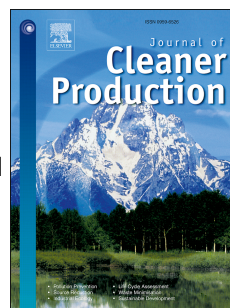


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Precise Evaluation the Effect of Microwave Irradiation on the Properties of Palm Kernel Oil Biodiesel Used in a Diesel Engine

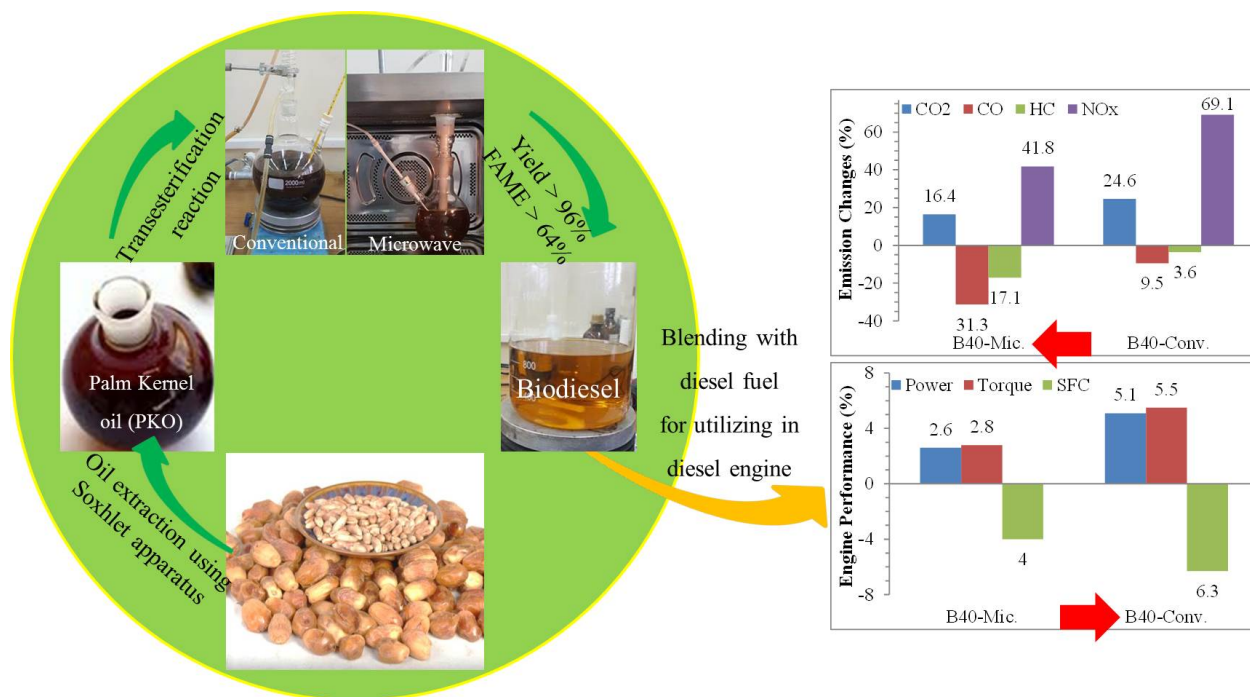
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Precise evaluation the effect of microwave irradiation on the properties of palm kernel oil biodiesel used in a diesel engine

Abstract

Palm kernel oil (PKO) has an appropriate oil content which can be utilized for biodiesel production. Sparse studies have been performed on its ability as well as the produced biodiesel properties and performance in the diesel engine. Further, no study has been performed on the conversion of PKO via microwave irradiation and comparing the PKO biodiesel abilities combusted in diesel engines with those prepared by conventional methods. For this purpose, PKO was directly extracted from date palm fruits (*Phoenix dactylifera*) with microwave and conventional heating systems utilized for conversion of PKO to biodiesel. In addition to optimization of microwave-assisted transesterification reaction conditions, variations of temperature during each run were carefully monitored. The results revealed that palm kernel has 10 wt.% of oil containing high unsaturated fatty acids and free fatty acid (FFA). The transesterification reaction was sharply accelerated by microwave power such that the reaction time diminished from 90 min for conventional method to 2.5 min. The results of temperature monitoring confirmed great elevation in the reaction temperature (over boiling point of methanol) with the rise of microwave power and methanol/oil ratio. Moreover, reduction of temperature occurred with more loading of catalyst due to greater formation of soap. Both high and low temperatures showed negative effects on the yield of transesterification reaction. The performance and emissions gas evaluation of the engine fueled by PKO biodiesel produced by microwave and conventional heating system indicated

that the fuel produced by microwave irradiation can sharply reduce the CO and HC and insignificantly increase NO_x in exhaust emission as compared to fuel produced by the conventional method. Also, higher amounts of microwave-assisted produced PKO biodiesel can be blended with net diesel fuel to use in diesel engines. The results suggested that microwave irradiation can considerably influence the phytochemical properties of biodiesel and improve its combustion profile in the diesel engine and exhaust gas emissions.

Keywords: Palm kernel oil (PKO); Microwave irradiation; Biodiesel; Engine performance, Exhaust emissions.

1. Introduction

The world production of dates has increased considerably over the last 30 years. Nowadays, palm fruits are widely cultivated around the world especially in Middle East which produces around 91% of the world's dates (Ali et al. 2015). Increasing in the palm production has caused the palm oil to claim the first rank in the amount of oil produced in the world (Rupilius and Ahmad 2007). Palm kernel, as an important by-product from the process of palm oil production, can be a suitable source for biodiesel production given its appropriate oil content (Jamil et al. 2017). The researchers have reported that the palm kernel has 5-12% oil depending on its type and cultivating conditions. Palm kernel oil (PKO) presents different compositions with most of them possessing high unsaturated carbon bonds, although the saturated short-chain fatty acids have also been detected (Lin et al. 2008, Bello et al. 2015).

Biodiesel contains fatty acid alkyl (methyl) ester (FAME) which is usually produced by transesterification of triglycerides with methanol in the presence of a catalyst. This fuel is non-toxic, biodegradable, sulfur and aromatics free compound which is of high interest due to

environmental problems caused by consumption of petroleum fuels such as air pollution, global warming, and climate change (Chuah et al. 2017, Mahmudul et al. 2017).

The researchers have been trying to find new sources as feedstock for biodiesel production to reduce the biodiesel production cost (Phoon et al. 2017, Ong et al. 2019, Xie et al. 2019). In this case, palm oil has been extensively evaluated in the transesterification reaction and tested in the diesel engine (Abdul Kapur et al. 2017, Fazal et al. 2018, Bautista et al. 2019). However, fewer studies have been performed on the biodiesel production from PKO and its ability in the diesel engine. Aladetuyi et al. (2014) studied the reaction conditions of biodiesel production from PKO and obtained 90% yield at the conditions of 100 °C, 2 h reaction time, 1 wt.% of catalyst (KOH) and oil-methanol ratio of 5:1 (w/v). Bello et al. (2015) reported that PKO biodiesel produced at the conditions of 60 °C, catalyst-to-oil ratio of 0.24:1 (w/v), and oil-methanol molar ratio of 10:1 contained 78% saturated fatty acid groups. Ojolo et al. (2012) presented PKO transesterified at 55 °C, 5:1 (w/w) ratio of methanol-to-oil, 0.5 wt.% of catalyst (NaOH) and obtained a yield of 92%. In addition, PKO biodiesel production using heterogeneous catalysts such as Al₂O₃-supported alkali earth metal oxides (Benjapornkulaphong et al. 2009), Ca and Zn mixed oxide (Ngamcharussrivichai et al. 2008), sulfated zirconia and stannic oxide (Jitputti et al. 2006), and modified dolomites (Ngamcharussrivichai et al. 2007) was also evaluated. However, higher reaction temperatures (over 100 °C), time (around 3 h), alcohol/oil molar ratio (around 15), and catalyst amount (≈ 10 wt.%) are required to achieve proper conversion of PKO to biodiesel, heterogeneously.

New technologies such as supercritical fluid (García-Martínez et al. 2017), microwave irradiation (Nayebzadeh et al. 2017) and ultrasonic wave (Hoseini et al. 2017) are utilized for biodiesel production, with microwave irradiation offering more desirable properties. Microwave energy makes a uniform heating profile at a molecular level in the materials whose thermal effects include a combination of heating rate, hot spots, and selective

absorption of radiation by polar substances (Hashemzahi et al. 2016). Due to the accelerated reaction rate, milder reaction conditions, higher chemical yield, lower energy usage, and different reaction selectivity, microwave irradiation is widely used in today's industries (Quirino et al. 2016). PKO biodiesel was tested in a diesel engine and offered a lower power, torque, and specific fuel consumption compared to diesel fuel (Lin et al. 2008, Bello et al. 2015). It can be related to high kinetic viscosity and low heating value of PKO which has a negative effect on the engine performance. On the other hand, B20 (20 vol.% biodiesel-80 vol.% net diesel) improved its properties (Igbokwe et al. 2015, Igbokwe and Nwafor 2016, Shote et al. 2019).

However, to the best of our knowledge no study has been done on the conversion of PKO to biodiesel under microwave irradiation assessing the reaction conditions and variations of temperature during the reaction. In addition, the effect of microwave irradiation on the properties and performance of produced biodiesel in the diesel engine has not been evaluated either.

Therefore, in this study, microwave-assisted biodiesel production from PKO using NaOH as homogeneous catalyst was assessed in detail. For this purpose, after extraction of PKO by solvent extraction method via soxhlet apparatus, it was transesterified using microwave irradiation and conventional method. The reaction conditions under microwave heating such as microwave power, reaction time, methanol-to-oil molar ratio, and catalyst concentration were optimized. In addition, the changes in the reaction temperature during each run were monitored. Finally, the physicochemical properties of the PKO biodiesel produced via the two heating systems (microwave and conventional) along with their performance and exhaust gas emissions in the diesel engine were evaluated.

2. Materials and methods

The operation processes for production of biodiesel via two heating systems and testing them in the diesel engine is completely summarized in figure S1.

2.1. Palm kernel oil extraction

Date palm fruits (*Phoenix dactylifera*) were purchased from a local store. Then, their kernel was separated from the pulp and washed completely with hot distilled water to eliminate the remaining pulp. After drying the kernels in the oven for overnight, they were crushed to the particle with a diameter lower than 1 mm. Then, the solvent method via the Soxhlet apparatus was utilized for oil extraction where hexane was used as solvent with a 4 mL/1 g kernel ratio (Ali et al. 2015). After 8 h, the solvent was separated from the oil through evaporation of mixture at 45 °C and 450 mm Hg. Finally, the yield and composition of PKO were obtained respectively in terms of the proportion of PKO weight to kernels' weight and gas chromatography (GC) as well as other physical properties of PKO such as density (ASTM D1298), viscosity (ASTM D445), acid value, and molecular weight.

2.2. Biodiesel production process

2.2.1. Esterification reaction

The extracted PKO includes high FFA contents which must be firstly esterified to reduce the FFA content due to sensitivity of alkali homogeneous catalyst to the amount of FFA causing soap formation (Hashemzahi et al. 2016). Therefore, a two-stage process involving esterification by acid catalyst and the transesterification by alkali catalyst is used for biodiesel production from PKO (Zullaikah et al. 2005). The esterification reaction was performed under the conditions of 60 °C, 6 methanol/PKO molar ratio, 1 wt.% of catalyst (H₂SO₄), and 60 min reaction time (Aranda et al. 2008, Hayyan et al. 2010). After the reaction, the product mixture was poured in the separation funnel to separate the oil and ester layer (bottom layer)

from the by-product layer (water and catalyst) using gravity (see Figure S2). Finally, the acid value was measured to obtain the FFA content of esterified PKO, which met the standard range.

2.2.2. Transesterification reaction

After reduction of the FFA content, the transesterification reaction was performed by two heating systems (conventional and microwave), as shown in Figure S3. The conventional biodiesel production from PKO was carried out in a two-neck glass reactor coupled with a condenser to condense the methanol from vapor to liquid phase and a thermocouple to sense the reaction temperature. The reactor was poured with 1000 g PKO, 280 cc methanol (6 molar ratio of methanol/PKO) and 10 g NaOH as catalyst (1 wt.%). The reaction was performed at 60 °C for 90 min (Alamu et al. 2007, Lubes and Zakaria 2009). Since no study had been carried out on the microwave-assisted biodiesel production from PKO, the reaction conditions were evaluated and optimized. The microwave-assisted transesterification reaction was performed in a 100 mL two-neck glass reactor poured with 20 g of PKO and desirable amounts of methanol and catalyst. Then, the reactor was placed in a modified domestic microwave oven (Daewoo, Model No. KOC9N2TB, 900 watts, 2.45 GHz) with a hole of 20 mm at its top to connect the glass reactor to a condenser for refluxing the methanol. The transesterification reaction conditions of microwave power (90 180, 270 and 360 W), reaction time (1, 1.5, 2, 2.5 and 3 min), methanol/PKO molar ratio (3, 6, 9 and 12), and catalyst concentration (0.5, 0.75, 1, 1.25 and 1.5 wt.%) were evaluated further.

After each reaction, the product mixture was poured in a decanter to separate the biodiesel (top layer) from glycerol as a by-product (see Figure S2). After elimination of methanol from the biodiesel layer through evaporation, the yield of reaction and FAME content of produced PKO biodiesel were measured by the following Eqs.:

$$\text{Yield (\%)} = (\text{Weight of produced PKO biodiesel} / \text{Weight of PKO}) \times 100 \quad \text{Eq.1}$$

$$\text{FAME content (\%)} = \frac{\text{area of all FAME} \times \text{weight of internal standard}}{\text{area of internal standard} \times \text{weight of biodiesel sample}} \times 100 \quad \text{Eq.2}$$

Where, FAME content was calculated by GC (Perkin Elmer Claus 580) equipped with a Flame Ionization Detector (FID) and capillary column Select Biodiesel CP9080 (30 m × 0.32 mm × 0.25 μm) and methyl nonadecanoate (C19:0) as the internal standard.

2.3. Fuel characterization

The density (Hydrometer, accuracy: ±2 Kg/m³), kinematic viscosity at 40 °C (Red wood viscometer, accuracy: ±0.02 mm²/s), flash point (Penksy martins apparatus, accuracy: ±2 °C), cloud point and pour point (11010-2, Stanhope SETA, accuracy: ±0.5 °C), acid value, iodine value, and Linoleic acid ME content of the PKO biodiesel produced via conventional and microwave heating systems were determined. Further, the chemical components of PKO biodiesel containing fatty acids, free glycerin and total glycerine were also measured by a gas chromatograph (GC) according to recommended ASTM standard method.

2.4. Testing the engine performance and exhaust emissions

To evaluate the performance of the produced fuels and assess the effect of microwave irradiation on the combustion behavior of PKO biodiesel, the fuels were tested in the diesel engine. A single-cylinder engine equipped with an eddy current dynamometer (WE400) was used whose specifications are listed in Table S1. Moreover, an AVL gas analyzer (DIGAS 1000) was used to measure CO₂, CO, HC, and NO_x emissions with its specifications summarized in Table S2. Various blends of PKO biodiesel-net diesel fuel (BX where X refers

174 to volume percentage of biodiesel (x=0, 10, 20 and 40)) were prepared. Then, the engine
175 performance and exhaust gas emissions of the diesel engine fueled by blend fuels were
176 measured. The performance and exhaust gas emissions were evaluated at engine speeds of
177 1800, 2150, and 2500 rpm at full load. The schematic diagram of the engine experiment is
178 depicted in Figure 1.

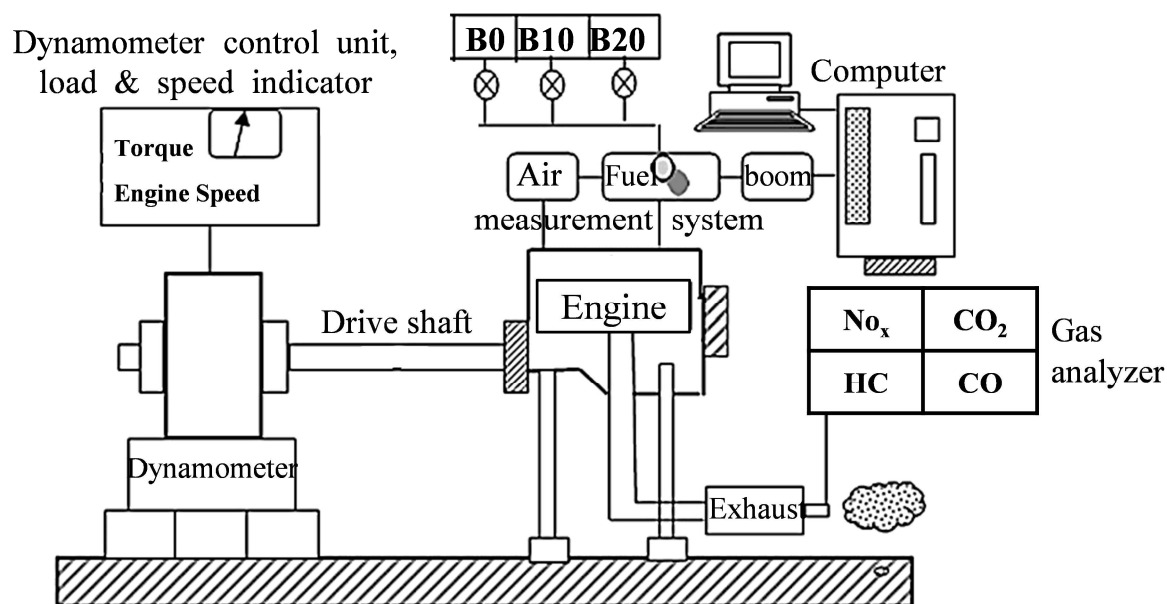


Figure 1. Schematic diagram of engine experiment

3. Results and discussion

3.1. Evaluation of palm kernel oil properties

184 According to ratio of the weight of the obtained PKO to weight of palm kernels, the palm
185 kernels of Zahidi type had around 10 wt.% oil which can be an appropriate feedstock for
186 biodiesel process. The density of PKO at 25 °C was obtained as 916 kg/m³. The PKO
187 revealed a high kinematic viscosity (28 mm²/s) causing problem in its flow and spraying in
188 the engine chamber. Therefore, it should be converted to ester (biodiesel) for reducing its
189 viscosity to be used in the engine. Meanwhile, 4.25 wt.% of FFA content (acid value of 8.5
190 mg KOH/g) of PKO exceeds the limitation for utilization in alkali homogeneous

transesterification reaction. Therefore, the esterification reaction with an acid catalyst (H_2SO_4) must have been done to reduce its FFA content. The FFA compositions of PKO are listed in Table 1.

Table 1. FFA compositions of PKO and produced PKO biodiesel by conventional and microwave methods

| FFA compositions | Unit | PKO | PKO biodiesel | |
|---------------------------------------|------|-------|--------------------|-------------------|
| | | | Conv. ^b | Mic. ^c |
| Lauric acid (C12:0) ^a | wt.% | 21.08 | 14.8 | 15.6 |
| Mysteric Acid (C14:0) ^a | wt.% | 13.85 | 9.9 | 10.4 |
| Palmitic acid (C16:0) ^a | wt.% | 12.38 | 10.8 | 11.2 |
| Palmitoleic acid (C16:1) ^a | wt.% | - | 1.0 | 1.1 |
| Stearic acid (C18:0) ^a | wt.% | 2.73 | 3.1 | 3.2 |
| Oleic acid (C18:1) ^a | wt.% | 43.23 | 45.6 | 46.5 |
| Linoleic acid (C18:2) ^a | wt.% | 5.94 | 11.4 | 8.8 |
| Other component | wt.% | 0.79 | 3.2 | 4.3 |

^a Carbon atoms number: double bond number

^b Conv.: Conventional heating system

^c Mic.: Microwave heating system

PKO has high unsaturated fatty acid components (58.7 wt.%) with a high unsaturation degree. It contains lauric acid (21.08%), mysteric Acid (13.85%), palmitic acid (12.38%), stearic acid (2.73%), oleic acid (43.23%), and linoleic acid (5.94%). According to the PKO structure, the molecular weight was obtained as 784 g/gmole which was used for measuring the methanol amount for each reaction.

3.2. Optimizing the microwave-assisted transesterification reaction parameters

3.2.1. Effect of microwave power

Assessment of the microwave power is very important to obtain the highest yield and the lowest energy consumption. The effect of microwave power is depicted in Figure 2 (a). The yield and FAME content of PKO biodiesel increase by increasing the microwave power from 90 W to 270 W due to elevation of the reaction rate. However, the reaction conversion diminished when the microwave power was set at 360 W. It can be related to considerable rise of the reaction temperature medium causing elimination of methanol from liquid to vapor phase. This phenomenon can be proven by detecting the changes in the reaction temperature with elevation of microwave power, as shown in Figure 2 (b). An inverse relationship has been observed between the reaction rate enhancement and the boiling point of the solvent in a series of esterification reactions (Jacob et al. 1995).

As seen in the Figure 2 (b), the time of reaching the desirable reaction temperature (around 50 °C) shortened sharply from 80 to 30 sec with the rise of the microwave power from 90 W to 270 W. However, when the microwave power was adjusted on 360 W, the reaction temperature passed the boiling point of methanol (64.7 °C) after 30 sec leading to evaporation of methanol and reduction of its amount in the reaction medium (liquid phase) (Hojjat et al. 2016). Therefore, microwave power of 270 W was selected as optimum for further studies.

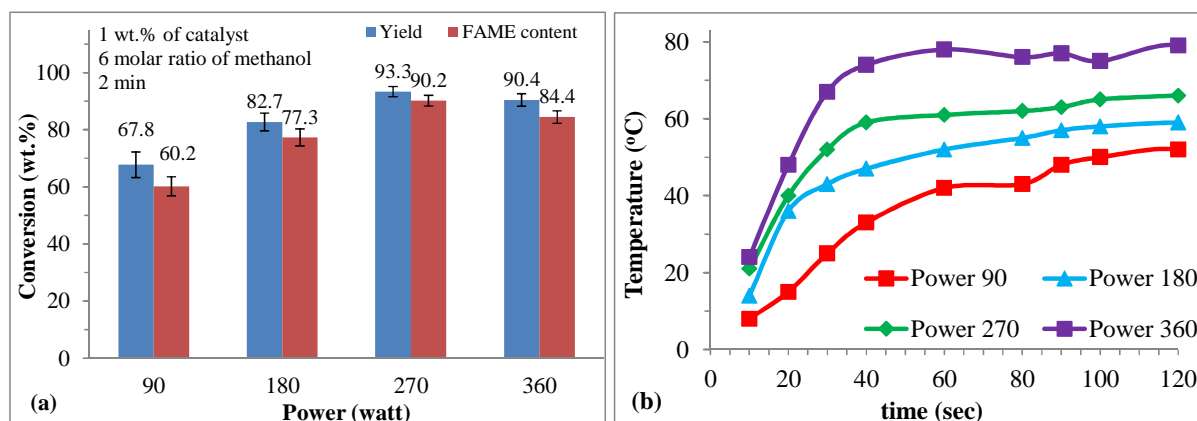


Figure 2. Effect of microwave power on (a) conversion of PKO to biodiesel and (b) temperature of transesterification reaction

3.2.2. Effect of reaction time

The effect of reaction time on transesterification of PKO was examined at 270 W, 6 molar ratios of methanol/PKO, and 1 wt.% of catalyst with the results illustrated in Figure 3 (a). The conversion rate significantly increased as the time of reaction lengthened from 1 to 2.5 min, as sufficient time was provided for the interaction between the catalyst and reactants. Further, Figure 3 (b) displays the temperature of microwave-assisted transesterification reaction during 5 min. The reaction temperature reached 60 °C after 40 sec. Therefore, more than 40 sec was required for the reaction of the reactants. After 150 sec, the levels of conversion decreased slightly due to saponification side reaction (Hojjat et al. 2016). It must be mentioned that the microwave irradiation increased all reactions including saponification reaction. However, since the transesterification is faster than the saponification reaction, methyl esters losses with saponification were negligible at the first moments of reaction. However, at longer reaction times, saponification effect has to be taken into account (Casas et al. 2010). Therefore, the equilibrium conversion was almost 97.6% (96.3. % of FAME content) for 150 seconds of reaction time.

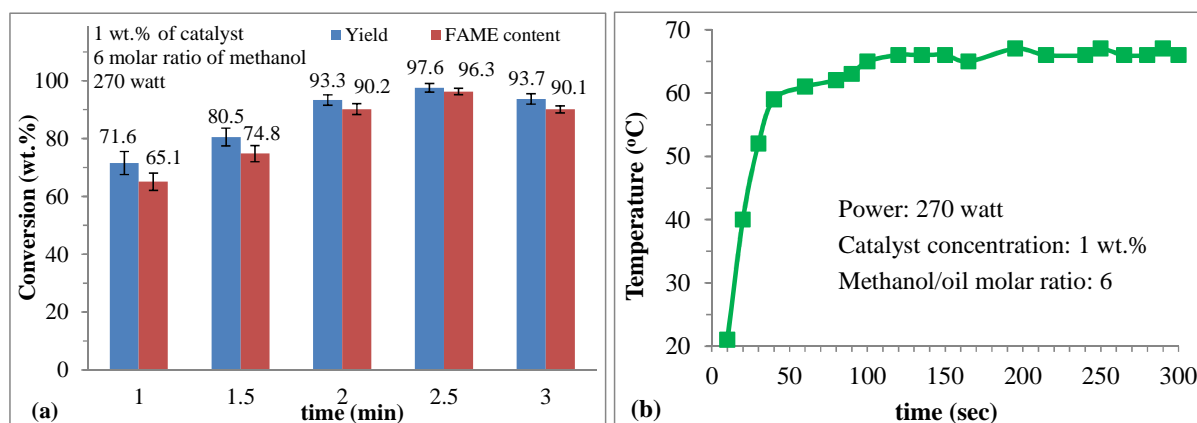


Figure 3. Effect of reaction time on (a) conversion of PKO to biodiesel under microwave irradiation and (b) temperature of transesterification reaction

3.2.3. Effect of methanol content

In addition to the positive effect of methanol on moving the transesterification reaction forward, methanol can also absorb the microwave irradiation to accelerate the reaction (Hashemzahi et al. 2016). Microwave-assisted transesterification reaction was examined at various methanol/oil molar ratios (3, 6, 9, and 12) with the results presented in Figure 4 (a). Expectedly, the conversion increased significantly by raising the the methanol amount. Greater adsorption of microwave irradiation using the reaction medium can be observed against the variations of reaction temperature as plotted in Figure 4 (b). It is clearly observed that when the methanol ratio increased from 3 to 6, the final temperature of reaction rose considerably from 53 °C to 66 °C; so did the reaction yield (FAME content) from 68.3% (59.6%) to 97.6% (93.3%). The reaction conversion diminished slightly by using methanol-to-oil molar ratio of 9, which can be related to insufficient rise of the reaction temperature, which reduces the methanol amount in the liquid medium (Hashemzahi et al. 2016). In addition, due to the high solubility of the by-product (glycerol) and FAME in excessive methanol, the separation becomes difficult and consequently the yield declines (Nayebzadeh et al. 2017).

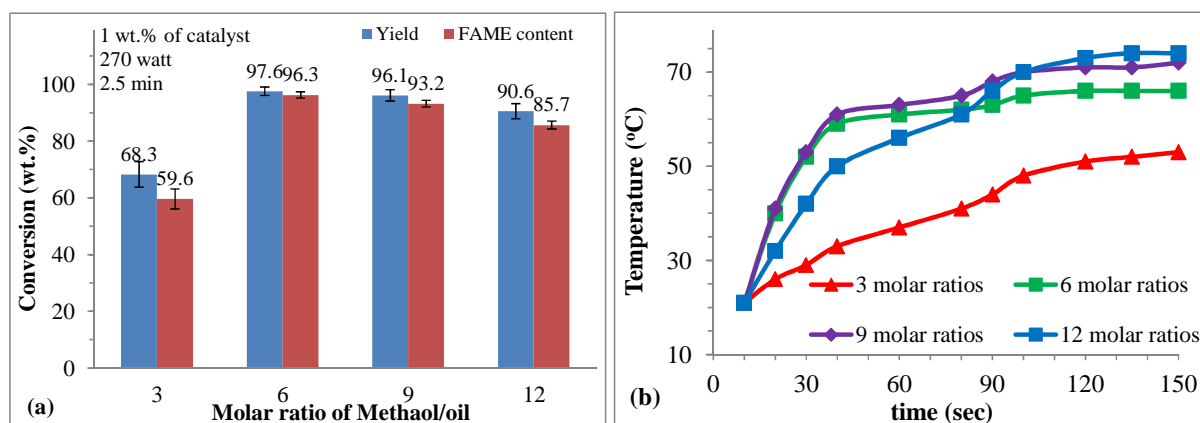


Figure 4. Effect of molar ratio of methanol/oil on (a) conversion of PKO to biodiesel under microwave irradiation and (b) temperature of transesterification reaction

3.2.4. Effect of catalyst concentration

A homogeneous catalyst in the transesterification reaction can have positive and negative effects. The catalyst speeds up a chemical reaction by lowering the amount of activation energy required for the reaction to take place. On the other hand, the base catalyst (NaOH) can react with FFA to form soap which has a negative influence on the yield of transesterification reaction. Therefore, the amount of catalyst must be evaluated with its results displayed in Figure 5 (a). The yield increased substantially from 73.2% to 97.6% with elevation of the catalyst loading from 0.5 to 1 wt.%. However, the conversion decreased drastically when higher amounts of the catalyst were introduced into the reaction. Formation of soap affects the viscosity of the reactants whereby the mass transfer occurs with difficulty (Patil et al. 2009).

The yield reduction can be also proven by monitoring the changes in transesterification reaction temperature as indicated in Figure 5 (b). It is observed that the rate of temperature elevation declines sharply with loading the catalyst to beyond 1 wt.%. Encinar et al. (2012) reported that dielectric constants of the product mixture (methyl ester and glycerol) are greater than those in the reactant (triglycerides and methanol). Soap adsorbs microwave irradiation by starting the saponification reaction, and inhibits the adsorption of microwave irradiation by the reactant or product to elevate the reaction temperature sufficiently. Therefore, the temperature did not grow enough and inappropriate yield was obtained. Accordingly, 1.0 wt.% of catalyst was set as the optimum catalyst amount which is consistent with earlier findings (Liao and Chung 2013, Nayebyzadeh et al. 2013).

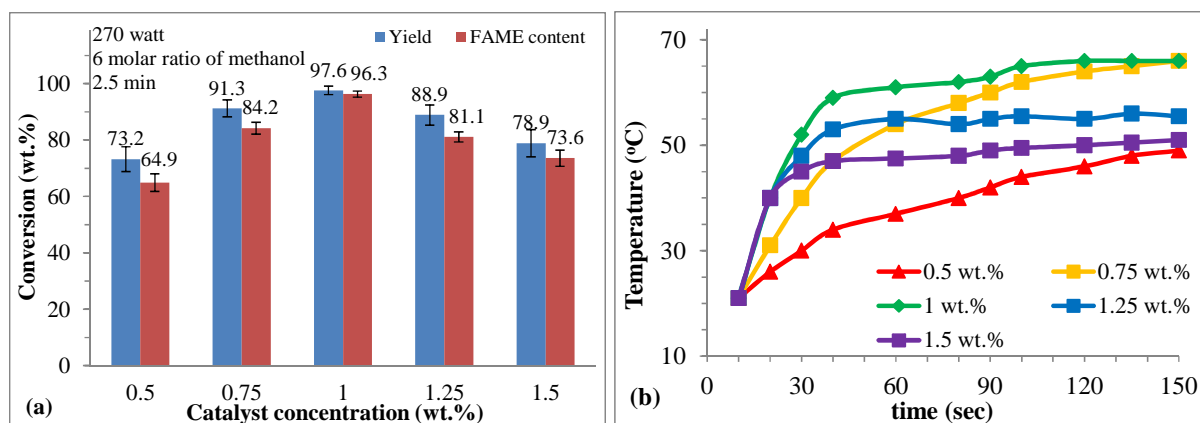


Figure 5. Effect of catalyst concentration on (a) conversion of PKO to biodiesel under microwave irradiation and (b) temperature of transesterification reaction

3.3. Biodiesel fuel characteristics and properties

The characterization of fatty acid compositions of the PKO biodiesel produced via conventional and microwave heating systems performed by GC is demonstrated in Table 1. The yield and FAME content of PKO biodiesel produced by conventional method were obtained as 96.4% and 96.3%, respectively. The biodiesel produced by conventional method contained 38.6% saturated fatty acids and 58% unsaturated components. On the other hand, the PKO biodiesel produced by microwave method had 40.4% saturated fatty acids and 56.4% unsaturated components with a 65.2% degree of unsaturation. Note that the duration of conventional transesterification reaction was 90 min, while the transesterification was completed after 2.5 min under microwave irradiation. The biodiesel produced by microwave irradiation showed lower unsaturation degree that has positive influence on the stability of biodiesel. It can be seen from the content of Linoleic acid ME of biodiesel produced by the both methods. Probably, microwave irradiation can accelerate the reaction between saturated components with alcohol instead of unsaturated components. It well known that microwave irradiation can significantly effect on the polar components such as methanol in transesterification reaction. On the other hands, nonpolar lipids are more saturated than polar

lipids (Nomanbhay and Ong 2017). Therefore, moving a component with the magnetic medium along with fix position a nonpolar component causes to more interaction between them. It can be consequently concluded that, for increasing the reaction between FFAs and methanol, the oils containing more saturated FFAs are more suitable.

Oleic acid is the most abundant methyl ester of PKO biodiesel. Further, PKO biodiesel contains around 36% short-chain fatty acids which have a positive effect on its viscosity, cloud point, and pour point.

The physical properties of PKO biodiesel produced by conventional and microwave methods are listed in Table 2. The kinematic viscosity of PKO was reduced from 28 mm²/s to 4.03 mm²/s by transesterification via microwave irradiation which meets the biodiesel standard. However, the kinematic viscosity was reduced to 4.85 mm²/s for PKO biodiesel produced by the conventional method. This parameter is important during injection of fuel in the diesel engine chamber where lower values are more desirable. Moreover, the density of both PKO biodiesels (microwave and conventional) decreased and obtained as 874 kg/m³ and 878 kg/m³, respectively.

The flash point (closed cup) of PKO biodiesel produced by the conventional (107 °C) and microwave transesterification reactions (119 °C) matched the ASTM D6751 (min 93 °C) and EN14214 (min 101 °C) standards of biodiesel. Cetane number and calorific value of both fuel are in the limitation range in which the fuel produced by microwave present higher amount. It can be referred to its lower unsaturation degree and higher amount of FAME component with longer carbon chain. Moreover, the linoleic acid methyl ester content of microwave and conventional PKO biodiesel was 8.8 wt.% and 11.4 wt.%, which are lower than the amount suggested by EN14214 standard (max 12 wt.%). Both biodiesel present low amount of free and total glycerine in their mixture that met the limitation of ASTM and EN standard.

Table 2. Properties of PKO biodiesel produced by conventional and microwave methods

| Property | Method | Unit | limit | | PKO biodiesel | |
|------------------------------|------------|-----------------------|------------|----------|---------------|-------|
| | | | ASTM D6751 | EN 14214 | Conv. | Mic. |
| Density at 15 °C | ASTM D1298 | kg/m ³ | - | 860-900 | 878 | 874 |
| Kinematic viscosity at 40 °C | ASTM D445 | mm ² /s | 1.9-6 | 3.5-5 | 4.85 | 4.03 |
| Flash point-closed cup | ASTM D93 | °C | 93 | 101 | 107 | 119 |
| Cetane number ^a | - | - | 48-65 | > 51 | 57.1 | 57.8 |
| Calorific value ^b | - | MJ/kg | > 35 | > 36 | 41 | 41.3 |
| Cloud point | - | °C | - | - | 6 | 2 |
| Pour point | - | °C | - | - | 0 | -6 |
| Acid value | ASTM D664 | mg KOH/g | Max 0.5 | Max 0.5 | 0.25 | 0.2 |
| Iodine value | EN 14111 | gI ₂ /100g | - | Max 120 | 63 | 59 |
| Linoleic acid ME | EN14103 | wt.% | - | Max 12 | 11.4 | 8.8 |
| Free glycerine | ASTM D6584 | wt.% | Max 0.02 | Max 0.02 | 0.03 | 0.02 |
| Total glycerin | ASTM D6584 | wt.% | Max 0.24 | Max 0.25 | 0.23 | 0.021 |

^a Cetane number calculated by the formula suggested by Gopinath et al. (2009) according to biodiesel composition

^b Calorific value calculated by the formula suggested by Demirbas (2008)

3.4. Effect of biodiesel production method on the engine performance

The blend fuels were labeled as BX-Y concerning the volume of biodiesel in the fuel and the production method, where X is related to volume percentage of biodiesel (0, 10, 20 and 40) and Y is associated to the production method (conventional (Conv.) and microwave (Mic.)).

3.4.1. Engine torque and power

The power and torque of engine fueled by blends of PKO biodiesel produced by the two heating methods with net diesel engine are displayed in Figure 6 and Figure 7, respectively.

The power is defined as the rate at which work is done by the engine (Zareh et al. 2017). It

was previously reported that a lower heating value and higher viscosity of biodiesel compared to net diesel fuel are attributed to diminished engine power. On the other hand, high oxygen content and flammability of biodiesel have a positive influence on the engine power (Miri et al. 2017). The results suggest that the power declines when biodiesel is added to net diesel fuel. However, B40 presents higher brake power compared to other blend fuels at the engine speed of 1800 rpm and 2150 rpm which is related to high oxygen content and flammability of biodiesel.

Some researchers believe that higher viscosity of biodiesel enhances fuel spray penetration whereas others reported that the higher viscosity decreases combustion efficiency due to bad fuel injection atomization (Damanik et al. 2018). Moreover, it is known that high lubricity of biodiesel might result in the reduced friction loss and thus improve the brake effective power. Therefore, it can be concluded that higher viscosity probably has positive effect such that the fuel produced by conventional method provides higher engine power. Increasing the power by more loading of biodiesel in the blend fuel can confirm the positive effect of viscosity such that the difference between the produced power by net diesel and B40.Mic. is not meaningful.

However, at higher engine speeds, although blend fuels presented a higher power compared to net diesel fuel, B10 fuels exhibited the maximum power. It is well known that higher amounts of fuel are required at high engine speeds, while blend fuels have a higher density and viscosity, affecting the fuel injection system. Therefore, B40 fuel leads to more injection problem where the power declines at higher engine speeds (Hoseini et al. 2017). Although a higher power was obtained at the maximum engine speeds such that the maximum power of 4.54 kW and 4.45 kW was obtained for B10-Conv. and B10.Mic. respectively, B40 can be a suitable choice for low engine speeds.

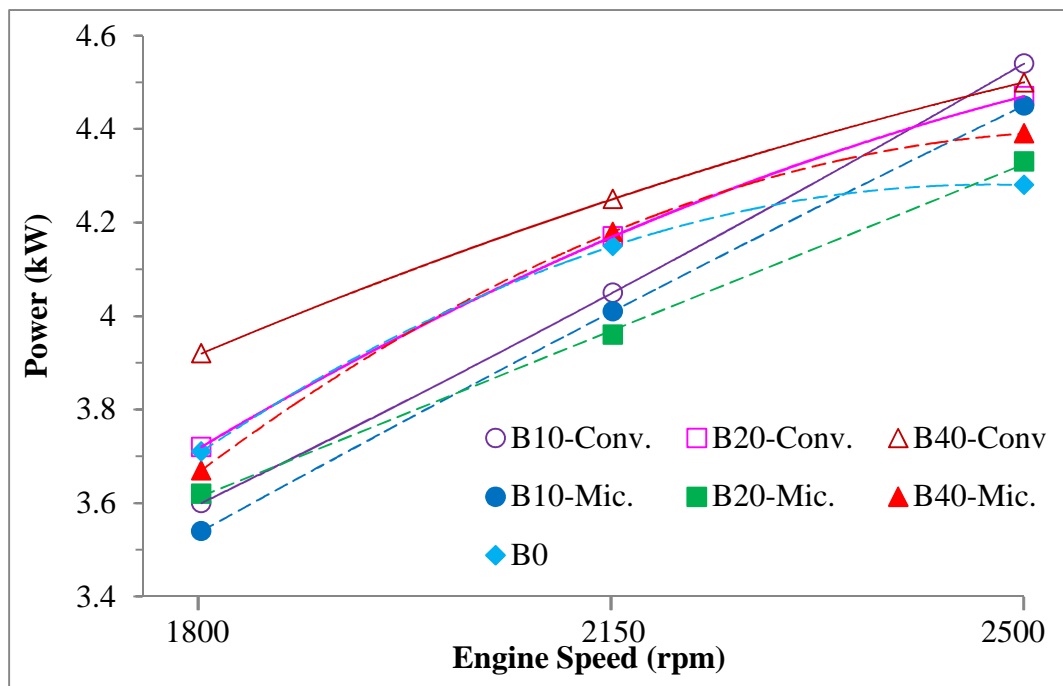


Figure 6. Effect of heating system used for biodiesel production process on the power of engine fueled by various diesel-biodiesel blends worked at different engine speeds

Since the produced power is directly proportional to the torque, the same trend as of power was observed for torque as well. The torque will decrease with elevation of engine speed and adding the biodiesel to fuel because of reducing the force on the piston and crankshaft and low heating value of the biodiesel, respectively (Noorollahi et al. 2018). Although low heating value of biodiesel negatively affects the engine ignition and reduces engine torque, biodiesel improves the lubricity of diesel fuel thereby reducing the friction loss and thus improving the effective torque (as can be seen for B40.Conv. at 1800 rpm). This grows for the fuels at the maximum engine speed (2500 rpm) in which higher torque is obtained because of higher injection of fuel to chamber, and increasing the lubricity and oxygen content of medium (Zaharin et al. 2017).

The difference in the torque provided by biodiesel produced by different method may be referred to higher viscosity of those produced by conventional method that leads to more injection of fuel in the engine camber, especially at higher engine speed (Zaharin et al. 2017).

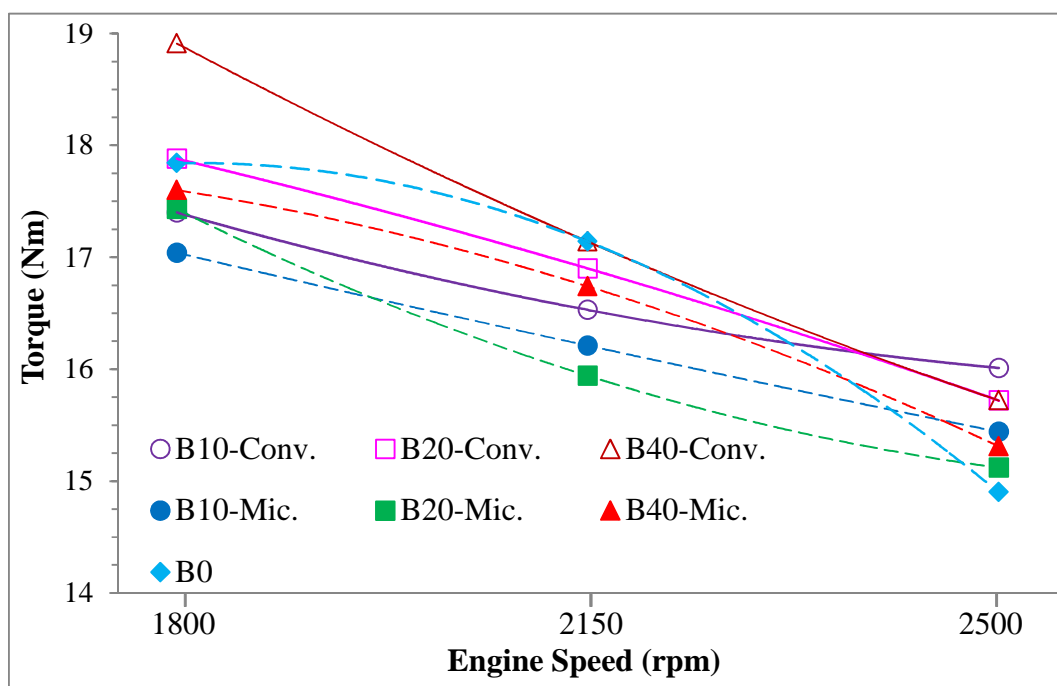


Figure 7. Effect of heating system used for biodiesel production process on the torque of engine fueled by various diesel-biodiesel blends worked at different engine speeds

3.4.2. Brake-Specific fuel consumption

The influence of blending the diesel fuel with PKO biodiesel, biodiesel production method, and engine speed on the Brake-specific fuel consumption (BSFC) is illustrated in Figure 8. The volume of injected fuel, fuel density, viscosity, and heating value of fuel affect the BSFC of diesel engine defined as the mass fuel flow rate to the brake power ratio (Ozsezen et al. 2009). BSFC increases by adding PKO biodiesel at low engine speeds due to lower heating and calorific values of blends fuel compared with net diesel fuel that causes to more amount of blends are required to produce the same amount of engine power output by the engine (Zaharin et al. 2017, Rajak and Verma 2018). In addition, the proper atomization of the fuel is probably prevented by the high viscosity of the blends, which in turn affects the combustion process (Soukht Saraee et al. 2017) However, the BSFC declines with further loading of biodiesel in the diesel fuel due to elevation of the oxygen content of the medium

and better combustion of the fuel (Lin and Lin 2006). This behavior can be proved with the rise of the brake power at high engine speeds. Across the entire engine speeds, B40 fuel presented the lowest SCF for the both produced biodiesel due to its lower viscosity, probably.

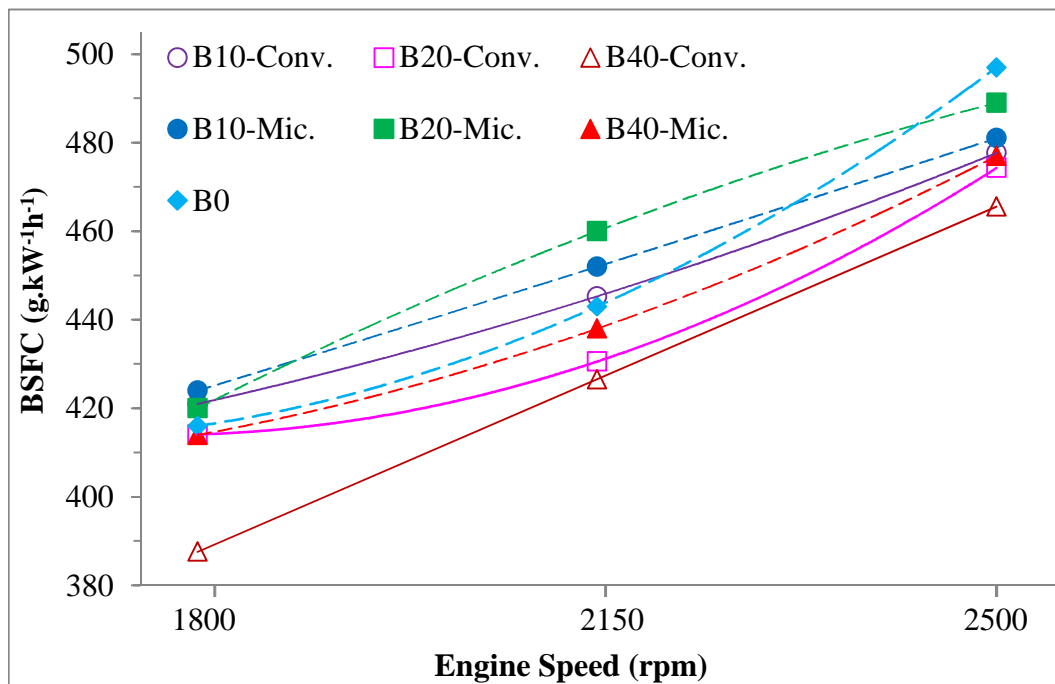


Figure 8. Effect of heating system used for biodiesel production process on BSFC of engine fueled by various diesel-biodiesel blends worked at different engine speeds

3.5. Emission analysis

3.5.1. CO₂ emissions

CO₂ emissions in the exhaust gas of the diesel engine fueled by different blend fuels and operating at various engine speeds are presented in Figure 9. It is expected for biodiesel-diesel fuel to release higher amounts of CO₂ due to the higher oxygen content of biodiesel compared to diesel fuel (Yusaf et al. 2011, Bayındır et al. 2017). However, it was observed that by increasing the ratio of PKO biodiesel produced by conventional method to the net diesel fuel, the amount of CO₂ in the emission gas rose, while this behavior was not observed for that produced by microwave irradiation.

This can be attributed to two reasons. Microwave-assisted produced PKO biodiesel has a lower viscosity and density which inhibits the high amount of fuel injection in the chamber, where lower amounts of CO₂ were released as compared to use of conventional produced PKO biodiesel. On the other hand, the higher flash point of PKO biodiesel produced by microwave irradiation probably accelerates other side reactions of carbon combustion leading to less CO₂ formation. Assessment of the other emissions in exhaust gas can determine the main reason for this behavior. On the other hands, it was pointed in the case of biodiesel emissions that the higher carbon dioxide emission should cause less concern because of Nature's recovery by raising biodiesel crops (Rajaeifar et al. 2014, Nguyen et al. 2017). The life cycle of CO₂ emissions of biodiesel revealed that biodiesel will cause 50–80% reduction in CO₂ emissions compared to petroleum diesel (Qi et al. 2010, Jørgensen et al. 2012, Esteves et al. 2017).

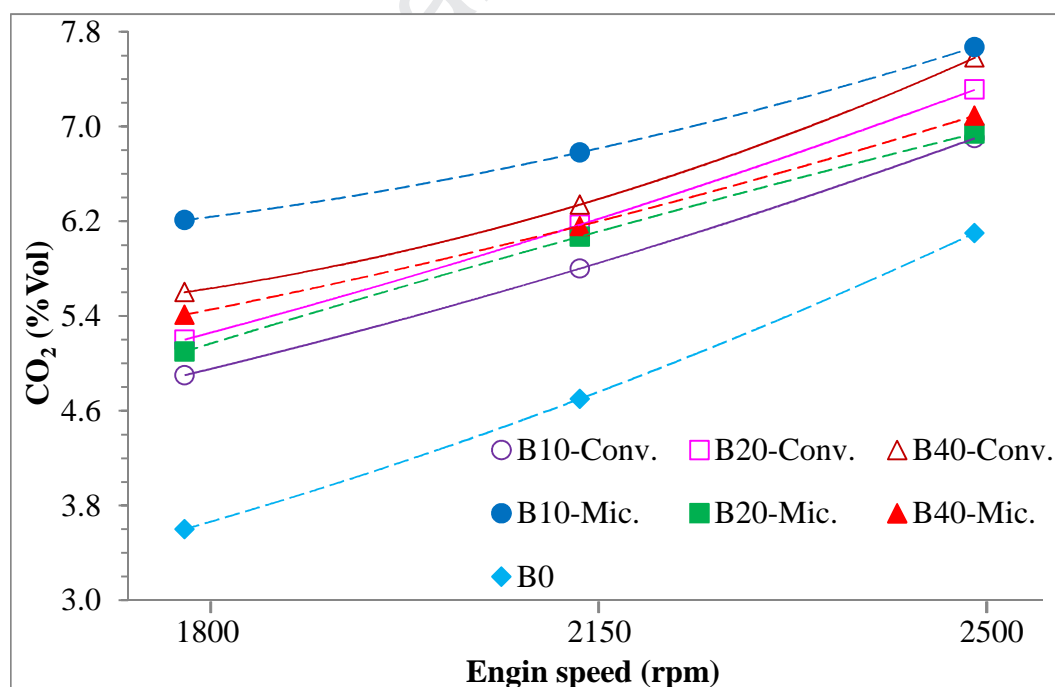


Figure 9. Effect of heating system used for biodiesel production process on CO₂ emission of engine fueled by various diesel-biodiesel blends at different engine speeds

3.5.2. CO emissions

The amount of CO released by different fuels at various engine speeds is depicted in Figure 10. When incomplete combustion or progression from CO to CO₂ occurs in the engine chamber, higher amounts of CO form in the exhaust gas emission. The results suggest that CO emission declines using blend fuels. This can be related to higher oxygen contents of fuel because of more complete combustion of fuel, which is consistent with the results of CO₂ content in the exhaust emission (Song and Zhang 2008, Gharehghani et al. 2019). Therefore, a significant reduction in the CO content with enlargement of the biodiesel volume in blends is acceptable with B20-Mic. and B40.Mic. presenting the lowest CO emissions at all engine speeds. Moreover, B40-Conv. also exhibited better fuel combustion in the engine chamber where the lowest CO was detected. The reduction in the CO content in the exhaust by raising the engine speed is a result of the better air–fuel mixing process and/or the increased fuel/air equivalence ratio (Pinto et al. 2005).

The PKO biodiesel produced by microwave irradiation showed more sufficient combustion compared to that prepared by the conventional method where very low CO emission was detected in the exhaust gas. It was mentioned that CO emissions reduced much higher with the increasing of chain length (Knothe et al. 2006). The biodiesel produced by microwave presented higher amount of all of FFA components, except of Linoleic acid ME, that effect on the well combustion of fuel in the engine chamber.

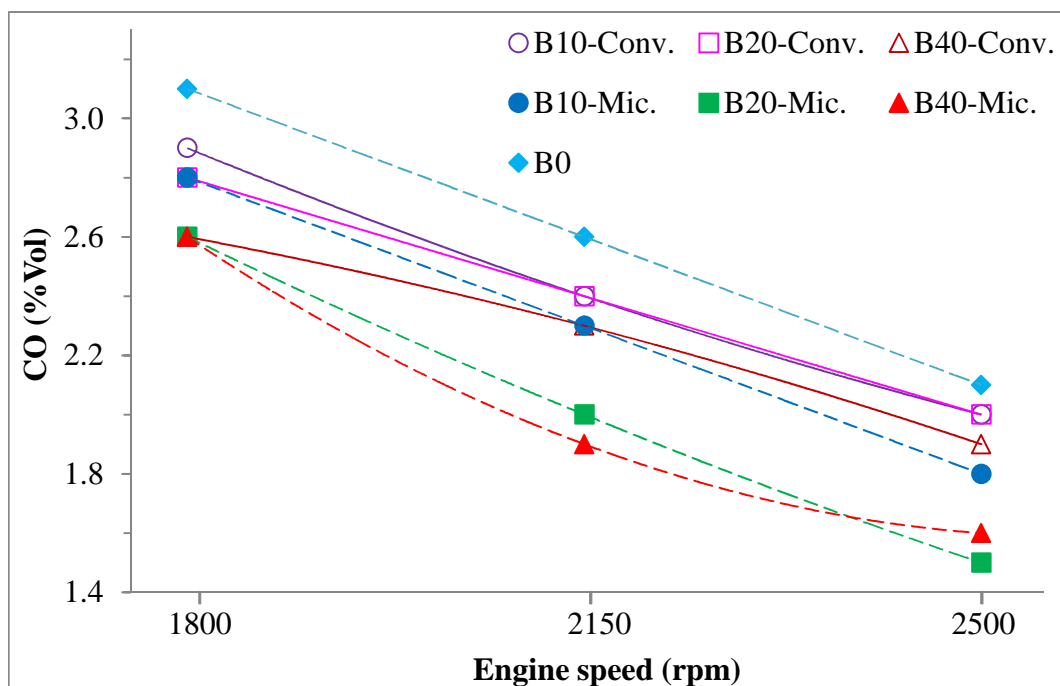


Figure 10. Effect of heating system used for biodiesel production process on CO emission of engine fueled by various diesel-biodiesel blends at different engine speeds

3.5.3. HC emissions

Figure 7 displays the effect of increasing the biodiesel to net diesel fuel ratio on the HC emission of the engine diesel working at various engine speeds and full load. It was described that the combustion of fuels in the engine chamber improves by blending the diesel fuel with biodiesel. Therefore, it is expected that the amount of unreacted hydrocarbon (HC) decreases. Furthermore, shortening the burning delay using biodiesel blends results in diminished HC emissions due to its higher cetane number (Yusaf et al. 2011, Soukht Saraee et al. 2017).

Note that PKO biodiesel produced by microwave irradiation exhibits a better behavior in the combustion of hydrocarbons into the engine chamber, which can be related to its lower density as well as viscosity and higher cetane number (Kumar et al. 2009, Sharma et al. 2019). Moreover, increase in chain length and saturation level of biodiesel leads to a higher reduction in HC emission (Knothe et al. 2006). The biodiesel produced by microwave

irradiation exhibit higher amount of ester with longer chain length and lower unsaturation degree that improves its combustion in the engine chamber.

Due to the high viscosity of PKO biodiesel produced by conventional method, high amounts of fuel were injected into the chamber causing incomplete fuel combustion. Therefore, higher CO and HC levels were released which is in good agreement with CO₂ results. Therefore, microwave-assisted produced PKO biodiesel is the best fuel for blending with biodiesel for more complete combustion of carbon groups in the engine chamber, with B40 presenting a great ability for mixing with net diesel fuel.

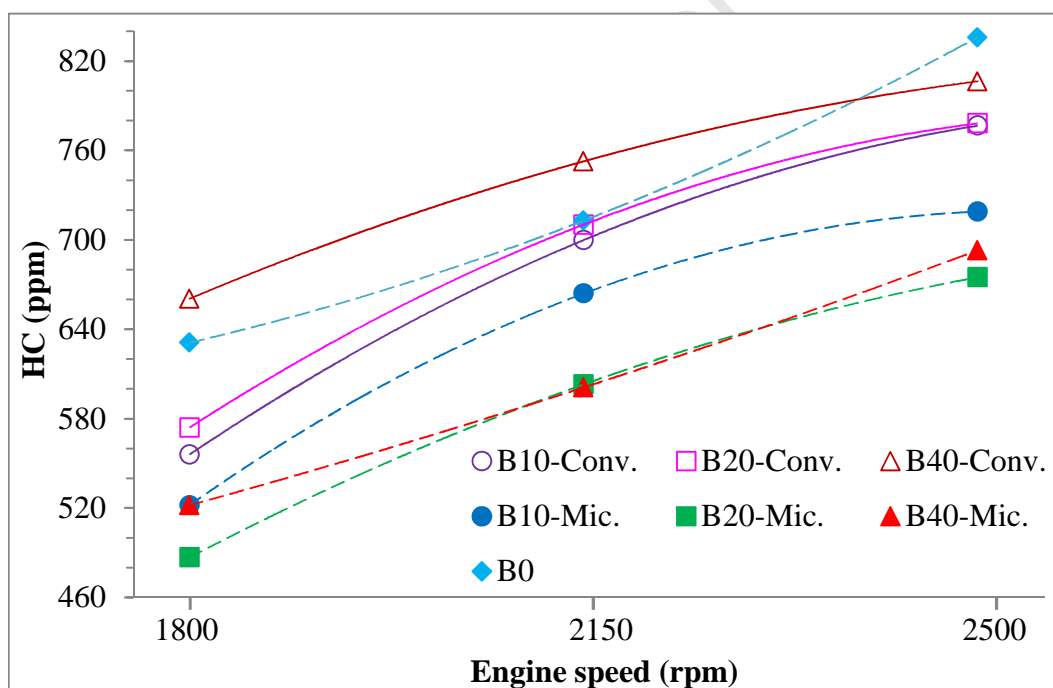


Figure 11. Effect of heating system used for biodiesel production process on HC emission of engine fueled by various diesel-biodiesel blends at different engine speeds

3.5.4. NO_x emissions

Figure 12 reveals the variations of NO_x emission with engine speed by running diesel engine with different fuel blends. Higher NO_x emissions occur in the exhaust using blend fuels due to the higher flash point and oxygen content of biodiesel, resulting in augmented

gas temperature in the engine chamber and accelerated interaction between oxygen and nitrogen (Xue et al. 2011). Faster premixed combustion by addition of the biodiesel to diesel fuel leads to elevated combustion temperature to over 1800 K causing NO_x formation (Zaharin et al. 2017, Sharma et al. 2019). B20-Mic. and B10-Conv. showed the lowest NO_x content in the exhaust, though B40-Mic. presented a similar NO_x amount in the exhaust gases at high engine speeds.

Further, the NO_x emission diminished continuously with elevation of the engine speed. It can be related to the shorter residence time available for NO_x formation, which may be owing to the rise in both the volumetric efficiency and flow velocity of the reactant mixture at higher engine speeds (Lin and Lin 2006). The minimum increase in the NO_x content was observed for B20-Mic. at the engine speed of 1800 rpm which is consistent with the results of other studies (Lin et al. 2008, Hoseini et al. 2017). Finally, B40-Mic. and B20-Mic. provided almost similar NO_x emissions at the other engine speeds.

It was mentioned that a less increase in NO_x emission can be observed by using the biodiesel containing the more saturated carbon bonds (Lin et al. 2009, Sharma et al. 2019). It can prove the similarity of NO_x emission when blend of diesel-biodiesel produced by microwave irradiation was utilized. In the other words, NO_x emissions increase by raising the degree of unsaturation of biodiesel (increase the unsaturated components) (Lin and Lin 2006). Moreover, advance in combustion for biodiesel due to shortens ignition delay, and advance of start of injection of biodiesel due to the higher density and viscosity are the reasons for higher NO_x of fuel blended with biodiesel produced by conventional method.

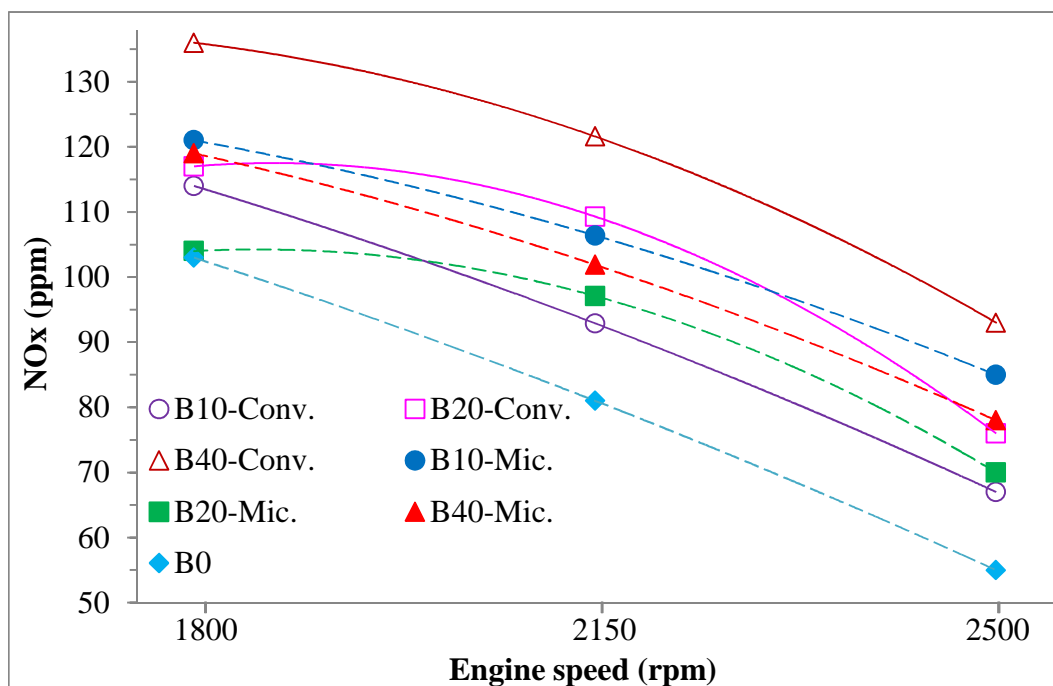


Figure 12. Effect of heating system used for biodiesel production process on NO_x emission of engine fueled by various diesel-biodiesel blends at different engine speeds

3.5.5. Comparison the emissions of B40

After chosen B40 as a suitable proposition for blending the biodiesel with diesel fuel, the CO₂, CO, HC and NO_x emission contents were summarized in Figure 13. It clearly observes that the fuel produced by microwave irradiation exhibits better emissions profile in all of engine speeds. Lower increasing in the amount of NO_x and CO₂ along with higher reduction of CO and HC prove that microwave irradiation changes the properties of produced biodiesel by effecting on the kind of FFA components. Probably under microwave medium, the nonpolar components (saturated FFA) easily react with polar component (methanol as alcohol) to form ester. It causes to saturation components form more than unsaturation components that lead to reduction the unsaturation degree and better combustion of fuel in the engine chamber, as mentioned above. Therefore, the microwave irradiation can concern as an effective method for fabrication of a same biodiesel fuel with low unsaturated

components that significantly decreases the emissions released from those produced by conventional method.

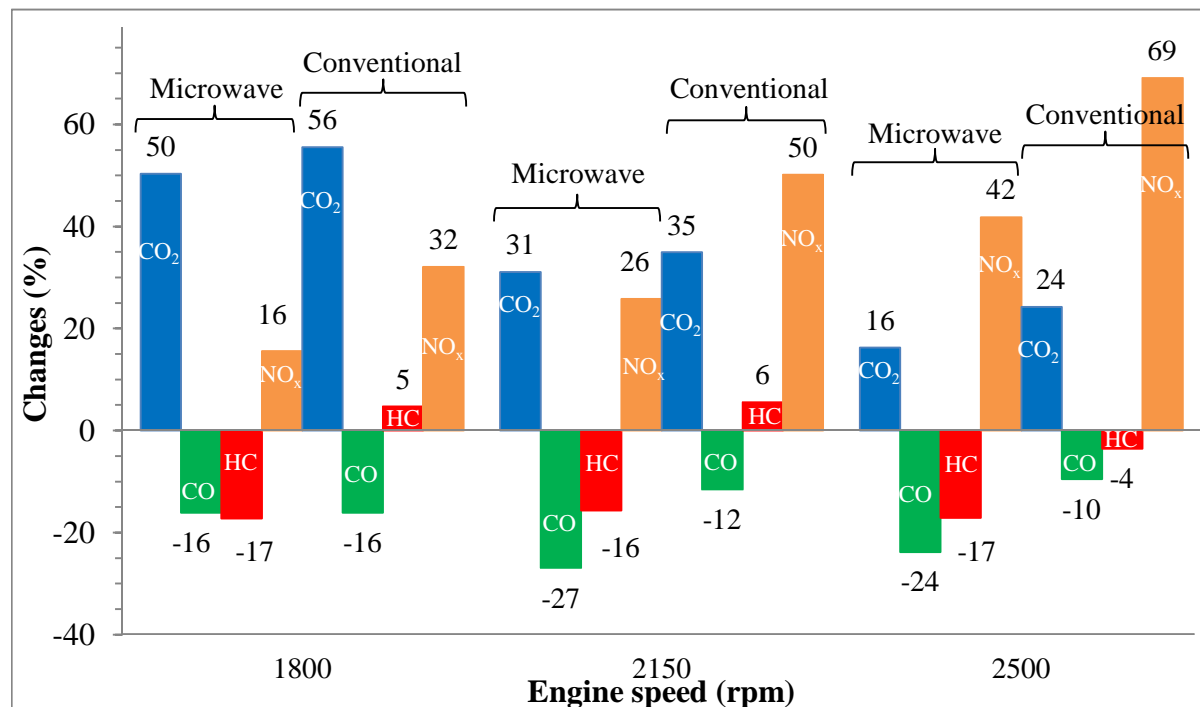


Figure 13. Comparison the emissions of B40 fuels produced by conventional and microwave heating systems fueled in diesel engine at different engine speeds

4. Conclusion

Palm kernel oil (PKO) contains appropriate amounts of oil making it a suitable source for biodiesel production. Accordingly, its performance in the diesel engine was firstly compared when microwave and conventional heating systems were utilized for converting PKO to biodiesel. The palm seed (Zahidi type) contained 10 wt.% oil in which a high FFA content was observed. After reducing the FFA content of PKO via esterification reaction, the PKO was transesterified via conventional and microwave irradiation heating systems with methanol and NaOH as a catalyst. A biodiesel yield of 96.4% was obtained at the conditions of 60 °C, methanol/PKO molar ratio of 6, 1 wt.% catalyst, and 90 min of the reaction time for

conventional method. On the other hand, microwave irradiation reduced the reaction time to 2.5 min and enhanced the yield to 97.6%. In addition to shortening the reaction time, the separation step was also curtailed from 4 h to 4 min using microwave irradiation. Both PKO biodiesels produced by conventional and microwave method met the ASTM D6751 and EN14214 standard specifications. The temperature monitoring of microwave-assisted transesterification reaction showed that the reaction temperature must be lower than the boiling point of the utilized alcohol to achieve the maximum conversion. Assessment of the performance and exhaust gas emissions of a single-cylinder engine fueled by blends of PKO biodiesel-diesel suggested that PKO biodiesel produced by the conventional method presented a higher brake power and torque and lower BSFC compared to that prepared by the microwave method. All fuels revealed a higher power and torque at the engine speed of 2500 rpm as compared to engine speeds of 1800 rpm and 2150 rpm.

Overall, B40 (both PKO biodiesels produced by different heating systems) can be a choice for improvement the problems of net diesel fuel by blending with biodiesel in which the biodiesel has higher proportion compared to commercial blend fuel (B20). The exhaust gas emissions analysis suggested that PKO biodiesel exhibited reduction in CO and HC emissions in exhaust due to elevation of oxygen content of the fuel leading to better combustion. On the other hands, increase of CO₂ and NO_x contents was observed by using biodiesel. Unlike the results of engine performance, PKO biodiesel produced by microwave irradiation showed better results in releasing the emissions which can be related to its lower density and viscosity. These properties mitigate the problem of fuel injection in the engine chamber. B40 also presented appropriate properties in the analysis of the emissions. The results confirmed that PKO biodiesel has very suitable properties which can be blended with net diesel fuel at a higher volume ratio (B40). Moreover, microwave irradiation, by shortening the transesterification time, improving the properties of produced biodiesel, and

significantly reducing the exhaust gas emissions, can be regarded as an alternative method for industrial biodiesel production to reduce greenhouse gas problems.

It must be mentioned that the FFAs compositions of PKO is strongly depends on the climate as well as engine performance that would be some limitations. Moreover, this study must be developed on assessment the engine load, broder engine speed, different engine type (containing more cylinder) that will be presented in our future work.

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Declarations of interest

None

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Journal Pre-proof

Precise Evaluation the Effect of Microwave Irradiation on the Properties of Palm Kernel Oil Biodiesel Used in a Diesel Engine

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Research Highlights

- Biodiesel production from palm kernel oil using conventional and microwave methods
- Optimization of transesterification reaction conditions under microwave irradiation
- Assessment the variations of reaction temperature by changing each parameter
- Evaluation the performance and emissions of a diesel engine fuelled by blend fuels
- Finding B40-Mic. and B40-Conv. fuels for using in the diesel engine.

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