with those of ULSD and checked with the acceptable limits of standard biodiesel. The important fuel properties of the mandarin biodiesel are presented in Table 5. The density of the biodiesel was measured at 15 °C using the ASTM D1298 standard and was found to be 861 kg/m^3 which is close to diesel and within the acceptable limits of the ASTM standard. The kinematic viscosity was measured by an ARES rheometer at 40 °C. The study found a mandarin biodiesel viscosity of 3.96 mm^2/s which is lower than the diesel viscosity of 4.10 mm^2/s. The measured value is within the acceptable range (3.50 to 5.0 mm^2/s) of standard biodiesel. The calorific value (CV) or heating value is one of the important fuel properties which indicates the total amount of heat content of the fuel. The study used a highly precise (0.1% precision and 0.0001 °C temperature resolution) isoperibolic calorimeter (Parr 6400, Parr, IL, USA) to measure the CV of diesel and biodiesel using the ASTM D240 standard. The results show that the CV of mandarin biodiesel is 39.94 MJ/kg, whereas it is 45.665 MJ/kg for diesel. In comparison with diesel, mandarin biodiesel contains about 3.48% less energy. It is reported in the literature that the minimum CV of biodiesel is 35.0 MJ/kg [115], however, neither ASTM nor EN standards have any specific limit for CV. Another important fuel property is flash point which indicates the safety of the fuel. It is the temperature at which the oil starts to ignite with the mixture of air. In this study, a flash point tester was used to determine the flash point of the produced biodiesel using the ASTM D93 standard. The flash point of the mandarin biodiesel was found to be 174 °C, whereas 60 °C was measured for diesel. The minimum limit for standard biodiesel is 100 °C.

Table 5. Physio-chemical fuel properties of mandarin biodiesel.

Properties	Unit	ULSD	Mandarin Biodiesel	ASTM Standard	Test Method
Density (at 15 °C temp.)	kg/m^3	866	861	860–900	ASTM D1298
Viscosity (at 40 °C temp.)	mm^2/s	4.10	3.96	3.5–5.0	ASTM D445
Calorific value (CV)	MJ/kg	45.665	41.446	-	ASTM D240
Cetane number	-	44	49.11	-	-
Flash point	°C	60	174	Min 100	ASTM D93
Pour point	°C	−15	−27	−15 to −16	ASTM D97
Cloud point	°C	−8.6	−4	−3 to −12	ASTM D5773
Smoke point	°C	293	256	-	ASTM D1322
Auto-ignition temperature	°C	256.9	296.15		ASTM E659
Acid value	mg KOH/g	Max 0.5	0.22	Max 0.5	ASTM D664
Carbon residue	m/m	0.01	0.01	-	ASTM D4530
Cold filter plugging point	°C	−3.0	−7.5	0, <−15 winter	ASTM D6371
Iodine value	-	-	106.21	-	-
Saponification number	-	-	204.39	-	-
Long chain saturated factor	-	-	5.56	-	-
Oxidation stability	hours	5.0	5.17	-	ASTM D2274

Some other properties such as density, viscosity, pour point, cloud point, cold filter plugging point etc. indicate the physical behaviour of the fuel. Density and viscosity are within the acceptable limits of the standard biodiesel. The pour point indicates the minimum temperature at which the fuel loses its flow characteristics and becomes semi-solid. The study obtained a pour point of −27 °C for mandarin biodiesel and −15°C for diesel using the ASTM D97 standard using a pour point tester. Under the ASTM D5773 standard, the cloud point was measured by a cloud point analyser and was found to be

−4 °C for biodiesel and –8.6 °C for diesel. This is the maximum temperature below which wax forms as a cloudy appearance in the fuel. The study found the smoke point for diesel is 293 °C and 256 °C for biodiesel. Another safety indication of the fuel is its auto-ignition temperature, the temperature at which the fuel starts burning automatically. The study measured the auto-ignition temperature for both diesel and biodiesel under the ASTM E659 standard and found 256.9 °C for diesel and 296.15 °C for biodiesel. It can therefore be noted that the mandarin biodiesel is safer for processing, handling and storing than diesel. The acid value is one of the important chemical properties which indicates the quantity of organic free fatty acid present in the biodiesel. The acid value of 0.22 mg KOH/g was measured after biodiesel conversion. Oxidation stability was found to be 5.0 h for diesel and 5.17 h for mandarin biodiesel. The cold filter plugging point (CFPP) is a parameter to describe the physical behaviour of the fuel, indicating the estimated lowest temperature at which the fuel gives trouble free flow under winter conditions. The study found CFPP of −3 °C for diesel and −7.5 °C for biodiesel under ASTM D6371 test conditions. Carbon residue for both fuels was found to be 0.01 m/m under the ASTM D4530 micro method.

Some fuel properties of saponification number, iodine value, cetane number (CN), and long chain saturated factor were calculated numerically using Equations (2)–(5), respectively. The numerical results were obtained based on the fatty acid methyl esters content of the biodiesel (Table 4). The cetane number (CN) is the combustion parameter of a fuel which indicates the ignition quality of that particular fuel. The higher the CN value, the better is the combustion speed and quality. The saponification number and iodine value for the mandarin biodiesel were determined as 204.39 and 106.21, respectively. The empirical result for the long chain saturated factor is 5.56 which was calculated based on the long chain fatty acid composition (C_{16} to C_{24}). Below is a brief discussion about the behaviour of the mandarin biodiesel at various temperatures.

3.4. Physical Behaviour of Mandarin Biodiesel at Various Temperatures

The biodiesel has some fuel properties which indicate the physical behaviour of the biodiesel. The study considered only two properties to analyse the behaviour of the biodiesel at different temperatures. The physical behaviour means the variation of physical properties such as density and viscosity for different weather condition throughout the year. For instance, a case study was done to identify the biodiesel behaviour for typical Australian seasonal weather conditions. According to the Australian Bureau of Meteorology (BoM), the average temperature range for winter is 8–15 °C, autumn is 15–23 °C, spring is 22–30 °C, and summer is 30–40 °C. Considering these temperature ranges, the study analysed the variation of density and kinematic viscosity of the mandarin biodiesel from 10 °C to 40 °C and results are presented in Figures 10 and 11, respectively. Figure 10 shows almost similar trend of density fluctuation with temperature compared with ULSD. For the ASTM D1298 standard test condition at 15 °C temperature, 8.58% higher biodiesel density was found compared to diesel (the density of the biodiesel and diesel are 861 kg/m^3 and 830 kg/m^3, respectively). The curves also show that the density decreases with increase of temperature. The mandarin density curve follows the second order polynomial equation of $y = -0.0159x^2 + 0.2232x + 861.5$ where the coefficient of determination (R^2) or goodness of fit is 0.9999. On the contrary, the diesel density curve follows the equation $y = -0.0029x^2 - 0.7143x + 840.36$ where the value of R^2 is 0.9904, so the derived mandarin biodiesel shows similar behaviour to diesel fuel for typical Australian weather conditions and remains within the acceptable range of the ASTM D6751 standard biodiesel.

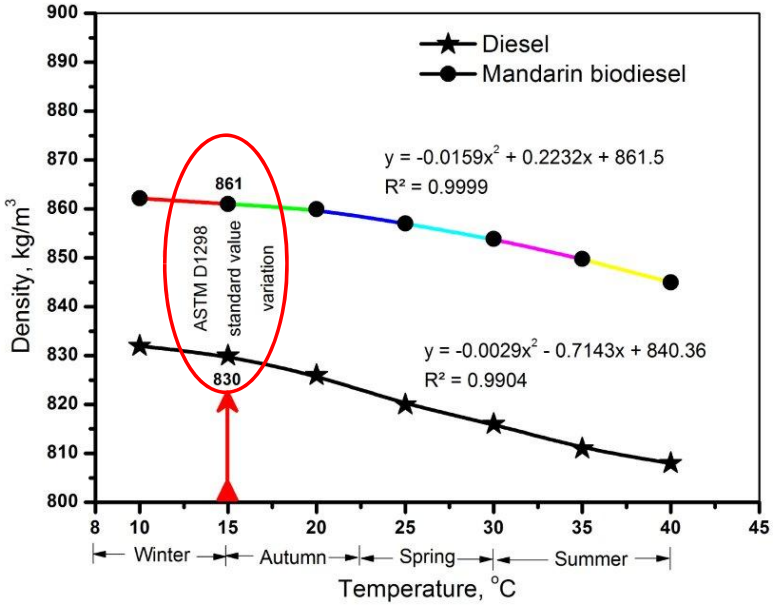

Figure 10. Variation of density with temperature.

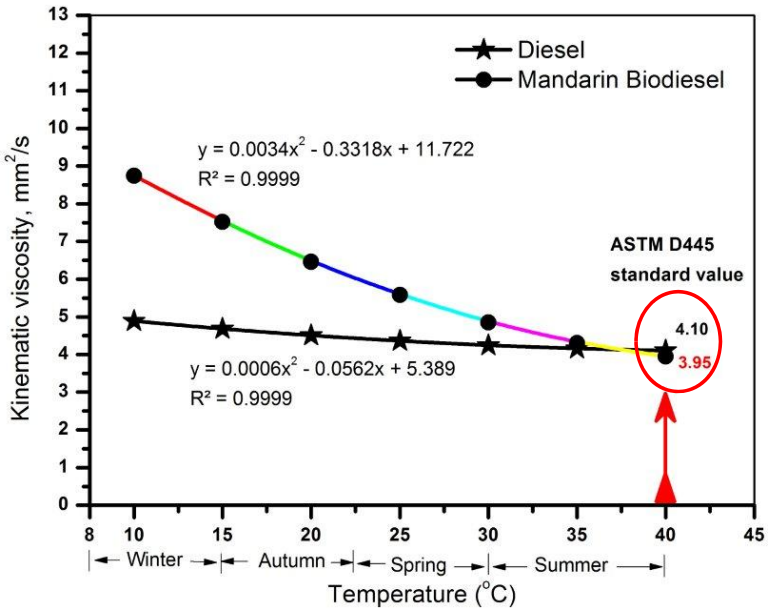

Figure 11. Variation of kinematic viscosity with temperature.

Figure 11 shows the variation with temperature of another important fuel property, kinematic viscosity in mm^2/s. For this analysis, the study used a highly precise rheometer by varying the temperature range from 10 °C to 40 °C. The ULSD viscosity curve follows the second order polynomial equation of $y = 0.0006x^2 - 0.0562x + 5.389$ where $R^2 = 0.9999$. The trend of the curve represents a minimal variation of the kinematic viscosity with temperature. On the other hand, the biodiesel viscosity curve follows the second order polynomial equation of $y = 0.0034x^2 - 0.3318x + 11.722$ where $R^2 = 0.9999$ and shows a converging trend at higher temperatures. From this curve, it can be clearly seen that the biodiesel has a higher viscosity in winter compared with diesel fuel. The viscosity decreases with increase in temperature and that of biodiesel is slightly lower (diesel 4.10 mm^2/s and biodiesel 3.95 mm^2/s) at 40 °C using the ASTM D445 standard test condition. It can be noted that the

biodiesel behaves very much like diesel in summer and the kinematic viscosity variation is within the range of the American standard ASTM D6751 and the European standard EN 14214.

3.5. Mass and Energy Balance for Mandarin Biodiesel Production

The study conducted mass and energy balances on both mandarin oil extraction (*n*-hexane) and biodiesel conversion. This analysis is important for minimising the process loss and optimising the process parameters. Mass balance was conducted based on input mass of the feedstock compared to the output mass of the crude bio-oil, converted biodiesel, cake material or other byproducts (according to Equation (7)). Energy balance was conducted based on input energy to the system compared with output energy recovery by the finished product and by-products (according to Equation (9)). Figure 12 shows the total mass balance for the entire process including oil extraction and biodiesel conversion.

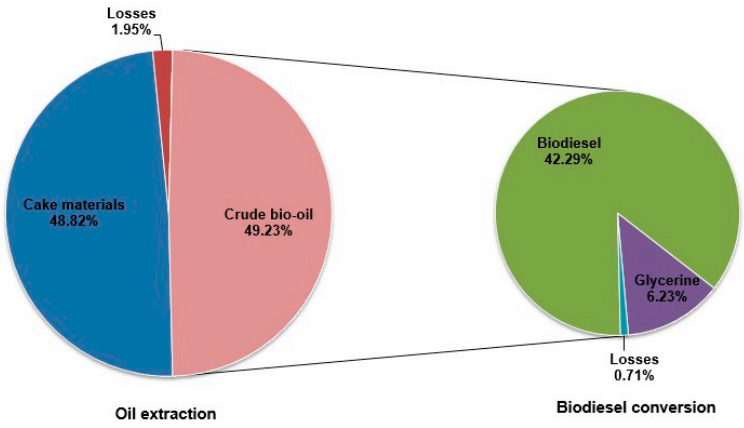

Figure 12. Mass balance for the total process (oil extraction and biodiesel conversion).

The results show a 49.23% oil yield of the mandarin seed which means that 49.23% by mass of crude bio-oil was extracted from the dried kernels whereas 48.82% was cake materials. The *n*-hexane oil extraction losses were found to be 1.95% by mass. The mass balance for biodiesel conversion was conducted based on the input mass of the crude bio-oil. The study found that 42.29% biodiesel was obtained from the total inputted biomass (kernels). In the designated conversion process, 6.23% of glycerine was found as a by-product which can be used as a raw material in the cosmetics industry. The calculated process loss for biodiesel conversion is 0.53%. The energy distribution for the biodiesel conversion is presented in Figure 13.

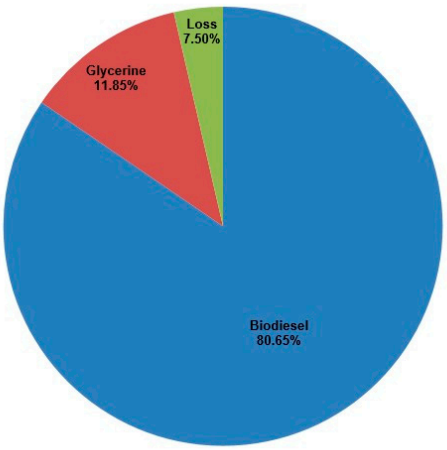

Figure 13. Energy balance for mandarin biodiesel conversion.

The energy recovery was calculated using Equation (9). For this analysis, the heating values for crude bio-oil, cake material, biodiesel and glycerine are presented in Table 6. From Figure 13, the study found that 80.65% energy was recovered as mandarin biodiesel, 11.85% as glycerine and 7.49% energy losses were calculated for the system. Compared with the recovery of mass, considerably more energy was recovered in the conversion process.

Table 6. Gross heating value or calorific value of the crude mandarin oil, cake materials, biodiesel and glycerine.

Name of the Product	Calorific Value (MJ/kg)
Crude bio-oil	39.24
Cake material	12.32
Biodiesel	41.446
Glycerine	23.92

4. Conclusions

The study investigated the oil rich mandarin seed as a potential, alternative and second generation transport fuel for diesel engines. The study found a 49.23% oil yield using the *n*-hexane method. The crude oil was converted to biodiesel by an alkali catalyst transesterification reaction. The FAME compositions were analysed under the EN 14103 standard and identified eleven fatty acids, mostly palmitic acid, stearic acid, *trans*- and *cis*-oleic acid and linolenic acid. Important physicochemical fuel properties were measured under relevant ASTM standards and compared with ultra-low sulphur diesel. The results show that the fuel properties are within the acceptable range of ASTM D6751 standards. The study analysed the physical behaviour of the biodiesel at typical Australian seasonal temperatures and found a similar trend of density variation compared with. The study also found a higher kinematic viscosity at low temperatures and a lower viscosity at higher temperatures compared with diesel. The mass and energy balances were conducted for the entire process and indicated a 42.29% mass recovery for the final product (biodiesel) from the total biomass feedstock. A total 84.65% of energy was recovered by the converted biodiesel and 11.85% by glycerine in the energy distribution. Further study is needed on tribological behaviour of the biodiesel and the engine performance, emission and combustion analysis of the fuel before its commercial application as an alternative fuel.

Acknowledgments: The author would like to acknowledge Mohammad Rasul, Masud Khan and Subhash Sharma for their fruitful advises and suggestion. The authors would also like to acknowledge Tim McSweeney, Adjunct Research Fellow, Centre for Railway Engineering at Central Queensland University for his contribution in English proof reading of this article.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Moghaddam, E.A.; Ahlgren, S.; Hulteberg, C.; Nordberg, Å. Energy balance and global warming potential of biogas-based fuels from a life cycle perspective. *Fuel Process. Technol.* **2015**, *132*, 74–82. [CrossRef]
2. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C.; Hazrat, M.A. Prospect of biofuels as an alternative transport fuel in Australia. *Renew. Sustain. Energy Rev.* **2015**, *43*, 331–351. [CrossRef]
3. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C.; Islam, R. Prospect of Moringa seed oil as a sustainable biodiesel fuel in Australia: A review. *Procedia Eng.* **2015**, *105*, 601–606. [CrossRef]
4. Conconi, C.C.; Crnkovic, P.M. Thermal behavior of renewable diesel from sugar cane, biodiesel, fossil diesel and their blends. *Fuel Process. Technol.* **2013**, *114*, 6–11. [CrossRef]
5. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Omri, A.; Bhuiya, M.M.K.; Hazrat, M.A. Modelling of renewable energy economy in Australia. *Energy Procedia* **2014**, *61*, 1902–1906. [CrossRef]
6. Senthil, M.; Visagavel, K.; Saravanan, C.G.; Rajendran, K. Investigations of red mud as a catalyst in Mahua oil biodiesel production and its engine performance. *Fuel Process. Technol.* **2016**, *149*, 7–14. [CrossRef]

7. Bartle, J.R.; Abadi, A. Toward Sustainable Production of Second Generation Bioenergy Feedstocks. *Energy Fuels* **2009**, *24*, 2–9. [CrossRef]
8. Rashid, U.; Ibrahim, M.; Yasin, S.; Yunus, R.; Taufiq-Yap, Y.; Knothe, G. Biodiesel from Citrus reticulata (mandarin orange) seed oil, a potential non-food feedstock. *Ind. Crops Prod.* **2013**, *45*, 355–359. [CrossRef]
9. Kamal, G.; Anwar, F.; Hussain, A.; Sarri, N.; Ashraf, M. Yield and chemical composition of Citrus essential oils as affected by drying pretreatment of peels. *Int. Food Res. J.* **2011**, *18*, 1275–1282.
10. Aussie Mandarins. Available online: http://www.aussiemandarins.com.au/industry (accessed on 16 April 2016).
11. ATLAS of Living Australia. Mandarin, Citrus Reticulata. Available online: http://bie.ala.org.au/species/Citrus+reticulata# (accessed on 22 July 2014).
12. Agarwal, D.; Agarwal, A.K. Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. *Appl. Therm. Eng.* **2007**, *27*, 2314–2323. [CrossRef]
13. Gresshoff, P.M.; Hayashi, S.; Biswas, B.; Mirzaei, S.; Indrasumunar, A.; Reid, D.; Samuel, S.; Tollenaere, A.; van Hameren, B.; Hastwell, A. The value of biodiversity in legume symbiotic nitrogen fixation and nodulation for biofuel and food production. *J. Plant Physiol.* **2015**, *172*, 128–136. [CrossRef] [PubMed]
14. Bhuiya, M.M.K.; Rasul, M.G.; Khan, M.M.K.; Ashwath, N.; Azad, A.K.; Mofijur, M. Optimisation of Oil Extraction Process from Australian Native Beauty Leaf Seed (*Calophyllum Inophyllum*). *Energy Procedia* **2015**, *75*, 56–61. [CrossRef]
15. Azad, A.K.; Rasul, M.G.; Giannangelo, B.; Islam, R. Comparative study of diesel engine performance and emission with soybean and waste oil biodiesel fuels. *Int. J. Automot. Mech. Eng.* **2015**, *12*, 2866–2881. [CrossRef]
16. Lee, R.A.; Lavoie, J.-M. From first-to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity. *Anim. Front.* **2013**, *3*, 6–11. [CrossRef]
17. Azad, A.K.; Ameer Uddin, S.M.; Alam, M.M. A Comprehensive Study of DI Diesel Engine Performance with Vegetable Oil: An Alternative Bio-fuel Source of Energy. *Int. J. Automot. Mech. Eng.* **2012**, *5*, 576–586. [CrossRef]
18. Du, W.; Xu, Y.; Liu, D.; Zeng, J. Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. *J. Mol. Catal. B Enzym.* **2004**, *30*, 125–129. [CrossRef]
19. Wang, L.; Du, W.; Liu, D.; Li, L.; Dai, N. Lipase-catalyzed biodiesel production from soybean oil deodorizer distillate with absorbent present in tert-butanol system. *J. Mol. Catal. B Enzym.* **2006**, *43*, 29–32. [CrossRef]
20. Pimentel, D.; Patzek, T.W. Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Nat. Resour. Res.* **2005**, *14*, 65–76. [CrossRef]
21. Bhuiya, M.M.K.; Rasul, M.G.; Khan, M.M.K.; Ashwath, N.; Azad, A.K. Prospects of 2nd generation biodiesel as a sustainable fuel—Part: 1 Selection of feedstocks, oil extraction techniques and conversion technologies. *Renew. Sustain. Energy Rev.* **2016**, *55*, 1109–1128. [CrossRef]
22. Kouzu, M.; Kasuno, T.; Tajika, M.; Sugimoto, Y.; Yamanaka, S.; Hidaka, J. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel* **2008**, *87*, 2798–2806. [CrossRef]
23. Noureddini, H.; Gao, X.; Philkana, R.S. Immobilized Pseudomonas cepacia lipase for biodiesel fuel production from soybean oil. *Bioresour. Technol.* **2005**, *96*, 769–777. [CrossRef] [PubMed]
24. Xie, W.; Li, H. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *J. Mol. Catal. A Chem.* **2006**, *255*, 1–9. [CrossRef]
25. Ha, S.H.; Lan, M.N.; Lee, S.H.; Hwang, S.M.; Koo, Y.-M. Lipase-catalyzed biodiesel production from soybean oil in ionic liquids. *Enzym. Microb. Technol.* **2007**, *41*, 480–483. [CrossRef]
26. Liu, X.; He, H.; Wang, Y.; Zhu, S.; Piao, X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel* **2008**, *87*, 216–221. [CrossRef]
27. Bhuiya, M.M.K.; Rasul, M.G.; Khan, M.M.K.; Ashwath, N.; Azad, A.K.; Hazrat, M.A. Prospects of 2nd generation biodiesel as a sustainable fuel—Part: 2 Selection of feedstocks, oil extraction techniques and conversion technologies. *Renew. Sustain. Energy Rev.* **2016**, *55*, 1129–1146. [CrossRef]
28. Barnwal, B.K.; Sharma, M.P. Prospects of biodiesel production from vegetable oils in India. *Renew. Sustain. Energy Rev.* **2005**, *9*, 363–378. [CrossRef]
29. Canakci, M.; Van Gerpen, J. Biodiesel production from oils and fats with high free fatty acids. *Trans. Am. Soc. Agric. Eng.* **2001**, *44*, 1429–1436. [CrossRef]

30. Bhuiya, M.M.K.; Rasul, M.G.; Khan, M.M.K.; Ashwath, N.; Azad, A.K.; Hazrat, M.A. Second generation biodiesel: Potential alternative to-edible oil-derived biodiesel. *Energy Procedia* **2014**, *61*, 1969–1972. [CrossRef]
31. Demirbas, A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Prog. Energy Combust. Sci.* **2005**, *31*, 466–487. [CrossRef]
32. Meneghetti, S.M.P.; Meneghetti, M.R.; Serra, T.M.; Barbosa, D.C.; Wolf, C.R. Biodiesel production from vegetable oil mixtures: Cottonseed, soybean, and castor oils. *Energy Fuels* **2007**, *21*, 3746–3747. [CrossRef]
33. Balat, M. Potential alternatives to edible oils for biodiesel production—A review of current work. *Energy Convers. Manag.* **2011**, *52*, 1479–1492. [CrossRef]
34. Sarin, R.; Kumar, R.; Srivastav, B.; Puri, S.K.; Tuli, D.K.; Malhotra, R.K.; Kumar, A. Biodiesel surrogates: Achieving performance demands. *Bioresour. Technol.* **2009**, *100*, 3022–3028. [CrossRef] [PubMed]
35. Hoekman, S.K.; Broch, A.; Robbins, C.; Ceniceros, E.; Natarajan, M. Review of biodiesel composition, properties, and specifications. *Renew. Sustain. Energy Rev.* **2012**, *16*, 143–169. [CrossRef]
36. Dorado, M.P.; Ballesteros, E.; Arnal, J.M.; Gómez, J.; López, F.J. Exhaust emissions from a Diesel engine fueled with transesterified waste olive oil. *Fuel* **2003**, *82*, 1311–1315. [CrossRef]
37. Demirbas, A. Importance of biodiesel as transportation fuel. *Energy Policy* **2007**, *35*, 4661–4670. [CrossRef]
38. Saka, S.; Kusdiana, D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel* **2001**, *80*, 225–231. [CrossRef]
39. Amir Uddin, M.A.; Azad, A.K.; Alam, M.M.; Ahamed, J.U. Performance of a diesel engine run with mustard-Kerosene blends. *Procedia Eng.* **2015**, *105*, 698–704. [CrossRef]
40. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C. Macadamia biodiesel as a sustainable and alternative transport fuel in Australia. *Energy Procedia* **2017**, *110*, 543–548. [CrossRef]
41. Demirbas, M.F. Biorefineries for biofuel upgrading: A critical review. *Appl. Energy* **2009**, *86*, S151–S161. [CrossRef]
42. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C.; Bhuiya, M.M.K. Study on Australian energy policy, socio-economic, and environment issues. *J. Renew. Sustain. Energy* **2015**, *7*, 063131. [CrossRef]
43. Zhang, Y.; Dubé, M.A.; McLean, D.D.; Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour. Technol.* **2003**, *89*, 1–16. [CrossRef]
44. Vasudevan, P.T.; Briggs, M. Biodiesel production—Current state of the art and challenges. *J. Ind. Microbiol. Biotechnol.* **2008**, *35*, 421–430. [CrossRef] [PubMed]
45. De Oliveira, J.S.; Leite, P.M.; de Souza, L.B.; Mello, V.M.; Silva, E.C.; Rubim, J.C.; Meneghetti, S.M.P.; Suarez, P.A.Z. Characteristics and composition of *Jatropha gossypiifoliaand Jatropha curcas* L. oils and application for biodiesel production. *Biomass Bioenergy* **2009**, *33*, 449–453. [CrossRef]
46. Sarin, A.; Arora, R.; Singh, N.P.; Sarin, R.; Malhotra, R.K.; Sharma, M.; Khan, A.A. Synergistic effect of metal deactivator and antioxidant on oxidation stability of metal contaminated Jatropha biodiesel. *Energy* **2010**, *35*, 2333–2337. [CrossRef]
47. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C.; Mofijur, M.; Bhuiya, M.M.K. Prospects, feedstocks and challenges of biodiesel production from beauty leaf oil and castor oil: A nonedible oil sources in Australia. *Renew. Sustain. Energy Rev.* **2016**, *61*, 302–318. [CrossRef]
48. Kumar, N.; Singh, A.S.; Kumari, S.; Reddy, M.P. Biotechnological approaches for the genetic improvement of *Jatropha curcas* L.: A biodiesel plant. *Ind. Crops Prod.* **2015**, *76*, 817–828. [CrossRef]
49. Maurya, R.; Gupta, A.; Singh, S.K.; Rai, K.M.; Chandrawati; Sawant, S.V.; Yadav, H.K. Microsatellite polymorphism in *Jatropha curcas* L.—A biodiesel plant. *Ind. Crops Prod.* **2013**, *49*, 136–142. [CrossRef]
50. Reyes-Trejo, B.; Guerra-Ramírez, D.; Zuleta-Prada, H.; Cuevas-Sánchez, J.A.; Reyes, L.; Reyes-Chumacero, A.; Rodríguez-Salazar, J.A. Annona diversifolia seed oil as a promising non-edible feedstock for biodiesel production. *Ind. Crops Prod.* **2014**, *52*, 400–404. [CrossRef]
51. Demirbaş, A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: A survey. *Energy Convers. Manag.* **2003**, *44*, 2093–2109. [CrossRef]
52. Sarin, A.; Arora, R.; Singh, N.; Sarin, R.; Sharma, M.; Malhotra, R. Effect of metal contaminants and antioxidants on the oxidation stability of the methyl ester of Pongamia. *J. Am. Oil Chem. Soc.* **2010**, *87*, 567–572. [CrossRef]
53. Habibullah, M.; Masjuki, H.H.; Kalam, M.A.; Zulkifli, N.W.M.; Masum, B.M.; Arslan, A.; Gulzar, M. Friction and wear characteristics of *Calophyllum inophyllum* biodiesel. *Ind. Crops Prod.* **2015**, *76*, 188–197. [CrossRef]

54. Mosarof, M.H.; Kalam, M.A.; Masjuki, H.H.; Alabdulkarem, A.; Habibullah, M.; Arslan, A.; Monirul, I.M. Assessment of friction and wear characteristics of *Calophyllum inophyllum* and palm biodiesel. *Ind. Crops Prod.* **2016**, *83*, 470–483. [CrossRef]
55. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C.; Bhuiya, M.M.K. Recent development of biodiesel combustion strategies and modelling for compression ignition engines. *Renew. Sustain. Energy Rev.* **2016**, *56*, 1068–1086. [CrossRef]
56. Da Silva, N.D.L.; Maciel, M.R.W.; Batistella, C.B.; Maciel Filho, R. Optimization of biodiesel production from castor oil. *Appl. Biochem. Biotechnol.* **2006**, *130*, 405–414. [CrossRef]
57. Conceição, M.M.; Candeia, R.A.; Silva, F.C.; Bezerra, A.F.; Fernandes, V.J., Jr.; Souza, A.G. Thermoanalytical characterization of castor oil biodiesel. *Renew. Sustain. Energy Rev.* **2007**, *11*, 964–975. [CrossRef]
58. Scholz, V.; da Silva, J.N. Prospects and risks of the use of castor oil as a fuel. *Biomass Bioenergy* **2008**, *32*, 95–100. [CrossRef]
59. Hazrat, M.A.; Rasul, M.G.; Khan, M.M.K.; Azad, A.K.; Bhuiya, M.M.K. Utilization of polymer wastes as transport fuel resources a recent development. *Energy Procedia* **2014**, *61*, 1681–1685. [CrossRef]
60. Silitonga, A.S.; Masjuki, H.H.; Ong, H.C.; Yusaf, T.; Kusumo, F.; Mahlia, T.M.I. Synthesis and optimization of Hevea brasiliensis and Ricinus communis as feedstock for biodiesel production: A comparative study. *Ind. Crops Prod.* **2016**, *85*, 274–286. [CrossRef]
61. Armendáriz, J.; Lapuerta, M.; Zavala, F.; García-Zambrano, E.; del Carmen Ojeda, M. Evaluation of eleven genotypes of castor oil plant (*Ricinus communis* L.) for the production of biodiesel. *Ind. Crops Prod.* **2015**, *77*, 484–490. [CrossRef]
62. Koutsouki, A.A.; Tegou, E.; Badeka, A.; Kontakos, S.; Pomonis, P.J.; Kontominas, M.G. In situ and conventional transesterification of rapeseeds for biodiesel production: The effect of direct sonication. *Ind. Crops Prod.* **2016**, *84*, 399–407. [CrossRef]
63. Modiba, E.; Osifo, P.; Rutto, H. Biodiesel production from baobab (*Adansonia digitata* L.) seed kernel oil and its fuel properties. *Ind. Crops Prod.* **2014**, *59*, 50–54. [CrossRef]
64. Theam, K.L.; Islam, A.; Choo, Y.M.; Taufiq-Yap, Y.H. Biodiesel from low cost palm stearin using metal doped methoxide solid catalyst. *Ind. Crops Prod.* **2015**, *76*, 281–289. [CrossRef]
65. Wang, R.; Sun, L.; Xie, X.; Ma, L.; Liu, Z.; Liu, X.; Ji, N.; Xie, G. Biodiesel production from Stauntonia chinensis seed oil (waste from food processing): Heterogeneous catalysis by modified calcite, biodiesel purification, and fuel properties. *Ind. Crops Prod.* **2014**, *62*, 8–13. [CrossRef]
66. Brennan, L.; Owende, P. Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renew. Sustain. Energy Rev.* **2010**, *14*, 557–577. [CrossRef]
67. Anwar, F.; Naseer, R.; Bhanger, M.; Ashraf, S.; Talpur, F.N.; Aladedunye, F.A. Physico-chemical characteristics of citrus seeds and seed oils from Pakistan. *J. Am. Oil Chem. Soc.* **2008**, *85*, 321–330. [CrossRef]
68. Jahirul, M.I.; Brown, J.R.; Senadeera, W.; Ashwath, N.; Laing, C.; Leski-Taylor, J.; Rasul, M.G. Optimisation of Bio-Oil Extraction Process from Beauty Leaf (*Calophyllum Inophyllum*) Oil Seed as a Second Generation Biodiesel Source. *Procedia Eng.* **2013**, *56*, 619–624. [CrossRef]
69. Mofijur, M.; Rasul, M.G.; Hyde, J.; Azad, A.K.; Mamat, R.; Bhuiya, M.M.K. Role of biofuel and their binary (diesel-biodiesel) and ternary (ethanol-biodiesel-diesel) blends on internal combustion engines emission reduction. *Renew. Sustain. Energy Rev.* **2016**, *53*, 265–278. [CrossRef]
70. Ullah, Z.; Bustam, M.A.; Man, Z. Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst. *Renew. Energy* **2015**, *77*, 521–526. [CrossRef]
71. Taufiqurrahmi, N.; Bhatia, S. Catalytic cracking of edible and non-edible oils for the production of biofuels. *Energy Environ. Sci.* **2011**, *4*, 1087–1112. [CrossRef]
72. Ghaly, A.E.; Dave, D.; Brooks, M.; Budge, S. Production of biodiesel by enzymatic transesterification: Review. *Am. J. Biochem. Biotechnol.* **2010**, *6*, 54–76. [CrossRef]
73. Azad, A.K.; Rasul, M.G.; Bhuiya, M.M.K.; Islam, R. Effect of first and second generation biodiesel blends on engine performance and emission. *AIP Conf. Proc.* **2016**, *1754*, 050031.
74. Atabani, A.E.; Silitonga, A.S.; Ong, H.C.; Mahlia, T.M.I.; Masjuki, H.H.; Badruddin, I.A.; Fayaz, H. Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renew. Sustain. Energy Rev.* **2013**, *18*, 211–245. [CrossRef]

75. Atabani, A.E.; Silitonga, A.S.; Badruddin, I.A.; Mahlia, T.M.I.; Masjuki, H.H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2070–2093. [CrossRef]
76. Balat, M.; Balat, H. Progress in biodiesel processing. *Appl. Energy* **2010**, *87*, 1815–1835. [CrossRef]
77. Salvi, B.L.; Panwar, N.L. Biodiesel resources and production technologies—A review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3680–3689. [CrossRef]
78. Meher, L.C.; Vidya Sagar, D.; Naik, S.N. Technical aspects of biodiesel production by transesterification—A review. *Renew. Sustain. Energy Rev.* **2006**, *10*, 248–268. [CrossRef]
79. Mofijur, M.M.; Rasul, M.G.; Hassain, N.M.S.; Azad, A.K.; Uddin, M.N. Effect of small proportion of butanol additive on the performance, emission, and combustion of Australian native first-and second-generation biodiesel in a diesel engine. *Environ. Sci. Pollut. Res.* **2017**, *24*, 22402–22413.
80. Balat, M.; Balat, H. A critical review of bio-diesel as a vehicular fuel. *Energy Convers. Manag.* **2008**, *49*, 2727–2741. [CrossRef]
81. Jain, S.; Sharma, M.P. Prospects of biodiesel from Jatropha in India: A review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 763–771. [CrossRef]
82. Koh, M.Y.; Ghazi, T.I.M. A review of biodiesel production from *Jatropha curcas* L. oil. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2240–2251. [CrossRef]
83. Mahanta, P.; Shrivastava, A. *Technology Development of Bio-Diesel as an Energy Alternative*; Department of Mechanical Engineering Indian Institute of Technology: Guwahati, India, 2004; pp. 1–19.
84. Murugesan, A.; Umarani, C.; Subramanian, R.; Nedunchezhian, N. Bio-diesel as an alternative fuel for diesel engines—A review. *Renew. Sustain. Energy Rev.* **2009**, *13*, 653–662. [CrossRef]
85. Singh, S.P.; Singh, D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 200–216. [CrossRef]
86. Yusuf, N.N.A.N.; Kamarudin, S.K.; Yaakub, Z. Overview on the current trends in biodiesel production. *Energy Convers. Manag.* **2011**, *52*, 2741–2751. [CrossRef]
87. Dias, J.M.; Alvim-Ferraz, M.C.M.; Almeida, M.F.; Méndez Díaz, J.D.; Polo, M.S.; Utrilla, J.R. Selection of heterogeneous catalysts for biodiesel production from animal fat. *Fuel* **2012**, *94*, 418–425. [CrossRef]
88. Berrios, M.; Skelton, R.L. Comparison of purification methods for biodiesel. *Chem. Eng. J.* **2008**, *144*, 459–465. [CrossRef]
89. Royon, D.; Daz, M.; Ellenrieder, G.; Locatelli, S. Enzymatic production of biodiesel from cotton seed oil using *t*-butanol as a solvent. *Bioresour. Technol.* **2007**, *98*, 648–653. [CrossRef] [PubMed]
90. Azad, A.K.; Rasul, M.G.; Khan, M.M.K.; Sharma, S.C.; Bhuiya, M.M.K.; Mofijur, M. A review on socio-economic aspects of sustainable biofuels. *Int. J. Glob. Warm.* **2016**, *10*, 32–54. [CrossRef]
91. Semwal, S.; Arora, A.K.; Badoni, R.P.; Tuli, D.K. Biodiesel production using heterogeneous catalysts. *Bioresour. Technol.* **2011**, *102*, 2151–2161. [CrossRef] [PubMed]
92. Parawira, W. Biotechnological production of biodiesel fuel using biocatalysed transesterification: A review. *Crit. Rev. Biotechnol.* **2009**, *29*, 82–93. [CrossRef] [PubMed]
93. Ramachandran, K.; Suganya, T.; Nagendra Gandhi, N.; Renganathan, S. Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review. *Renew. Sustain. Energy Rev.* **2013**, *22*, 410–418. [CrossRef]
94. Narasimharao, K.; Lee, A.; Wilson, K. Catalysts in production of biodiesel: A review. *J. Biobased Mater. Bioenergy* **2007**, *1*, 19–30.
95. Kim, H.-J.; Kang, B.-S.; Kim, M.-J.; Park, Y.M.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catal. Today* **2004**, *93*, 315–320. [CrossRef]
96. Rashid, U.; Anwar, F. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel* **2008**, *87*, 265–273. [CrossRef]
97. Dorado, M.P.; Ballesteros, E.; López, F.J.; Mittelbach, M. Optimization of alkali-catalyzed transesterification of Brassica C arinata oil for biodiesel production. *Energy Fuels* **2004**, *18*, 77–83. [CrossRef]
98. Demirbas, A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. *Energy Convers. Manag.* **2009**, *50*, 923–927. [CrossRef]
99. Suehara, K.-I.; Kawamoto, Y.; Fujii, E.; Kohda, J.; Nakano, Y.; Yano, T. Biological treatment of wastewater discharged from biodiesel fuel production plant with alkali-catalyzed transesterification. *J. Biosci. Bioeng.* **2005**, *100*, 437–442. [CrossRef] [PubMed]

100. Cao, C.-Y.; Zhao, Y.-H. Transesterification of castor oil to biodiesel using KOH/NaY as solid base catalyst. *Int. J. Green Energy* **2013**, *10*, 219–229. [CrossRef]
101. Canakci, M.; Van Gerpen, J. Biodiesel production via acid catalysis. *Trans. ASAE Am. Soc. Agric. Eng.* **1999**, *42*, 1203–1210. [CrossRef]
102. Lotero, E.; Liu, Y.; Lopez, D.E.; Suwannakarn, K.; Bruce, D.A.; Goodwin, J.G. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353–5363. [CrossRef]
103. Jothiramalingam, R.; Wang, M.K. Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production via transesterification. *Ind. Eng. Chem. Res.* **2009**, *48*, 6162–6172. [CrossRef]
104. Azad, A.K.; Uddin, S.M.M. Performance study of a diesel engine by first generation bio-fuel blends with fossil fuel: An experimental study. *J. Renew. Sustain. Energy* **2013**, *5*, 013118. [CrossRef]
105. Demirbaş, A. Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy Convers. Manag.* **2002**, *43*, 2349–2356. [CrossRef]
106. Minami, E.; Saka, S. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. *Fuel* **2006**, *85*, 2479–2483. [CrossRef]
107. He, H.; Wang, T.; Zhu, S. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. *Fuel* **2007**, *86*, 442–447. [CrossRef]
108. Pinnarat, T.; Savage, P.E. Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions. *Ind. Eng. Chem. Res.* **2008**, *47*, 6801–6808. [CrossRef]
109. Rashid, U.; Anwar, F.; Ashraf, M.; Saleem, M.; Yusup, S. Application of response surface methodology for optimizing transesterification of Moringa oleifera oil: Biodiesel production. *Energy Convers. Manag.* **2011**, *52*, 3034–3042. [CrossRef]
110. Fan, M.; Huang, J.; Yang, J.; Zhang, P. Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst. *Appl. Energy* **2013**, *108*, 333–339. [CrossRef]
111. Talebi, A.F.; Tabatabaei, M.; Chisti, Y. BiodieselAnalyzer: A user-friendly software for predicting the properties of prospective biodiesel. *Biofuel Res. J.* **2014**, *1*, 55–57. [CrossRef]
112. Ramos, M.J.; Fernández, C.M.; Casas, A.; Rodríguez, L.; Pérez, Á. Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresour. Technol.* **2009**, *100*, 261–268. [CrossRef] [PubMed]
113. Rizwanul Fattah, I.M.; Masjuki, H.H.; Kalam, M.A.; Wakil, M.A.; Rashedul, H.K.; Abedin, M.J. Performance and emission characteristics of a CI engine fueled with Cocos nucifera and Jatropha curcas B20 blends accompanying antioxidants. *Ind. Crops Prod.* **2014**, *57*, 132–140. [CrossRef]
114. Kongkasawan, J.; Capareda, S.C. Jatropha Oil Refining Process and Biodiesel Conversion: Mass and Energy Balance. *Int. Energy J.* **2012**, *13*, 1–4.
115. Knothe, G. Biodiesel derived from a model oil enriched in palmitoleic acid, macadamia nut oil. *Energy Fuels* **2010**, *24*, 2098–2103. [CrossRef]