

Optimization of biodiesel production by microwave irradiation-assisted transesterification for waste cooking oil-*Calophyllum inophyllum* oil via response surface methodology

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ABSTRACT

In this study, microwave irradiation-assisted alkaline-catalysed transesterification was used to produce W70CI30 biodiesel from a mixture of waste cooking oil and *Calophyllum inophyllum* oil. The methanol/oil ratio, catalyst concentration, stirring speed, and reaction time were optimized using response surface methodology based on the Box-Behnken experimental design in order to maximize the biodiesel yield. The quadratic response surface regression model was used to predict the biodiesel yield. It is found that the optimum methanol/oil ratio, catalyst concentration, stirring speed, and reaction time are 59.60 (v/v)%, 0.774 (w/w)%, 600 rpm, and 7.15 min, respectively, and the predicted biodiesel yield is 97.40%. Experiments were conducted using the optimum process parameters and the average biodiesel yield is 97.65%, which is in excellent agreement with the predicted value. The physicochemical properties of the W70CI30 biodiesel produced using the optimum process parameters were measured and it is found that the biodiesel has significantly higher oxidation stability (18.03 h) compared with the waste cooking oil biodiesel (4.61 h). In addition, the physicochemical properties and cold flow properties of the biodiesel fulfil the fuel specifications stipulated in the ASTM D6751 and EN 14214 standards. It can be concluded that microwave irradiation-assisted transesterification is effective to boost the biodiesel yield and produce biodiesel of superior quality. In addition, this method significantly reduces the reaction time of the transesterification process to 9.15 min and the process is energy-efficient. It is believed that the findings of this study will be beneficial for microwave irradiation-assisted biodiesel synthesis on the industrial scale.

1. Introduction

It is known that global energy demands are mainly fulfilled by fossil fuels. However, global energy demands seem to increase at a slower pace in recent years due to unprecedented efficiencies created by novel renewable energy technologies as well as the enforcement of stringent energy policies and environmental legislations. There is a dramatic shift in the energy pattern where the demand for energy harvesting from fossil fuels has declined since year 2014. The current state of global energy is called 'The Grand Transition' [1]. In this state, there is a strong demand for renewable energy due to the emergence of new technologies, greater environmental challenges, and swiftness in economics and geopolitical power [2]. It is well-known that the burning of

fossil fuels such as coal and oil leads to environmental problems and decarbonization of energy systems (increasing the utilization of low-carbon energy sources such as renewable energy) to address environmental issues such as climate change is one of the toughest challenges that require full commitment from all relevant parties [3,4]. The carbon intensity contributed by the transportation sector in particular, plays a crucial role on environmental health [5–7].

Hence, efforts are being made to diversify the fuels used by vehicles and it is believed that this approach is one of the efficient solutions to address environmental problems resulting from fossil fuel combustion [8,9]. Biodiesels play an important role to fulfil the demand for alternative fuels, which will help reduce carbon emissions [10,11] due to the fact that biodiesels are biodegradable and environmentally friendly

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compared with fossil fuels. First-generation biodiesels are produced from edible vegetable oils such as sunflower, soybean, and palm oils. However, using edible vegetable oils for biodiesel production is not a feasible solution in the long term because this approach leads to global food insecurity and fluctuations in food prices [12–14]. For this reason, second-generation biodiesels come into play and these fuels are produced from non-edible plant-based oils such as *Calophyllum inophyllum* [15,16], *Ceiba pentandra* [17], *Schleichera triguga* [18], and *Pongamia pinnata* [19] oils. In addition, second-generation biodiesels are proven to have high biodiesel yields, good oxidation stabilities, and favourable cold flow properties. Furthermore, second-generation biodiesels fulfil the fuel specifications given in the ASTM D6751 and EN 14214 standards, rendering these fuels promising as diesel substitutes. However, the main disadvantage of second-generation biodiesels is their high acidity since these fuels are produced from non-edible feedstocks with high free fatty acid (FFA) content.

While improving the physicochemical properties of biodiesels is one of the key areas in biodiesel research, the cost of biodiesel production remains the primary interest in the biodiesel industry in order to achieve energy and environmental sustainability [12,20–22]. In this regard, waste cooking oils are among the low-cost feedstocks that can be easily collected from restaurants in the food and beverage industry. It is a great idea to recycle waste cooking oils because these oils can be used as a continuous supply in order to create useful products (biodiesels), which will help to fulfil the ever-increasing global energy demands. Converting waste cooking oils into biodiesels is a practical approach since the oils are recycled rather than being disposed into the landfill. In addition, this approach will help minimize environmental pollution caused by illegal handling of waste cooking oils. However, it is particularly challenging to convert waste cooking oils into biodiesels with high biodiesel yields, good oxidation stabilities, favourable cold flow properties, as well as low FFA content, trace elements, and acid values [23,24]. In order to address this issue, waste cooking oil can be blended with non-edible plant-based oil in order to improve the physicochemical properties of the biodiesel. In this study, waste cooking oil is blended with non-edible *Calophyllum inophyllum* oil in order to improve the physicochemical properties of the biodiesel which will fulfil the fuel specifications given in the ASTM D6751 and EN 14214 standards [25,26].

Besides the prices of the raw materials, the technology used for biodiesel production is equally important in order to produce biodiesel with competitive prices as those for diesel [27,28]. Biodiesels produced from conventional alkaline-catalysed transesterification requires long reaction times (typically more than 60 min) due to the heat transfer from the heating surface to the oil by conduction, convection, and radiation [29]. The mode of heat transfer between the surface and interior of the material is thermal conduction. The chemical reaction is dependent on the heat transfer efficiency, which is why conventional heating results in long reaction time in order to achieve a high conversion of crude oil into biodiesel. Therefore, it is crucial to use the appropriate technology for biodiesel production. In this regard, microwave irradiation-assisted alkaline-catalysed transesterification process helps improve the heat transfer efficiency, which results in shorter chemical reactions [30–32]. Microwave irradiation creates a magnetic field in the oil which forces the original random thermal motion of the reactants to follow the orientation of the electric field in order to generate heat. The heat transfer efficiency is dependent on the dielectric properties of the material used. The heating characteristics of a material subject to microwave irradiation are dependent on the ability of a specific substance to convert the electromagnetic energy into heat. Therefore, synthesis of organic materials such as oil with high ionic liquids such as potassium hydroxide (KOH)-methanol reagent mixture results in strong polarity, which will increase the efficiency of microwave heating. In addition, microwave irradiation-assisted alkaline-catalysed transesterification is a feasible biodiesel production method because the results are repeatable and reproducible at extreme temperatures and pressures.

Naor et al. [33] adopted microwave irradiation-assisted transesterification to produce biodiesel from *Nannochloropsis* microalgae oil in 2 min. Strontium oxide/silicon dioxide (SrO/SiO₂) nanopowders were used in the biodiesel synthesis. El Sherbiny et al. [34] produced *Jatropha* biodiesel by using both conventional and microwave irradiation-assisted transesterification methods. The results showed that the reaction rate was significantly reduced from 150 min (conventional transesterification) to 2 min (microwave irradiation-assisted transesterification). Xiang et al. [35] produced biodiesel from waste cooking oil using microwave irradiation-assisted transesterification with a fixed reaction time of 6 min. The optimum process parameters used in their study were (1) methanol/oil molar ratio: 9.67:1, (2) modified coal fly ash: 3.99%, and (3) reaction temperature: 66.2 °C. The corresponding biodiesel yield was 94.5%. Hong et al. [36] produced biodiesel from waste cooking oil using microwave irradiation-assisted transesterification and the fatty acid methyl ester (FAME) content was 96.8 (w/w)%. The following process parameters were used in their study: (1) reaction time: 6 min, (2) methanol/oil molar ratio: 8:1, (3) microwave power: 500 W, and (4) KOH catalyst concentration: 1 (w/w)%. In general, the results of these studies indicate that microwave irradiation-assisted transesterification is one of the promising methods for biodiesel production. Microwave irradiation provides unique thermal effects that are beneficial to chemical synthesis. Microwave irradiation boosts biodiesel yields, reduces the time of chemical reaction, improves the separation process, and reduces the net energy to produce biodiesel.

Response surface methodology (RSM) is an effective statistical tool used to examine the effects of various independent variables on the dependent variable. This tool greatly facilitates researchers in determining the optimum parameters by reducing the large number of experiments [37,38] that supposedly need to be performed with conventional experimental methods. Thus, RSM helps boost productivity and minimizes the time, material, and cost consumption required for optimization [39,40].

Due to the advantages of microwave irradiation-assisted transesterification, this method is adopted in this study to produce biodiesel from waste cooking oil blended with *Calophyllum inophyllum* oil. RSM based on the Box-Behnken experimental design is used to optimize the methanol/oil ratio, KOH catalyst concentration, stirring speed, and reaction time in order to maximize the biodiesel yield. RSM is also used to examine the interaction effects of the aforementioned process parameters on the biodiesel yield. The procedure used for biodiesel production using microwave irradiation-assisted transesterification and conventional transesterification is described in detail in this paper. The procedure used to determine the FAME content, linolenic methyl ester content, as well as glyceride and glycerol composition is also described in detail. The physicochemical properties of the biodiesel are measured and the effect of blending waste cooking oil with *Calophyllum inophyllum* oil on the physicochemical properties of the biodiesel is discussed. The results obtained from microwave irradiation-assisted transesterification and conventional transesterification are compared and discussed. The novelty of this work lies in the optimization of the process parameters for microwave irradiation-assisted alkaline-catalysed transesterification using RSM in order to maximize the yield of biodiesel produced from waste cooking oil blended with *Calophyllum inophyllum* oil. The use of a microwave reactor significantly reduces the reaction time and produces biodiesel of superior quality, as shown in the results of this study.

2. Material and methods

2.1. Materials

Crude *Calophyllum inophyllum* crude oil was purchased from Kebumen, Central Java, Indonesia, whereas the waste cooking oil was collected from various restaurants in the food and beverage industry. The following chemicals were used for biodiesel production: (1)

methanol (purity: 99.9%, grade: ACS reagent), (2) sulphuric acid (purity: > 98.9%), (3) ortho-phosphoric acid (purity: 85%), (4) anhydrous sodium sulphate (purity: 99%), (5) sodium hydrogen carbonate (purity: > 99%), (6) potassium hydroxide pellets (purity: 99%), (7) FAME mix C₈–C₂₄, (brand: Sigma-Aldrich, packaging: 100 mg, grade: analytical standard), (8) methyl nonadecanoate, C₁₉ (brand: Sigma-Aldrich, purity: > 99.5%), (9) 1,2,4-butanetriol, (10) glyceryl mononadecanoate, mono C₁₉, (11) glyceryl dinonadecanoate, di C₃₈, (12) glyceryl trinonadecanoate, tri C₅₇, and (13) Fluka® Analytical phenolphthalein solution (1% in ethanol). These chemicals were purchased from It Tech Research (M) Sdn. Bhd., Malaysia.

2.2. Experimental set-up and procedure

The collected waste cooking oil was refined using a filter in order to remove solid impurities and then heated to remove traces of water. Next, the waste cooking oil was mixed with *Calophyllum inophyllum* oil at a volume ratio of 7:3. This oil sample was labelled as W70CI30. The free fatty acid (FFA) content of the oil mixture was measured and it was found that the FFA content was 9.92%, which was more than the permissible limit (2%) for the transesterification process. Therefore, the W70CI30 oil mixture was degummed with 5% of diluted ortho-phosphoric acid (20%) in a 2-L double-jacketed reactor set at a temperature of 60 °C and stirring speed of 1500 rpm for 30 min. The degummed oil was then esterified with 70 (v/v)% of methanol and 1.5 (v/v)% of sulphuric acid (H₂SO₄) in a 2-L double-jacketed reactor set at a temperature of 60 °C and stirring speed of 1500 rpm for 2 h. The physico-chemical properties (kinematic viscosity at 40 °C, dynamic viscosity at 40 °C, density at 40 °C, density at 15 °C, oxidation stability, calorific value, and acid value) of the waste cooking oil, *Calophyllum inophyllum* oil, and W70CI30 oil mixture are presented in Table 1. The schematic diagram of the experimental set-up for degumming and esterification processes is shown in Fig. 1. It is found that the FFA content of the esterified W70CI30 oil is reduced to less than 2%, indicating that the oil can be used for the transesterification reaction. Anton Paar Monowave 400 high-performance microwave reactor with Autosampler MAS24 was used because it is suitable for small-scale microwave synthesis, which makes it an ideal equipment for optimization studies.

2.3. Microwave irradiation-assisted alkaline-catalysed transesterification

As mentioned previously, Anton Paar Monowave 400 high-performance microwave reactor with Autosampler MAS24 was used for the microwave irradiation-assisted alkaline-catalysed transesterification, where the esterified W70CI30 oil was converted into fatty acid methyl ester. The technical specifications and photograph of the microwave reactor are presented in Table 2 and Fig. 2, respectively.

The Anton Paar Monowave 400 microwave reactor with

Table 1

Physicochemical properties of the waste cooking oil, *Calophyllum inophyllum* oil, and W70CI30 oil mixture.

Properties	Units	Waste cooking oil	<i>Calophyllum inophyllum</i> oil	W70CI30 oil mixture
Kinematic viscosity at 40 °C	mm ² /s	49.05	65.48	54.12
Dynamic viscosity at 40 °C	mPa s	44.27	60.73	49.27
Density at 40 °C	kg/m ³	902.7	927.5	910.5
Density at 15 °C	kg/m ³	904.4	929.2	912.2
Oxidation stability	h	1.26	10.3	3.25
Calorific value	MJ/kg	38.59	37.16	37.29
Acid value	mg KOH/g	2.30	63.05	19.75

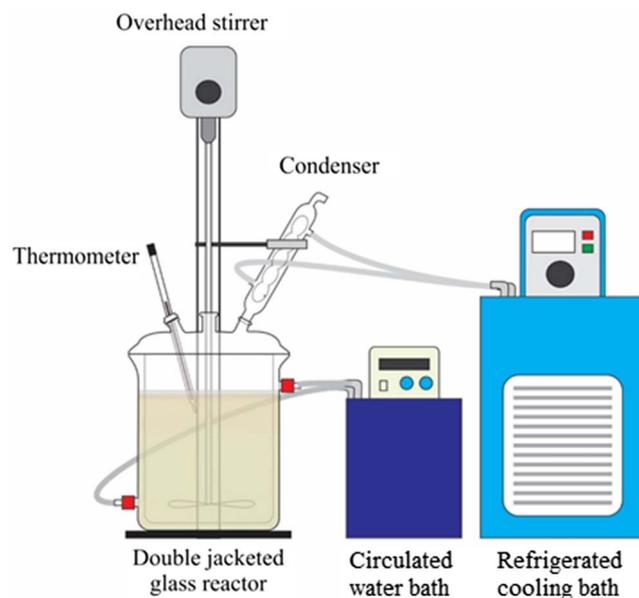


Fig. 1. Schematic diagram of the experimental set-up for degumming and esterification processes.

Table 2

Technical specifications of the Anton Paar Monowave 400 high-performance microwave reactor.

Specifications	Monowave 400
Maximum filling volume	20 mL for 30 mL vial
Maximum operation pressure	30 bars (435 psi)
Maximum infrared temperature	300 °C
Maximum fibre-optic temperature	300 °C
Maximum power	850 W
Vial material	Borosilicate glass
Cap material	Polyetheretherketone (PEEK)
Camera	Integrated
Autosampler MAS24	Yes
Seal material	Teflon-coated silicone

Autosampler MAS 24 is equipped with infrared sensors for temperature control, pressure sensors to monitor the reaction that takes place in the closed vessel, and a built-in magnetic stirrer which provides optimum agitation of the reaction mixture. The temperature and pressure profiles during the experiments were automatically recorded by the microwave reactor. The heating profile of the microwave reactor consists of three steps: (1) the closed vessel is heated to the set temperature, (2) the set temperature is kept constant over a specific period, and (3) the closed vessel is cooled to a set temperature in order to terminate the chemical reaction. During the reaction, the power output was controlled based on the temperature chosen for the experiment. The power output was monitored continuously in order to prevent the reaction from becoming exothermic during the microwave irradiation-assisted transesterification process.

2.4. Optimization of microwave irradiation-assisted alkaline-catalysed transesterification

2.4.1. Box-Behnken experimental design

The parameters of the microwave irradiation-assisted alkaline-catalysed transesterification process chosen for optimization are the methanol/oil ratio, KOH catalyst concentration, speed of rotation of the magnetic stirrer (stirring speed), and duration of microwave irradiation (reaction time), as shown in Table 3. RSM based on the Box-Behnken experimental design was used to determine the optimum process parameters (independent variables) and study the effect of each

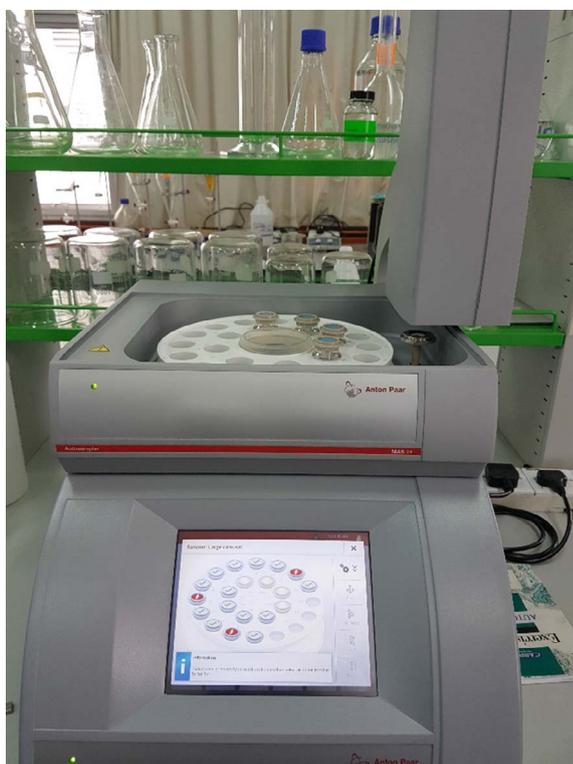


Fig. 2. Anton Paar Monowave 400 high-performance microwave reactor.

Table 3
Parameters (independent variables) chosen for optimization of microwave irradiation-assisted alkaline-catalysed transesterification of W70CI30 oil mixture.

Process parameters	Units	Levels		
		-1	0	1
(A) Methanol/oil ratio	(v/v)%	40	55	70
(B) KOH catalyst concentration	(w/w)%	0.4	0.7	1.0
(C) Stirring speed	rpm	600	800	1000
(D) Reaction time	min	2	6	10

parameter on the W70CI30 methyl ester yield (dependent variable). Since there are four process parameters with three coded levels for each parameter, the total number of experimental runs is 29, as shown in Table 4. The experiments were designed based on the heating profile described in the preceding section: (1) the closed vessel was heated to 100 °C in 2 min, (2) the closed vessel was held at the set temperature over a specific period (this specific period is the duration of microwave irradiation (holding time) or rather, the reaction time (D) investigated in this study), and (3) the closed vessel was cooled down to 55 °C in order to terminate the transesterification process. The response variable (dependent variable) chosen in this study is the experimental W70CI30 methyl ester yield. Response surface regression model was used to fit the data obtained from the Box-Behnken design of experiments:

$$Q = c_0 + \sum_{i=1}^k c_i Y_i + \sum_{i=1}^k c_{ii} Y_i^2 + \sum_{i,i>j}^k c_{ij} Y_i Y_j + e \tag{1}$$

In Eq. (1), Q is the response variable (dependent variable), Y_i is the predictor variable, (independent variable), c_0 is a constant, c_i is the regression coefficient of the linear i th predictor variable, c_{ii} is the regression coefficient of the quadratic i th predictor variable, c_{ij} is the regression coefficient of the product term (product of i th and j th predictor variables), k is the number of factors (predictor variables) studied and optimized in the experiment, and e is the value that is attributed to the uncertainty of Q.

Analysis of variance (ANOVA) was carried out to evaluate significance of the model and all terms in the model within the 95% confidence interval. Two-dimensional array plots and three-dimensional response surface plots were also plotted in order to visualize the main and interaction effects of the process parameters on the W70CI30 methyl ester yield.

2.5. Determination of the FAME content and linolenic acid methyl ester content according to the EN 14103:2011 standard test method

Gas chromatograph fitted with a flame ionization detector was used to determine the FAME content and linolenic acid methyl ester content of the W70CI30 methyl ester according to the EN 14103:2011 standard test method. This method is also suitable to determine the FAME content of biodiesels containing methyl esters between C_6 and C_{24} as well as to determine the linolenic acid methyl ester content ($C_{18:3}$). According to the EN 14103:2011 method, the FAME content should be greater than 90 (w/w)% whereas the linolenic acid methyl acid content should be within a range of 1–15 (w/w)%. This method is suitable for use with the gas chromatograph equipped with HP-INNOWax high-polarity column (length \times inner diameter \times film thickness: 30 m \times 0.25 mm \times 0.25 μ m, stationary phase: polyethylene glycol). Helium gas was used as the carrier gas. The operating conditions for the gas chromatography measurements used to determine the FAME content and linolenic acid methyl ester content according to the EN 14103:2011 standard test method are presented in Table 5. The FAME content and linolenic acid methyl ester content were determined using Eqs. (2) and (3) respectively:

$$FAME((w/w)\%) = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{W_{EI}}{W} \times 100 \tag{2}$$

$$L((w/w)\%) = \frac{A_L}{A_{EI}} \times \frac{W_{EI}}{W} \times 100 \tag{3}$$

Here, FAME represents the fatty acid methyl ester content in percent by weight ((w/w)%), $\sum A$ is the total peak area from methyl ester $C_{6:0}$ to $C_{24:0}$, A_{EI} is the peak area corresponding to methyl nonadecanoate (methyl ester C_{19}), W_{EI} is the weight of the methyl nonadecanoate (C_{19}) chosen as the internal standard in milligrams (mg), W is the weight of the sample in milligrams (mg), L represents the linolenic acid methyl ester in percent by weight ((w/w)%), and A_L is the peak area corresponding to the linolenic acid methyl ester.

2.6. Determination of glycerol, monoglycerides, diglycerides, and triglycerides according to the EN 14105:2011 standard test method

Agilent Cool On-Column inlet was used to determine the glycerol, monoglyceride, diglyceride, and triglyceride contents in the W70CI30 methyl ester. The operating conditions used to determine the glycerol and glycerides according to the EN 14105:2011 standard test method are presented in Table 6. To prepare the sample for analysis, 50 mg of the sample was measured and added into a 12-mL amber vial, followed by the addition of 40 μ L of 1,2,4-butanetriol (internal standard solution 1 or IS1), 100 μ L of standard glyceride stock solution (G3440-85018), 100 μ L of pyridine, and lastly, 100 μ L of N-methyl-N-trimethylsilyltri-fluoroacetamide (MSTFA). Next, the amber vial was sealed and shaken vigorously to ensure that a homogeneous liquid mixture was obtained. The amber vial was stored in a dark area at room temperature (25–30 °C) for 15 min. Next, 4 mL of n-heptane was added into the solution using a graduated cylinder and then 1.5 mL of the solution was transferred into a gas chromatography amber vial. Next, 1 μ L of the solution was injected into the Agilent Cool On-Column inlet for analysis and the glycerol and glycerides were determined using the following equations:

Table 4

Box-Behnken experimental design of the microwave irradiation-assisted alkaline-catalysed transesterification of W70CI30 oil mixture with four process parameters and three coded levels for each parameter.

Experimental run	Methanol/oil ratio, A ((v/v)%)	KOH catalyst concentration, B ((w/w)%)	Stirring speed, C (rpm)	Reaction time, D (min)	Experimental W70CI30 methyl ester yield (%)	Predicted W70CI30 methyl ester yield (%)
1	55	0.4	1000	6	93.72	93.55
2	55	1.0	1000	6	95.09	95.90
3	40	1.0	800	6	88.70	88.68
4	55	0.7	1000	10	95.12	95.17
5	40	0.7	600	6	89.15	89.15
6	55	1.0	800	10	93.85	93.76
7	55	0.4	800	2	90.63	90.51
8	40	0.7	800	2	87.71	87.66
9	40	0.4	800	6	85.35	86.16
10	40	0.7	800	10	88.77	88.61
11	70	0.7	800	10	92.73	92.77
12	70	1.0	800	6	93.54	92.95
13	55	0.7	800	6	96.03	96.49
14	55	0.7	800	6	96.72	96.49
15	55	0.7	800	6	96.82	96.49
16	70	0.4	800	6	90.30	90.54
17	70	0.7	1000	6	94.05	93.83
18	70	0.7	800	2	92.01	92.15
19	55	0.7	600	10	96.03	96.14
20	70	0.7	600	6	94.50	94.88
21	55	1.0	600	6	95.50	95.66
22	55	0.7	600	2	93.85	94.03
23	55	1.0	800	2	94.27	94.00
24	40	0.7	1000	6	91.50	90.91
25	55	0.7	800	6	96.25	96.49
26	55	0.7	1000	2	95.59	95.71
27	55	0.4	800	10	92.26	92.32
28	55	0.7	800	6	96.62	96.49
29	55	0.4	600	6	93.90	93.08

Table 5

Operating conditions for the gas chromatography measurements used to determine the FAME content and linolenic methyl ester content in the W70CI30 methyl ester according to the EN 14103:2011 standard test method.

Parameters	Specifications
Capillary column	Agilent HP-INNOWax column Length × inner diameter × film thickness: 30 m × 0.25 mm × 0.25 μm
Oven temperature	60 °C, hold for 2 min 60–200 °C at 10 °C/min 200–240 °C at 5 °C/min 240 °C, hold for 7 min Post-run at 255 °C for 0.5 min
Carrier gas	Helium
Helium pressure	70 kPa
Flow rate	1.5 mL/min
Split flow	100 mL/min
Split ratio	100:1.5
Injector temperature	250 °C
Detector temperature	250 °C
Type of injector	Split/splitless
Type of detector	Flame ionization detector
Injection volume	1 μL
Flame ionization detector makeup gas	Helium
FAME standard	FAME mix C ₈ –C ₂₄ , Brand: Sigma-Aldrich, Packaging size: 100 mg
Internal standard	Methyl nonadecanoate, C ₁₉ , Brand: Sigma-Aldrich, Purity: > 99.5%

$$\text{Free glycerol}((w/w)\%), G = \left[a_G \left(\frac{A_G}{A_{EI1}} \right) + b_G \right] \times \left(\frac{M_{EI}}{m} \right) \times 100 \quad (4)$$

$$\text{Monoglycerides}((w/w)\%), M = \left(\frac{A_{Mono}}{A_{MonoC19}} \right) \times \left(\frac{M_{MonoC19}}{m} \right) \times 100 \quad (5)$$

Table 6

Operating conditions for the gas chromatography measurements used to determine the glycerol and glycerides in the W70CI30 methyl ester according to the EN 14105:2011 standard test method.

Parameters	Specifications
Column	Agilent VF-5ht Ultimetall Length × inner diameter × film thickness: 15 m × 0.32 mm × 0.1 μm
Oven temperature	50 °C, hold for 1 min 50–180 °C at 15 °C/min 180–230 °C at 7 °C/min 230–370 °C at 10 °C/min 370 °C, hold for 15 min
Carrier gas	Helium
Helium pressure	80 kPa
Flow rate	2.5 mL/min
Injector temperature	Track oven
Detector temperature	380 °C
Type of injector	Cool on-column
Type of detector	Flame ionization detector
Injection volume	1 μL
Flame ionization detector makeup gas	Helium
Internal standard for glycerol	1,2,4-Butanetriol
Internal standard for glycerides	Glyceryl mononadecanoate (mono C ₁₉) Glyceryl dinonadecanoate (di C ₃₈) Glyceryl trinonadecanoate (tri C ₅₇)

$$\text{Diglycerides}((w/w)\%), D = \left(\frac{A_{Di}}{A_{DiC38}} \right) \times \left(\frac{M_{DiC38}}{m} \right) \times 100 \quad (6)$$

$$\text{Triglycerides}((w/w)\%), T = \left(\frac{A_{Tri}}{A_{TriC57}} \right) \times \left(\frac{M_{TriC57}}{m} \right) \times 100 \quad (7)$$

$$\text{Total glycerol}((w/w)\%) = G + 0.255M + 0.146D + 0.103T \quad (8)$$

Here, a_G and b_G represent the regression coefficients of the calibration

function of glycerol, A_G is the peak area of glycerol, A_{EI} is the peak area of the internal standard, 1,2,4-butanetriol, M_{EI} is the weight of the 1,2,4-butanetriol in milligrams (mg), A_{Mono} , A_{Di} , and A_{Tri} are the sum of the peak areas of the monoglycerides, diglycerides, and triglycerides, respectively, $A_{MonoC19}$ is the peak area of the internal standard, mono C₁₉, $M_{MonoC19}$ is the weight of mono C₁₉ in milligrams (mg), A_{DiC38} is the peak area of the internal standard, di C₃₈, M_{DiC38} is the weight of di C₃₈ in milligrams (mg), A_{TriC57} is the peak area of the internal standard, tri C₅₇, M_{TriC57} is the weight of tri C₅₇ in milligrams (mg), and m is the weight of the biodiesel sample in milligrams (mg).

2.7. Measurement of physicochemical properties

The physicochemical properties of the waste cooking oil biodiesel and W70CI30 biodiesels produced from microwave irradiation-assisted transesterification and conventional transesterification methods were measured and the results were compared with those for *Ceiba pentandra-Nigella sativa* biodiesel and diesel. The physicochemical properties (kinematic viscosity at 40 °C, density at 15 °C, acid value, calorific value, oxidation stability, flash point, copper strip corrosion, Conradson carbon residue) and cold flow properties (pour point, cloud point, and cold filter plugging point) were measured according to the ASTM D6751 and EN 14214 standards.

3. Results and discussion

3.1. Excellent parameter control by the high-performance microwave reactor

The microwave reactor provides direct in-core heating to the glass vial, which ensures an energy-efficient process. Fig. 3(a) shows the glass vial partially filled with esterified W70CI30 oil (bottom layer) and KOH catalyst dissolved in methanol (top layer). A magnetic stirring bar was placed gently into the glass vial, which ensures homogeneous mixing of the reaction mixture in the microwave reactor during the transesterification process. The KOH catalyst-methanol mixture is essential to accelerate the transesterification reaction, which will prevent biases in the experiments since all of the processes take place within several minutes. Fig. 3(b) shows the W70CI30 methyl ester produced from the microwave irradiation-assisted alkaline-catalysed transesterification process. The transparent glass vial reveals that the transesterification reaction is complete, with the formation of W70CI30 methyl ester at the

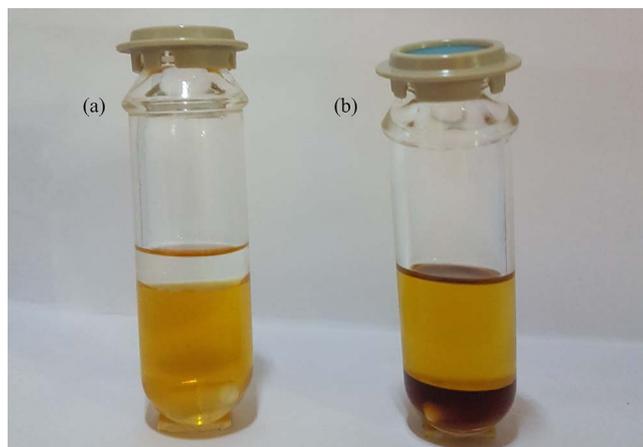


Fig. 3. (a) Esterified W70CI30 oil before the glass vial is placed in the microwave reactor, where the top layer consists of KOH catalyst dissolved in methanol and the bottom layer is the esterified oil W70CI30 oil; (b) W70CI30 methyl ester after the glass vial is removed from the microwave reactor, where the top layer is the W70CI30 methyl ester whereas the bottom layer is a mixture of glycerol, KOH catalyst, and methanol. Note that the magnetic stirring bar used to ensure homogeneous mixing of the reactants is present at the bottom of the glass vial.

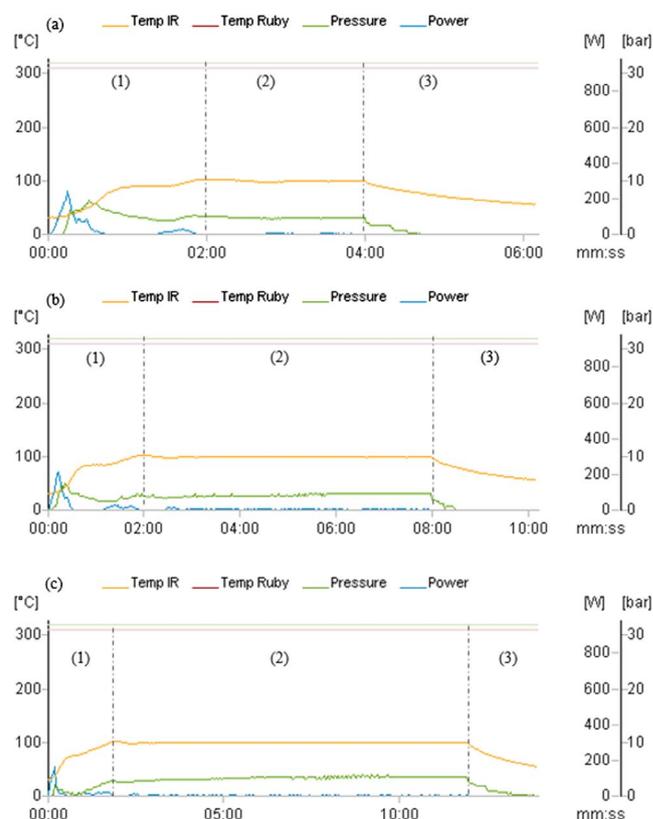


Fig. 4. Heating profile of the reaction mixture which is heated to 100 °C and then held at this temperature for (a) 2 min (Run 7), (b) 6 min (Run 1), and (c) 10 min (Run 4).

top layer whereas the bottom layer consists of methanol, glycerol, KOH catalyst, and other impurities. As expected, the transesterification reaction is completed less than 10 min with the aid of the microwave reactor unlike conventional transesterification which typically requires more than 60 min to complete. In addition, the parameters of the microwave reactor (infrared temperature, fibre optic temperature, operating pressure, and power) can be measured and monitored accurately throughout the experiment, which ensures excellent parameter control.

Fig. 4 shows the heating profiles of reaction mixture, which include the infrared temperature, operating pressure, and power recorded during the experiment. It can be seen from the heating profiles that the heating process consists of three steps: (a) the closed vessel is heated to 100 °C for 2 min, (b) the temperature of the closed vessel is maintained at 100 °C within a specific period, and (c) the closed vessel is then cooled down to a touchable surface temperature of 55 °C. The heating profiles vary in terms of the holding time (i.e. reaction time) in order to investigate its effect on the W70CI30 methyl ester yield. The microwave reactor features a built-in magnetic stirrer which ensures proper agitation and uniform temperature distribution throughout the reaction mixture. The power output shown in the heating profile indicates the amount and continuous power output needed in order to reach the required temperature and hold the set reaction temperature. This means that the mean power output is automatically adjusted by the microwave reactor in order to maintain the temperature. This will prevent the reaction from becoming exothermic and reduce the formation of hot spots.

3.2. Optimization of the microwave irradiation-assisted alkaline-catalysed transesterification process parameters using RSM

The process parameters optimized in this study are the methanol/oil ratio, KOH catalyst concentration, stirring speed, and reaction time in order to maximize the W70CI30 methyl ester yield. The results obtained

Table 7
ANOVA results for the quadratic response surface regression model (Partial sum of squares — Type III).

Source	Coefficient	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
Model	96.49	250.7	14	17.91	68.69	< .0001
A: Methanol/oil ratio	2.16	56.07	1	56.07	215.07	< .0001
B: KOH catalyst concentration	1.23	18.21	1	18.21	69.86	< .0001
C: Stirring speed	0.18	0.37	1	0.37	1.43	.2509
D: Reaction time	0.39	1.85	1	1.85	7.09	.0186
AB	−0.003	3.5(10 ^{−3})	1	3.53(10 ^{−3})	0.014	.9090
AC	0.70	1.97	1	1.97	7.57	.0156
AD	0.085	0.029	1	0.029	0.11	.7453
BC	0.057	0.013	1	0.013	0.049	.8277
BD	−0.51	1.04	1	1.04	4	.0653
CD	−0.66	1.75	1	1.75	6.72	.0213
A ²	−4.63	138.91	1	138.91	532.85	< .0001
B ²	−2.28	33.66	1	33.66	129.12	< .0001
C ²	0.33	0.73	1	0.73	2.79	.1173
D ²	−1.56	15.82	1	15.82	60.69	< .0001
Residual		3.65	14	0.26		
Lack of fit		3.21	10	0.32	2.88	.1595
Pure error		0.44	4	0.11		
Correlated total sum of squares		254.35	28			
Standard deviation	0.51					
Mean	93.12			Adjusted R ²		.9713
Coefficient of variation	0.55			Predicted R ²		.9247
R ²	0.9857			Adequate precision		28.128

p is the significance level

If *p* < .05, this means that the model or parameter is significant.

from the Box-Behnken experimental design (29 experimental runs) and the results predicted using the response surface regression model (Eq. (1)) are presented in Table 4. The results from the Box-Behnken experimental design were subjected to multiple regression analyses and it is found that the quadratic response surface regression model is the best estimator. Hence, the quadratic response surface regression model used to predict the W70CI30 methyl ester yield in terms of the process parameters (coded factors) is given by:

$$Y = 96.49 + 2.16A + 1.23B + 0.18C + 0.39D - 0.030AB - 0.7AC - 0.085AD - 0.057BC - 0.51BD - 0.66CD - 4.63A^2 - 2.28B^2 + 0.33C^2 - 1.56D^2 \quad (9)$$

where *Y* represents the W70CI30 methyl ester yield and *A*, *B*, *C*, and *D* represent the methanol/oil ratio, KOH catalyst concentration, stirring speed, and reaction time, respectively.

Table 7 shows the ANOVA results for the quadratic response surface regression model and the significance of the regression coefficients in order to maximize the W70CI30 methyl ester yield. The *F*-value of the model is 68.69 and its *p*-value is less than .0001, indicating that the model is significant in predicting the W70CI30 methyl ester yield. The lack of fit *F*-value is 3.21, which is not significant relative to the pure error. This indicates that there is 15.95% probability that the lack of fit *F*-value is due to noise and its corresponding *p*-value is .1595, indicating that the model fits well with the experimental data. The coefficient of determination (*R*²) is found to be 0.9857, which indicates that 98.57% of the variability in the W70CI30 methyl ester yield is explained by this model. This shows that the predicted W70CI30 methyl ester yield values are close to those from Box-Behnken experimental design, which confirms the reliability of the model. The adequate precision is a measure of the signal to noise ratio and it is found that the adequate precision is 28.128, which is significantly greater than 4, and this indicates that the model is adequate to navigate through the design space and predict the W70CI30 methyl ester yield. The difference between the predicted *R*² (0.9247) and adjusted *R*² (0.9713) is less than 0.2, which indicates there is reasonable agreement in the regression polynomial.

The model terms are considered to be significant if *p* < .05 and the model terms that fulfil this criterion are *A* (methanol/oil ratio), *B* (KOH catalyst concentration), *D* (reaction time), *AC* (methanol/oil ratio and stirring speed), *CD* (stirring speed and reaction time), *A*² (quadratic effect of methanol/oil ratio), *B*² (quadratic effect of KOH catalyst

concentration), and *D*² (quadratic effect of reaction time). The aforementioned terms are the significant terms that influence the W70CI30 methyl ester yield. Based on the results in Table 7, the stirring speed (*C*) is not a factor that has a significant effect on the W70CI30 methyl ester yield.

The perturbation plot is plotted, as shown in Fig. 5(b). Perturbation plot helps to identify the priority of each factor (process parameter) and its effect while other factors are kept constant. The curvature shown in Fig. 5(b) reflects the sensitivity of factors *A* (methanol/oil ratio: 55 (v/v)%), *B* (KOH catalyst concentration: 0.7 (w/w)%), *C* (stirring speed: 800 rpm), and *D* (reaction time: 6 min) on the W70CI30 methyl ester yield. In general, a steeper slope in the perturbation plot indicates that the factor has a more pronounced effect on the W70CI30 methyl ester yield compared with a flatter slope. Hence, it is evident from the perturbation plot that factor *A* has the most pronounced effect on the W70CI30 methyl ester yield (since it has the steepest slope) followed by factors *B* and *D*. Similar to the results in Table 7, factor *C* does not have a significant effect on the W70CI30 methyl ester yield judging from its flatter slope. The effect of each process parameter and the interaction effects of the process parameters on the W70CI30 methyl ester yield were also investigated in this study in order to gain an in-depth understanding on how these process affects the conversion of W70CI30 oil into methyl ester and the results are presented and discussed in the following sub-sections.

3.2.1. Main effects of the process parameters on the W70CI30 methyl ester yield

3.2.1.1. Effect of methanol/oil ratio. Fig. 6(a) shows the effect of methanol/oil ratio on the W70CI30 methyl ester yield. The methanol/oil ratio is varied from 40 to 70 (v/v)% whereas the KOH catalyst concentration, stirring speed, and reaction time are kept fixed at 0.7 (w/w)%, 800 rpm, and 6 min, respectively. The methyl ester yield is lowest (~90.00%) when the methanol/oil ratio is at the lowest coded level (−1) whereas the methyl ester yield is highest (96.82%) when the methanol/oil ratio is at the intermediate coded level (0). The methyl ester yield decreases to ~94.00% when the methanol/oil ratio is 70 (v/v)%. The highest methyl ester yield (97.40%) is achieved when the methanol/oil ratio is ~59 (v/v)% while other process parameters are invariant.

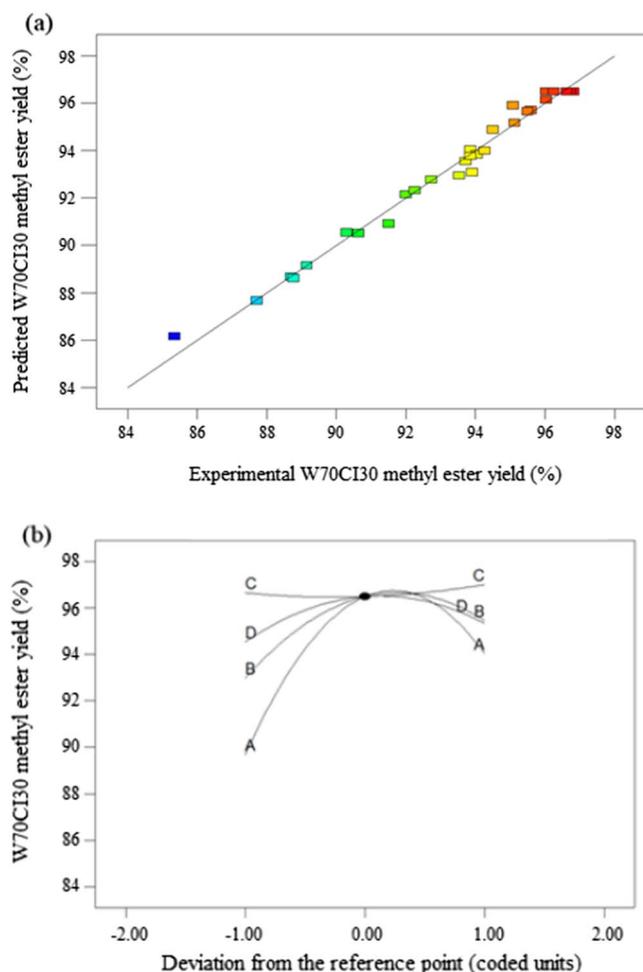


Fig. 5. (a) Comparison between the predicted and experimental W70CI30 methyl ester yield; (b) Perturbation plot.

Determining a suitable methanol/oil ratio is indeed important to determine the quantity of the methyl ester produced. If the methanol/oil ratio is insufficient for transesterification, this will reduce the methyl ester yield because the glycerides are not converted into fatty acid methyl ester. The presence of methanol increases the solubility and compatibility of the KOH catalyst in the reaction mixture, which favours forward transesterification reaction and boost the methyl ester yield. In addition, in this study, the microwave irradiation-assisted alkaline-catalysed transesterification is carried out in a closed vessel, which prevents evaporation of the methanol, unlike conventional alkaline-catalysed transesterification. For this reason, if the methanol/oil ratio is exceptionally high, this will significantly reduce the quantity of methyl ester produced, which may be due to the high solubility of glycerol, which complicates the separation and purification processes [41–44]. Thus, the methanol/oil ratio used during the transesterification process is crucial to achieve high methyl ester yields. Excessive amounts of methanol are unnecessary and wasteful because this will reduce the methyl ester yield, inhibit the recovery of glycerol, and increase the cost of biodiesel production, especially when microwave reactor is used for biodiesel production.

3.2.1.2. Effect of KOH catalyst concentration. The KOH catalyst concentration is varied from 0.4 to 1.0 (w/w)% and its effect on the W70CI30 methyl ester yield is shown in Fig. 6(b). KOH is an excellent choice as a homogeneous catalyst because it promotes methyl ester yield due to its higher catalytic activity in methanol solution. It is crucial to determine the appropriate amount of KOH catalyst for transesterification reaction since a high KOH catalyst concentration

will result in overwhelming amounts of free ions in the reaction mixture, which leads to massive collisions of ions and reduces the activation energy needed by the oil to increase the rate of reaction. On the other hand, when the reaction mixture reaches an equilibrium state, excessive amounts of KOH catalyst does not result in a methyl ester yield of 100% since the transesterification reaction is reversed. The reaction becomes endothermic during the cooling process based on Le Chatelier's Principle. Therefore, excessive amounts of catalyst used will cause a shift of equilibrium of the reaction mixture towards backward reaction, which will reduce the conversion of oil into methyl ester and glycerol. Moreover, excessive usage of KOH catalyst will result in formation of metal salt (soap), which makes it difficult to separate soap, glycerol, and biodiesel during the washing process. The presence of water and large amounts of KOH catalyst will result in a cloudy mixture with water, biodiesel, and glycerol as its constituents, which complicates the separation process and reduces the biodiesel yield [45–51]. This was also observed by Muthukumaran et al. [37], who found that the *Madhuca indica* methyl ester yield was maximized when the catalyst concentration was 1 (w/w)%. However, the *Madhuca indica* methyl ester yield decreased when the catalyst concentration was increased from 1 to 4 (w/w)%. Similar results were also reported by Verma et al. [43] who observed that the Karanja biodiesel yield decreased by 20% when the catalyst concentration was increased from 1.30 to 1.52 (w/w)%. Excessive amounts of catalyst will increase the time required to wash and purify the biodiesel, which is highly unfavourable in regions with water scarcity. Even more alarming, washing biodiesels containing large amounts of catalyst will lead to water pollution when the washing water is disposed into water bodies in the absence of proper industrial wastewater treatment facilities. For this reason, it is essential to determine the suitable KOH catalyst concentration prior to industrial-scale production of biodiesel from waste cooking oil in order to impede illegal disposal of waste cooking oil, reduce wastage of KOH catalyst, and prevent contamination of water bodies.

3.2.1.3. Effect of stirring speed. Fig. 6(c) shows the effect of stirring speed on the W70CI30 methyl ester yield. It can be observed that stirring speed does not have a marked effect on the methyl ester yield. However, the methyl ester yield is slightly higher at a stirring speed of 600 rpm compared with that at 1000 rpm. Even though the effect of stirring speed is not significant in this study, it is still important to control the stirring speed during the transesterification reaction because this will ensure homogeneous mixing between the oil, methanol, and catalyst, which in turn, accelerates the rate of reaction [25,52,53]. In addition, stirring speed is an essential parameter of the transesterification process because without any mixing, the transesterification reaction will be inhibited, which prolongs the reaction time. Therefore, the stirring speed plays a vital role to accelerate the rate of reaction by promoting reaction between the triglycerides and alcohol in the presence of catalyst. The stirring speed ensures thorough mixing of the reactants, ensures uniform temperature distribution of the reaction mixture, and promotes collision of the particles travelling through the medium (i.e. mass diffusion).

3.2.1.4. Effect of reaction time. The reaction time is an important parameter which needs to be optimized because it plays a critical role in influencing the methyl ester yield. It is expected that the reaction time will be reduced by half when the temperature of the reaction mixture is increased by 10 °C. This is why the W70CI30 methyl ester yield is significantly influenced by the holding time of the microwave reactor. Fig. 6(d) shows the W70CI30 methyl ester yield when the reaction time is varied from 2 to 10 min. It shall be noted that the methanol/oil ratio, KOH catalyst concentration, and stirring speed are kept fixed at 55 (v/v)%, 0.7 (w/w)%, and 800 rpm, respectively. It is found that the methyl ester yield increases by 2% when the reaction time is extended to 6 min. However, the methyl ester yield decreases by 1% when the reaction

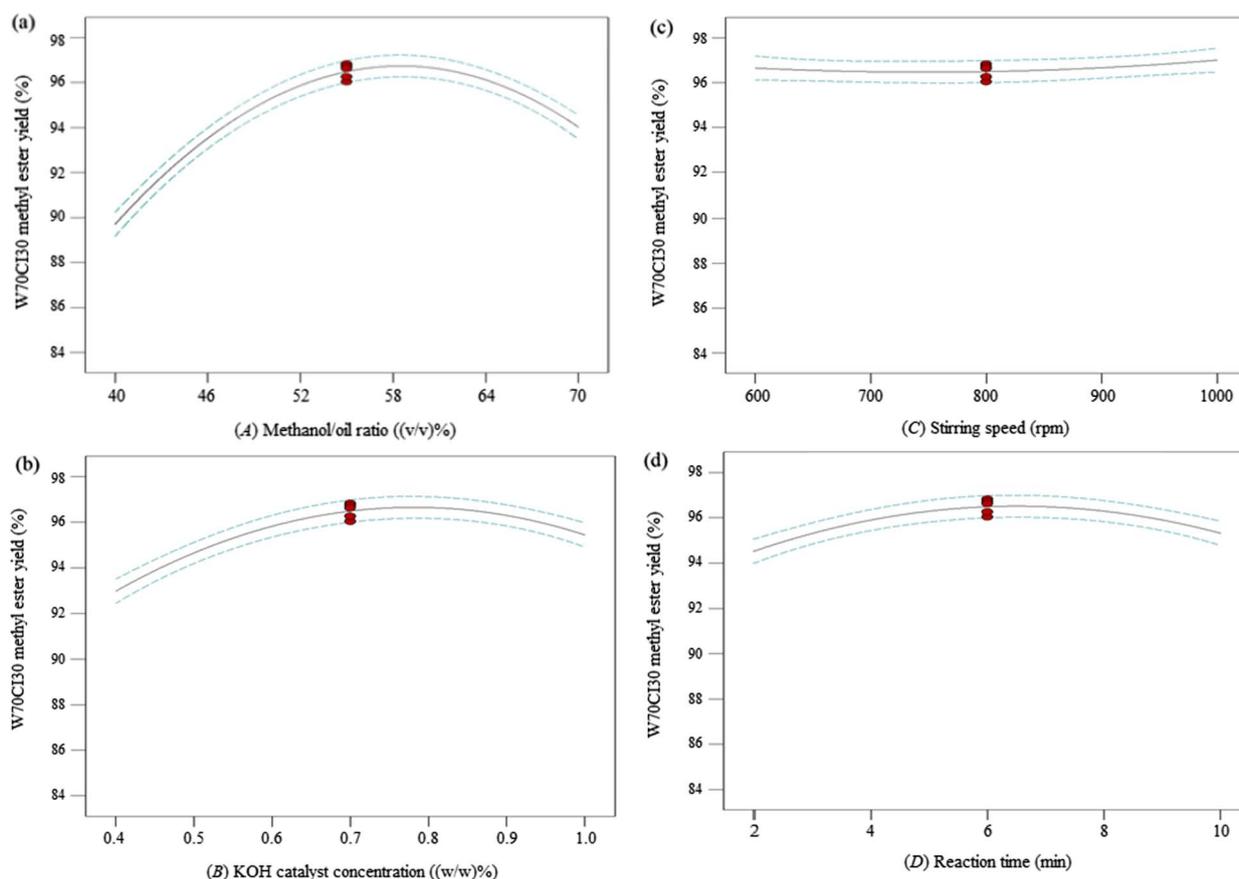


Fig. 6. Effect of (a) methanol/oil ratio, (b) KOH catalyst concentration, (c) stirring speed, and (d) reaction time on the W70CI30 methyl ester yield.

time is further extended to 10 min. This indicates that the transesterification reaction is complete and the reaction mixture reaches an equilibrium state at 6 min. In general, the reaction time significantly affects the amount of methyl ester produced and sufficient time is needed to ensure complete diffusion between the methanol, oil, and KOH catalyst, as well as increase the rate of reaction. In general, increasing the reaction time will boost the methyl ester yield by enhancing diffusivity of the reaction mixture, which facilitates each step in the transesterification process (conversion of triglycerides into diglycerides, diglycerides into monoglycerides, and lastly, monoglycerides into methyl ester) [54]. While examining the effect of the individual process parameters provides some insight on how these parameters affect the W70CI30 methyl ester yield, it does not provide a holistic view on the interactions between these parameters and their effect on the W70CI30 methyl ester yield. For this reason, three-dimensional response surface plots were plotted in order to visualize the interaction effects of the process parameters on the W70CI30 methyl ester yield.

3.2.2. Interaction effects of the process parameters on the W70CI30 methyl ester yield

Three-dimensional response surface plots are plotted in order to visualize the interaction effects of the process parameters on the W70CI30 methyl ester yield, as shown in Fig. 7. In general, it is expected that the W70CI30 methyl ester yield will increase at the optimum process parameters; however, the methyl ester yield will decrease if the process parameters are increased beyond the optimum values. The interaction effects of the process parameters are explained in detail in the following sub-sections.

3.2.2.1. Interaction effect of methanol/oil ratio and KOH catalyst concentration.

Fig. 7(a) shows the three-dimensional response surface

plot of the W70CI30 methyl ester yield as a function of the methanol/oil ratio and KOH catalyst concentration based on the conditions defined by the Box-Behnken experimental design. It is found that a high methyl ester yield (97.40%) is achieved at a methanol/oil ratio of 59.60 (v/v)% and KOH catalyst concentration of 0.774 (w/w)%, as evidenced from the red region in the response surface plot. Moreover, a high methyl ester yield (96.82%) is achieved at Run 15 when the methanol/oil ratio and KOH catalyst concentration are 55 (v/v)% and 0.7 (w/w)%, respectively. It is apparent that these process parameters are close to the optimum values. The catalyst concentration is known to be an important factor in order to maximize the methyl ester yield. By increasing the KOH catalyst concentration to 1 (w/w)%, the methyl ester yield decreases due to higher amount of catalyst in the reaction mixture, which results in emulsification when water is introduced to the reaction mixture. Emulsification is highly undesirable because it leads to difficulties during phase separation, which will reduce the methyl ester yield. However, based on the ANOVA results (Table 7), it is found that the interaction effect of methanol/oil ratio and KOH catalyst concentration is not significant since the p -value is .909, which is larger than .05.

3.2.2.2. Interaction effect of methanol/oil ratio and stirring speed.

Fig. 7(b) shows the interaction effect of methanol/oil ratio and stirring speed on the W70CI30 methyl ester yield while the KOH catalyst concentration and reaction time are kept constant. A high W70CI30 methyl ester yield (96.82%) is attained at a methanol/oil ratio of 55 (v/v)% and stirring speed of 800 rpm. It can be observed that the methyl ester yield increases when the methanol/oil ratio increases from 52 to 66 (v/v)% within a stirring speed range of 600–1000 rpm. Increasing the methanol/oil ratio more than 66 (v/v)% slightly decreases the W70CI30 methyl ester yield to 94.00%. When the methanol/oil ratio is less than 50 (v/v)%, the W70CI30 methyl ester

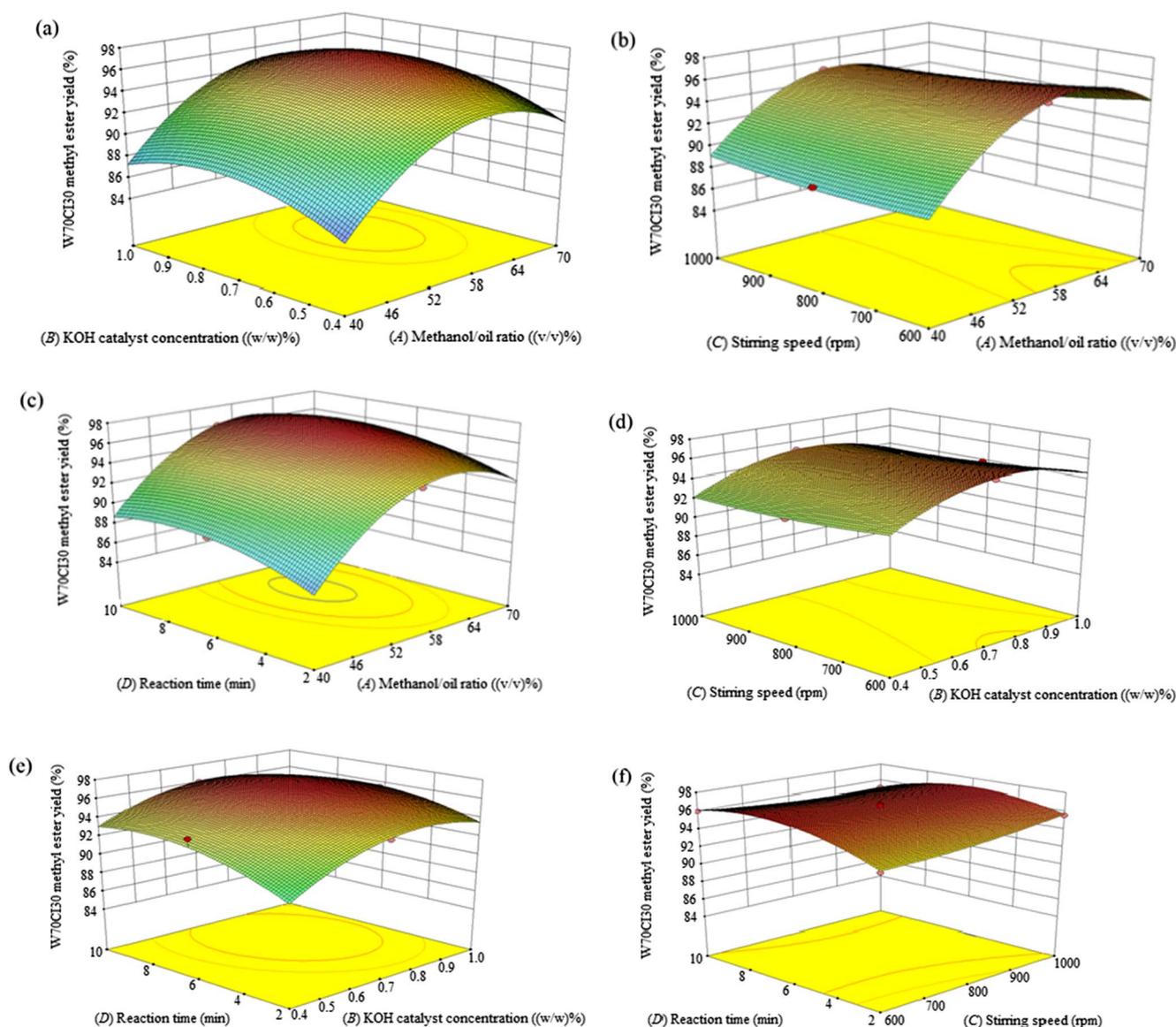


Fig. 7. Three-dimensional response surface plots showing the interaction effects of (a) KOH catalyst concentration and methanol/oil ratio, (b) stirring speed and methanol/oil ratio, (c) reaction time and methanol/oil ratio, (d) stirring speed and KOH catalyst concentration, (e) reaction time and KOH catalyst concentration, and (f) reaction time and stirring speed on the W70Cl30 methyl ester yield.

yield is relatively constant with a maximum value of 94.00% even though the stirring speed is increased. It is apparent from the response surface plot that methanol/oil ratio has a more significant effect on the methyl ester yield compared with the stirring speed. Therefore, it is crucial to determine the optimum methanol/oil ratio since the methyl ester yield is directly proportional to the methanol/oil ratio. However, the methyl ester yield decreases if the methanol/oil ratio exceeds the optimum value. Excessive amounts of methanol are undesirable because this will lead to high solubility of glycerol, which makes it difficult to separate the methyl ester from glycerol and other impurities at the end of the transesterification reaction. In general, both of these process parameters influence the methyl ester yield by 5.6–16.4%.

3.2.2.3. Interaction effect of methanol/oil ratio and reaction time. The interaction effect of methanol/oil ratio and reaction time on the W70Cl30 methyl ester yield is shown in Fig. 7(c). The KOH catalyst concentration and stirring speed are kept fixed at 0.7 (w/w)% and 600 rpm, respectively. It is found that the highest methyl ester yield (96.82%) is achieved at a methanol/oil ratio of 55 (v/v)% and reaction time of 6 min. It can be observed from the response surface plot that

increasing the methanol/oil ratio has a marked effect on the methyl ester yield. As discussed previously, it is important to determine the optimum methanol/oil ratio since this will maximize the methyl ester yield. However, excessive amounts of methanol have an opposite effect on the methyl ester yield, where the methyl ester yield will decrease beyond the optimum methanol/oil ratio. In this study, it is found that the reaction time has a minor effect on the methyl ester yield since increasing the reaction time of the microwave irradiation-assisted transesterification process only slightly increases the methyl ester yield up to a certain value at a particular methanol/oil ratio. At a methanol/oil ratio of 55 (v/v)%, the methyl ester yield is directly proportional to the reaction time. When the reaction time is increased from 2 to 10 min, there is a gradual increase in the methyl ester yield. It can be deduced that the methanol/oil ratio is an important factor that determines the quantity of methyl ester produced. Inadequate or excessive amounts of methanol will have a detrimental effect on the methyl ester yield. It is imperative to optimize the methanol/oil ratio due to the fact that the transesterification reaction takes place in a closed vessel (microwave reactor), where it can be reasonably assumed that there is no evaporation of methanol and thus, excessive amounts of

methanol will lead to more free diatomic anions (OH^-) which will lead to difficulties in separating the methyl ester at a later stage.

3.2.2.4. Interaction effect of KOH catalyst concentration and stirring speed. In this case, the methanol/oil ratio and reaction time are kept fixed at 55 (v/v)% and 10 min, respectively. Fig. 7(d) shows that the interaction effect of KOH catalyst concentration and stirring speed is not really significant. Within a KOH catalyst concentration range of 0.4–0.65 (w/w)%, increasing the stirring speed slightly increases the W70CI30 methyl ester yield. The highest methyl ester yield (96.82%) is achieved when the KOH catalyst concentration is within a range of 0.65–0.85 (w/w)% at lower stirring speeds. However, increasing the KOH catalyst concentration to more than 0.85 (w/w)% reduces the methyl ester yield. In general, increasing the stirring speed will increase the methyl ester yield because it promotes homogeneous mixing between the methanol, KOH catalyst, and oil during the transesterification reaction. It is found that the effect of KOH catalyst concentration is not really pronounced, which may be due to the fact that the solid catalyst is dissolved in methanol before the methanol-KOH catalyst mixture is added into the oil. The methanol and KOH catalyst were premixed prior to the transesterification process in order to ensure homogeneity between the methanol, KOH catalyst, and oil during microwave irradiation-assisted transesterification since it was expected the reaction will be completed within a matter of minutes. Thus, the methanol-KOH catalyst mixture helps prevent biases in the results due to inhomogeneity between the reactants. At the same time, the methanol-KOH catalyst mixture will significantly increase the rate of reaction compared with the KOH solid catalyst since the mixture is in a free radical state which will reduce the activation energy during the transesterification reaction.

3.2.2.5. Interaction effect of KOH catalyst concentration and reaction time. The interaction effect of KOH catalyst concentration and reaction time on the W70CI30 methyl ester yield is shown in Fig. 7(e). The methanol/oil ratio and stirring speed are kept fixed at 55 (v/v)% and 600 rpm, respectively. It can be observed that at low catalyst concentrations, increasing the reaction time to ~8 min significantly boosts the W70CI30 methyl ester yield (96.82%). However, a further increase in the KOH catalyst concentration beyond 0.7 (w/w)% gradually decreases the methyl ester yield. Based on the results of the Box-Behnken experimental design for Runs 5, 8, and 10 (Table 4), it can be seen that the methyl ester increases with an increase in reaction time while other process parameters are kept constant. However, the methyl ester yield decreases as the reaction time approaches 10 min. In general, it can be observed that the interaction effect of the KOH catalyst concentration and reaction time on the W70CI30 methyl ester yield is pronounced, particularly at low catalyst concentrations (< 0.7 (w/w)%). Based on the results, it can be deduced that the reaction time does not play a vital role in enhancing the methyl ester yield compared with the KOH catalyst concentration. It is found that the lowest methyl ester yield is achieved at a KOH catalyst concentration and reaction time of 0.4 (w/w)% and 2 min, respectively. This is due to the low mass transfer, which inhibits the rate of reaction between the oil, methanol, and catalyst.

3.2.2.6. Interaction effect of stirring speed and reaction time. Fig. 7(f) shows the three-dimensional response surface plot of the interaction effect of stirring speed and reaction time on the W70CI30 methyl ester yield. The methanol/oil ratio and KOH catalyst concentration are kept fixed at 55 (v/v)% and 0.7 (w/w)%, respectively. It is found that the maximum methyl ester yield (96.82%) is attained at a stirring speed and reaction time of 800 rpm and 6 min, respectively. Interestingly, the methyl ester yield appears almost invariant, judging from the flat response surface, and one may conclude that the interaction effect of these process parameters is not significant. However, the ANOVA results (Table 7) prove otherwise, since the interaction effect of the

stirring speed and reaction time on the W70CI30 methyl ester yield is significant, with a p -value of .0213, which is less than .05. This indicates that the stirring speed and reaction time have a significant effect on the W70CI30 methyl ester yield.

When the reaction time increases from 5 to 10 min, a high methyl ester yield (96.82%) is observed at a stirring speed of 600 rpm. It can be seen that there is no enhancement in the methyl ester yield within a reaction time of 4–10 min. In contrast, at a stirring speed of 1000 rpm, the highest methyl ester yield is attained within a shorter reaction time (3 min) and the methyl ester yield remains relatively constant up to a reaction time of 9 min. The methyl ester yield gradually decreases after 9 min, which means that there is no enhancement in the methyl ester yield within a reaction time of 3–9 min. Therefore, even though the ANOVA results indicate that the interaction effect of both of these process parameters is significant, the response surface plot indicates otherwise.

In general, the interaction effect is slightly significant at low values of stirring speed and reaction time. At a stirring speed of 600 rpm, as the reaction time increases from 2 to 5 min, there is a stepwise increase in the methyl ester yield. Hence, the reaction time should be sufficiently long to ensure complete transesterification, which will promote the methyl ester yield. A low methyl ester yield is attained when the reaction time is reduced, which may be due to low mass transfer. It is known that oil and methanol have poor miscibility and for this reason, the reaction mixture is stirred continuously throughout the transesterification process to promote mixing and mass diffusion of the reactants. Therefore, applying the optimum reaction time will ensure complete mass diffusion between the different species, which in turn, enhances the methyl ester yield.

3.3. Validation of the quadratic response surface regression model

Design-Expert® software version 9 (Stat-Ease, Inc., USA) was used to conduct the Box-Behnken design of experiments and predict the optimum process parameters in order to maximize the W70CI30 methyl ester yield. The optimum methanol/oil ratio, KOH catalyst concentration, stirring speed, and reaction time predicted by the quadratic response surface regression model are 59.60 (v/v)%, 0.774 (w/w)%, 600 rpm, and 7.15 min, respectively. The microwave irradiation-assisted alkaline-catalysed transesterification process is maintained at a temperature of 100 °C and the corresponding predicted W70CI30 methyl ester yield is 97.40%. Experiments were conducted based on the optimum process parameters in order to validate the quadratic response surface regression model. The same process parameters used for the microwave irradiation-assisted transesterification were also used for conventional transesterification. Five experiments were replicated for both transesterification methods and the W70CI30 methyl ester yield values obtained from the experiments are presented in Table 8.

Based on the results, it is found that the average W70CI30 methyl ester yield obtained from the microwave irradiation-assisted alkaline-catalysed transesterification is 97.65%, which is only slightly higher than the predicted methyl ester yield (97.40%). The difference between the average predicted and experimental methyl ester yield is 0.25% with a standard error of 0.17. In contrast, for the conventional transesterification with the same optimum process parameters, the average W70CI30 methyl ester yield is 89.15%, which is significantly lower than that for the microwave irradiation-assisted transesterification method with a standard error of 0.26. It is evident that at the same process parameters, there is a significant difference in the quantity of methyl ester produced between the microwave irradiation-assisted and conventional transesterification methods, where the methyl ester yield is certainly higher for the former method.

This indicates that microwave irradiation effectively facilitates the transesterification process and reduces the reaction time because it promotes molecular vibrations and high oscillations of the charged particles, which accelerates the conversion of glycerides into methyl

Table 8

Comparison of the W70CI30 methyl ester yield between microwave irradiation-assisted transesterification and conventional transesterification using the optimum process parameters. Note that the W70CI30 methyl ester yield predicted by the quadratic response surface regression model is also included for comparison.

Experimental run	Methanol/oil ratio ((v/v)%)	KOH catalyst concentration ((w/w)%)	Stirring speed (rpm)	Reaction time (min)	W70CI30 methyl ester yield (%)		
					Microwave irradiation-assisted alkaline-catalysed transesterification		Conventional alkaline-catalysed transesterification
					Predicted ^a	Experimental ^b	Experimental ^c
1	59.60	0.774	600	7.15	97.40	97.57	89.81
2	59.60	0.774	600	7.15	97.40	97.42	89.24
3	59.60	0.774	600	7.15	97.40	97.57	88.37
4	59.60	0.774	600	7.15	97.40	97.37	89.53
5	59.60	0.774	600	7.15	97.40	98.33	88.78

^a Average W70CI30 methyl ester yield: 97.40%.

^b Average W70CI30 methyl ester yield: 97.65%.

^c Average W70CI30 methyl ester yield: 89.15%.

ester. In addition, microwave irradiation-assisted transesterification is carried out in a closed vessel, which prevents evaporation of methanol to the atmosphere, which helps boost the methyl ester yield. The results indicate that the microwave irradiation-assisted alkaline-catalysed transesterification is a promising method to produce biodiesel with high biodiesel yields. More importantly, there is good agreement between the average W70CI30 methyl ester yield determined from experiments and the quadratic response surface regression model, which indicates the reliability of the prediction model. This proves that RSM based on the Box-Behnken experimental design is an effective tool to predict the optimum process parameters of the microwave irradiation-assisted transesterification in order to maximize the methyl ester yield.

3.4. FAME content and physicochemical properties of the W70CI30 methyl ester

The FAME content and linolenic methyl ester content of the W70CI30 methyl ester was determined from gas chromatography measurements in accordance with the EN 14103:2011 standard test method and the results are summarized in Table 9. The FAME content and linolenic methyl ester content are presented for the W70CI30 methyl ester at Run 15 and W70CI30 methyl ester produced from microwave irradiation-assisted and conventional transesterification methods. The FAME content and linolenic methyl ester content for the waste

cooking oil methyl ester are also presented for comparison. As expected, it can be seen that the total FAME content (98.94 (w/w)%) is highest for the W70CI30 methyl ester produced from microwave irradiation-assisted transesterification compared with those for waste cooking oil methyl ester (97.45 (w/w)%) and W70CI30 methyl ester at Run 15 (97.70 (w/w)%). It is found that the linolenic methyl ester content is less than 0.6 (w/w)% for all methyl esters produced in this study, which is significantly lower than the value stipulated in the EN 14103:2011 standard (15 (w/w)%). This is due to the higher polyunsaturated fatty acid content as a result of adding *Calophyllum inophyllum* oil into waste cooking oil, which will increase the oxidation stability and improve the cold flow properties of the methyl ester [55,56].

The physicochemical properties of the W70CI30 methyl ester were measured and the results were compared with those of other fuels, as shown in Table 10. In general, it is found that the waste cooking oil methyl ester and W70CI30 methyl esters produced from the microwave irradiation-assisted and conventional transesterification methods fulfil the fuel specifications given in the ASTM D6751 and EN 14214 standards. The optimized W70CI30 methyl ester has lower kinematic viscosity at 40 °C (4.72 mm²/s) and density at 15 °C (861.8 kg/m³) and therefore, the methyl ester has favourable lubrication characteristics. The acid value of the optimized W70CI30 methyl ester is 0.46 mg KOH/g, which is less than the permissible limit (0.5 mg KOH/g) specified in

Table 9

FAME and linolenic methyl ester content of the W70CI30 methyl ester produced from the microwave-assisted and conventional alkaline-catalysed transesterification methods.

FAME ((w/w)%)	Structure of carbon	Waste cooking oil methyl ester	W70CI30 methyl ester (Run 15 ^a)	W70CI30 methyl ester (Conventional alkaline-catalysed transesterification ^b)	W70CI30 methyl ester (Microwave irradiation-assisted alkaline-catalysed transesterification ^b)
Octanoic	C8:0	0.06	0.00	0.00	0.00
Lauric	C12:0	0.20	0.17	0.15	0.18
Myristic	C14:0	0.82	0.65	0.64	0.66
Palmitic	C16:0	32.84	29.67	28.97	30.11
Palmitoleic	C16:1	0.19	0.21	0.21	0.22
Heptadecanoic	C17:0	0.00	0.00	0.00	0.00
Stearic	C18:0	3.91	7.37	7.40	7.49
Oleic	C18:1	45.82	44.35	44.15	44.78
Linoleic	C18:2	11.65	14.18	14.11	14.35
Linolenic	C18:3	0.47	0.54	0.58	0.56
Arachidic	C20:0	1.06	0.57	0.63	0.61
Eicosenoic	C20:1	0.00	0.00	0.00	0.00
Docosanoic	C22:0	0.16	0.00	0.00	0.00
Erucic	C22:1	0.11	0.00	0.00	0.00
Lignoceric	C24:0	0.16	0.00	0.00	0.00
Saturated		39.20	38.43	37.78	39.04
Unsaturated		58.25	59.27	59.06	59.90
Total		97.45	97.70	96.84	98.94

^a The highest W70CI30 methyl ester yield (96.82%) is attained at Run 15 with the following process parameters: methanol/oil ratio (A): 55 (v/v)%, KOH catalyst concentration (B): 0.7 (w/w)%, stirring speed (C): 800 rpm, and reaction time (D): 6 min.

^b The W70CI30 methyl ester yield is produced using the optimum process parameters.

Table 10
Comparison of the physicochemical properties of the W70C130 biodiesel produced from microwave irradiation-assisted and conventional alkaline-catalysed transesterification with those of other fuels.

Properties	Unit	Biodiesel ASTM D6751	Standard test method	EN 14214	Standard test method	Diesel	Waste cooking oil biodiesel	W70C130 biodiesel (conventional alkaline-catalysed transesterification)	Optimized W70C130 biodiesel (Microwave irradiation-assisted alkaline-catalysed transesterification)	<i>Ceiba pentandra-Nigella sativa</i> biodiesel (Conventional alkaline-catalysed transesterification) [17]
Kinematic viscosity at 40 °C	mm ² /s	1.9–6.0	D445	3.5–5.0	EN ISO 3104	2.96	5.01	5.12	4.72	4.42
Density at 15 °C	kg/m ³	880	D4052	860–900	EN ISO 3675	846.1	862.1	878.0	861.8	884.8
Acid value	mg KOH/g	0.5 (max.)	D664	0.5 (max.)	EN 14104	0.017	0.13	0.57	0.46	0.14
Calorific value	MJ/kg	—	D240	—	—	45.361	38.766	40.82	41.35	39.94
Oxidation stability at 110 °C	h	3 (min.)	EN 14112	6 (min.)	EN 14112	15.2	4.61	18.14	18.03	3.27
Flash point	°C	100–170	D93	101 (min.)	EN ISO 22719	75.5	154	163.5	160.5	186.5
Pour point	°C	–15–16	D2500	—	—	3	12	4	2	–1
Cloud point	°C	–3–12	D2500	—	—	2	2	3	2	0
Cold filter plugging point	°C	19 (max.)	D6371	0 (max.)	EN 116	0	7	4	1	–1
Copper strip corrosion residue	— (w/w)%	3 (max.)	D130	—	—	1a	1a	1a	1a	—
Conradson carbon	— (w/w)%	—	—	—	—	0.187	0.04	0.03	0.02	—
Fatty acid methyl ester content	— (w/w)%	—	—	90 (min.)	EN 14103:2011	—	97.45	96.84	98.94	—
Linoleic acid methyl ester content	— (w/w)%	—	—	1–15	EN 14103:2011	—	0.47	0.58	0.56	—
Monoglycerides	— (w/w)%	—	—	0.8	EN 14105	—	0.435	0.291	0.333	—
Diglycerides	— (w/w)%	—	—	0.2	EN 14105	—	0.205	0.153	0.064	—
Triglycerides	— (w/w)%	—	—	0.2	EN 14105	—	0.459	0.222	0.142	—
Free glycerol	— (w/w)%	0.02 (max.)	D6584	0.02	EN 14105	—	0.017	0.079	0.016	—
Total glycerol	— (w/w)%	0.24 (max.)	D6584	0.25	EN 14.105	—	0.205	0.198	0.125	—

Table 11
Energy consumption of the microwave reactor and conventional reactor.

Parameter	Energy consumption of the reactor				
	Microwave heating (2.00 min)	Microwave heating (6.00 min)	Microwave heating (10.00 min)	Microwave heating (7.15 min)	Conventional heating
Power (W)	850	850	850	850	260
Preheating time (min)	2.00	2.00	2.00	2.00	75.00
Reaction time (min)	2.00	6.00	10.00	7.15	7.15
Energy consumption for 10 mL (kJ)	4.66	6.17	7.44	6.49	—
Energy consumption for 100 mL (kJ)	46.65	61.73	74.41	64.92	1283.10

the ASTM D6751 and EN 14214 standards. The calorific value of the optimized W70CI30 methyl ester is 41.35 MJ/kg, which is slightly lower than that for diesel (45.361 MJ/kg), indicating that the energy content of the methyl ester is comparable to that for diesel.

The flash point of the optimized W70CI30 methyl ester is 160.5 °C, which is significantly higher than that for diesel (75.5 °C). The flash point of the methyl ester fulfils the requirements of the ASTM D6751 and EN 14214 standards, which specify that the flash point of the fuel should be within a range of 100–170 °C and more than 101 °C, respectively. The high flash point of the optimized W70CI30 methyl ester will reduce the risk of fire hazards when the fuel is exposed to an ignition source such as flame or spark. The cold flow properties are also significantly improved for the optimized W70CI30 methyl ester where the pour point, cloud point, and cold filter plugging point are 2, 2, and 1 °C, respectively, indicating that the methyl ester is suitable for use in cold-climate countries.

The oxidation stability at 110 °C of the waste cooking oil methyl ester is 4.61 h, which is higher than the minimum value specified in the ASTM D6751 (3h). However, the oxidation stability of the waste cooking oil methyl ester does not fulfil the requirement of the EN 14214, which specifies a minimum oxidation stability of 6 h. Hence, this problem is compensated by adding 30 (v/v)% of *Calophyllum inophyllum* oil into the waste cooking oil, since it is evident from the results that the oxidation stabilities of the W70CI30 methyl esters produced from microwave irradiation-assisted and conventional transesterification are significantly improved, with a value of 18.03 and 18.14 h, respectively. This indicates that the oxidation stability is quadrupled by blending the two types of feedstocks, and the oxidation stabilities of the W70CI30 methyl esters are superior to that for diesel (15.2 h). Oxidation stability is an important property since it indicates the rate of fuel degradation, which plays a vital role for storage, handling, and transportation of the fuel. Fuel oxidation is highly undesirable because it degrades the physicochemical properties of the fuel where the acid value is increased, which will lead to corrosiveness of engine components, and the kinematic viscosity is increased, which will clog the fuel injectors. Based on the results, blending waste cooking oil with *Calophyllum inophyllum* oil significantly enhances the oxidation stability of the methyl ester.

The total monoglyceride content (0.333 (w/w)%), total diglyceride content (0.064 (w/w)%), and total triglyceride content (0.142 (w/w)%) of the optimized W70CI30 methyl ester fulfils the requirements of the EN 14214 standard. In addition, the total glycerol (0.125 (w/w)%) and free glycerol (0.016 (w/w)%) fulfils the specifications since the values are less than 0.25 (w/w)% and 0.02 (w/w)%, respectively. The low values of monoglycerides, diglycerides, and triglycerides indicate that most of the glycerides have been successfully converted into methyl ester and most of the glycerol have been eliminated from the methyl ester during the separation and purification processes.

In general, the W70CI30 methyl ester produced from conventional transesterification has higher kinematic viscosity, density, and acid value as well as slightly lower calorific value compared with the W70CI30 methyl ester produced from microwave irradiation-assisted

transesterification. The pour point, cloud point, and cold filter plugging point are also slightly higher for the conventionally transesterified W70CI30 methyl ester. In addition, the FAME content of the W70CI30 methyl ester produced from conventional transesterification is 96.84 (w/w)%, which is slightly lower than that (98.94 (w/w)%) for the W70CI30 methyl ester produced from microwave irradiation-assisted transesterification. The total diglyceride content (0.153 (w/w)%), total triglyceride content (0.222 (w/w)%), free glycerol (0.079 (w/w)%), and total glycerol (0.198 (w/w)%) are also higher for the conventionally transesterified W70CI30 methyl ester. All of these indicate that the W70CI30 methyl ester produced from microwave irradiation-assisted transesterification is of superior quality compared with the conventionally transesterified W70CI30 methyl ester. More importantly, the W70CI30 methyl ester yield obtained from microwave irradiation-assisted transesterification is higher by ~8.5% compared with that from conventional transesterification, based on the results shown in Table 8.

Table 11 shows the energy consumption of the microwave reactor and conventional reactor. The energy consumption of the Anton Paar Monowave 400 microwave reactor was recorded for 100 mL of W70CI30 oil mixture for a preheating time of 2.00 min and reaction time of 2.00, 6.00, 7.15, and 10.00 min. The energy consumption of the microwave reactor is determined to be 46.65, 61.73, 64.92, and 74.41 kJ for a reaction time of 2.00, 6.00, 7.15, and 10.00 min, respectively. The power of the conventional reactor is 260 W and the time required to heat the reaction mixture to 100 °C (preheating time) is 75.00 min whereas the time required for a complete transesterification reaction (reaction time) is 7.15 min. Therefore, the energy consumption of the conventional reactor is 1283.10 kJ.

It is obvious that the preheating time is significantly longer for the conventional reactor compared with that for microwave reactor, which results in higher energy consumption. The difference in energy consumption indicates that microwave irradiation-assisted transesterification is more energy-efficient compared with conventional transesterification. With the aid of microwave technology, the W70CI30 methyl ester yield is higher (97.65%), the process is more energy-efficient (by a factor of 20), the total reaction time is significantly reduced (9.15 min including preheating time and reaction time) and more environmentally friendly. In contrast, conventional alkaline-catalysed transesterification results in lower W70CI30 yield (89.15%), longer total reaction time (82.15 min including preheating time and reaction time), and higher energy consumption (1283.10 kJ). Hence, it can be deduced that microwave irradiation-assisted transesterification is superior to conventional transesterification in many aspects.

Anton Paar Masterwave BTR microwave bench-top reactor can be used in replacement of the Anton Paar Monowave 400 microwave reactor in order to upscale the current microwave irradiation-assisted biodiesel synthesis to the kilogramme scale without the need to re-optimize the process parameters. The 1-L polytetrafluoroethylene (PTFE) reaction vessel is equipped with a magnetic paddle stirrer, which enables one to produce kilogrammes of biodiesel on a daily basis, which makes this equipment suitable for industrial applications.

4. Conclusions

In this study, microwave irradiation-assisted alkaline-catalysed transesterification was used to produce biodiesel from a mixture of waste cooking oil and *Calophyllum inophyllum* oil (W70CI30), where the oils were blended at a volume ratio of 7:3. The W70CI30 oil mixture has an acid value of 19.75 mg KOH/g and kinematic viscosity at 40 °C of 54.12 mm²/s, which reduce to 0.46 mg KOH/g and 4.72 mm²/s, respectively, after degumming, acid-catalysed esterification, and microwave irradiation-assisted alkaline-catalysed transesterification. The optimum methanol/oil molar ratio, KOH catalyst concentration, stirring speed, and reaction time are 59.60 (v/v)%, 0.774 (w/w)%, 600 rpm, and 7.15 min, respectively, resulting in a predicted methyl ester yield of 97.40%. It is found that the W70CI30 biodiesel has higher oxidation stability (18.03 h) and better cold flow properties (pour point, cloud point, and cold filter plugging point of 2, 2, and 1 °C, respectively) compared with those for the waste cooking oil biodiesel, which indicates the positive effect of blending *Calophyllum inophyllum* oil with waste cooking oil. In addition, it is found that the physicochemical properties of W70CI30 biodiesel fulfil the fuel specifications stipulated in the ASTM D6751 and EN 14214 standards. The use of microwave irradiation greatly accelerates the alkaline-catalysed transesterification reaction, which significantly shortens the total reaction time to 9.15 min compared with conventional alkaline-catalysed transesterification with a total reaction time of 82.15 min. The physicochemical properties of the W70CI30 biodiesels produced from both methods are comparable, though microwave irradiation-assisted alkaline-catalysed transesterification gives more competitive edge in terms of time and energy consumption.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.enconman.2017.12.027>.

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