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Low-Cost Alternative Biodiesel Production Apparatus Based on Household Food Blender for Continuous Biodiesel Production for Small Communities

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Abstract

Fatty acid methyl esters (FAMEs) are sustainable biofuel that can alleviate high oil cost and environmental impacts of petroleum-based fuel. A modified 1,200 W high efficiency fruit blender was employed for continuous transesterification of various refined vegetable oils and waste cooking oil (WCO) using sodium hydroxide as a homogeneous catalyst. The following factors have been investigated on their effects on FAME yield: baffles, reaction volume, total reactant flow rate, methanol-oil molar ratio, catalyst concentration and reaction temperature. Results indicated that the optimal conditions were: 2,000 mL reaction volume, 50 mL/min total flow rate, 1% and 1.25% catalyst concentration for refined palm oil and WCO, respectively, 6:1 methanol-to-oil molar ratio and 62 - 63ºC, obtaining yield efficiency over 96.5% FAME yield of 21.14×10^{-4} g.J^{-1} (for palm oil) and 19.39×10^{-4} g.J^{-1} (for WCO). All the properties of produced FAMEs meet the EN 14214 and ASTM D6751 standards. The modified household fruit blender could be a practical and low-cost alternative biodiesel production apparatus for continuous biodiesel production for small communities in remote areas.

Keywords: Biodiesel; Continuous; High-power fruit blender; Transesterification; Vegetable oil; Waste cooking oil

1. Introduction

Fossil fuels and their derivatives are the main sources for transportation, electricity generation and agriculture. However, it is widely accepted that fossil fuel leads to large greenhouse gas emissions[1] and particulate matter causing environmental consequences. Alternative non-petroleum-based fuels such as biodiesel has received considerable attentions recently due to the fact it is renewable, which is more environmentally-friendly than petroleum-derived diesel fuels in terms of reducing the exhaust emissions and high biodegradability[2]. Biodiesel is a compound of mono-alkyl esters derived from various types of vegetable oils, lard, waste cooking oil (WCO), and unicellular or multicellular plants including certain species of algae[3]. The first generation of biofuels, the raw material is extracted from crop plants, for instance, palm, soybean, corn, sunflower, rapeseed and so on [4, 5]. In 2018, Thailand was ranked as having the third largest palm oil plantation in the world with a planting area of over 8.5×10^3 km^2 and palm oil production of up to 15 million tons [6]. Nevertheless, domestic palm oil price tends to decrease. Therefore, the use of palm oil as the feedstock to produce biodiesel will stimulate the economy, help farmers indirectly and increase the value-added of palm oil. There are many studies on the use of waste cooking oil for biodiesel production which beneficially reduce waste to the environment. Also molecular structure of biodiesel derived from vegetable cooking oil is redefined leading to the reduction of emissions[7] which is one of the principles of sustainable biofuels.

Most commercial-level biodiesel production processes commonly use vegetable oil reacting with alcohol, mostly methanol, through a chemical process called transesterification to produce fatty acid methyl esters (FAMEs) and glycerol together with conventional homogeneous base or acid catalysts [8, 9]. For the base catalysts, potassium hydroxide and sodium hydroxide have been preferred by the industry because of their low cost, high reaction rates and faster process

[9, 10]. Generally, biodiesel synthesis using alkali catalysts requires 1 - 4 h under different reaction temperatures [11]. Homogeneous acid catalysts that have been used are such as sulfuric acid, sulfonic acid, hydrochloric acid and phosphoric acid. Acid-catalyzed biodiesel production accompanies the reaction through esterification which does not lead to soap formation, but the reaction is quite slow, requires high temperature and high alcohol to oil molar ratio, and may cause reactor corrosion [9]. Miao et al. [12] indicated that 2.0 M trifluoroacetic acid reacting with methanol to soybean oil molar ratio of 20:1 at 120^{o}C after 5 h of operation gave the FAME yield of 98.4%. With these regards, the use of an alkali catalyst in the present work offers a simple operation and can shorten the reaction time for biodiesel production.

Typically, when mixing oil with methanol, two-liquid phases will be generated, so advanced intensification technologies have been designed and developed to improve the miscibility of the liquids and to enhance speed, heat and mass transfer, reaction time, energy efficiency and cost effectiveness. Most intensified technologies require expensive equipment pieces that lead to costly maintenance expenses and consume large energy, while some conditions require high pressure and high temperature causing safety concerns.

The present research aimed to use a high-power kitchen fruit blender modified with a stainless steel chamber to produce biodiesel on a continuous basis for small communities. The high-power fruit blender can create process intensification from the cavitational effect taking place inside the reactor. The rapidly-spinning impeller causes a sufficient pressure reduction in the liquid generating numerous microbubbles. They flow through the tips and trailing edges of the spinning blades and they are then ripped into the surrounding fluid and eventually collapse and mix the liquid well [13]. Due to the high rotational speed of the impeller, rapid liquid circulation enhances the mixing efficiency as well as increase the reaction kinetics. Also, the price of the high-power

kitchen fruit blender used in the present work is much lower than those of the professional reactors and it is convenient to purchase.

The batch production has some drawbacks such as the requirement of a larger reaction volume and lower efficiency due to the natural start-up and shutdown system [14]. To eliminate these limitations, continuous biodiesel production processes have been put forward to increase the production efficiency overtime. Therefore, in the present work, a simple process for continuous biodiesel production based on vegetable oils and WCO using the efficient kitchen blender is proposed for small communities. This biodiesel production system offers the compact size of the reactor, simplicity of set up, control, operation, and maintenance.

2. Results and discussion

Effect of baffles in reactor

For large rectors, installation of baffles are common practices to provide more effective mixing and heat transfer in the reactor [15]. Without baffles, the fluid would spin freely without achieving good mixing and reaction yield. To ensure that the designed chemical reactor with the rapidly-spinning impeller does require baffles similar to conventional chemical reactors with lower spinning speeds, the effect of baffles was studied here. The reactor was studied with and without appropriate longitudinal flow baffles on the lid extending into the reactor. The dimensions of the baffles were as follows [16, 17]: number of baffles = 4, width = 12.5 mm, length = along the reactor terminating at 10 mm from the bottom, off-wall distance = 2.1 mm. The experiment on the effect of the baffles was based on the MeOH/refined palm oil molar ratio of 6:1, reaction volume of 1,000 mL, feed flow rate of 25 mL/min, NaOH loading of 1 wt% and at 62 - 63^{o}C. The result is shown in Fig. 1.

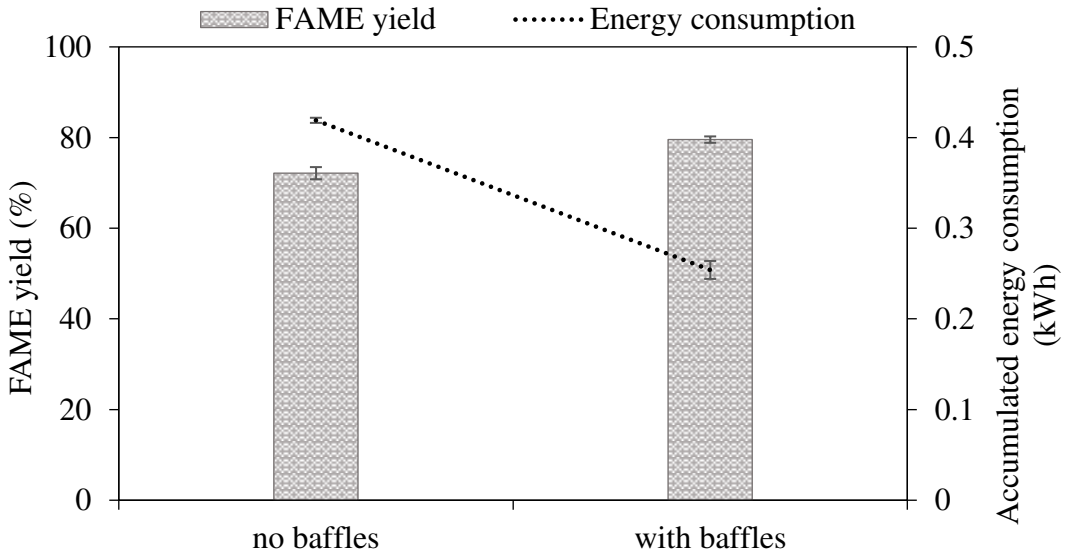


Fig. 1. Effect of baffle plates on steady state FAME yield (refined palm oil, 1,000 mL, 25 mL/min, 1 wt% NaOH, 6:1 MeOH:oil molar ratio, 62 - 63°C)

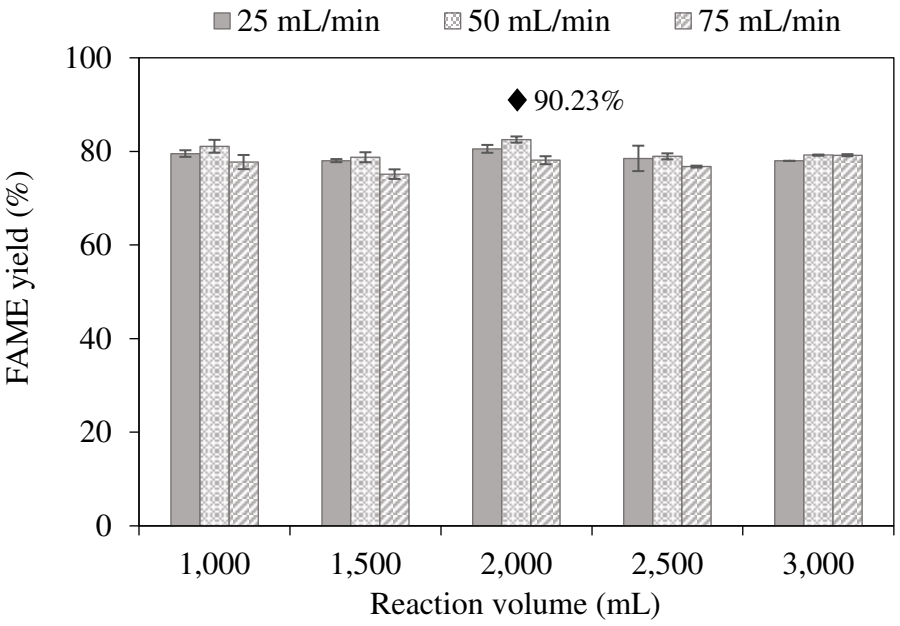
The presence of the baffles shows a significant effect on both steady-state FAME yield and energy consumption. The FAME yield increased from 72.5 to 80% after the reaction time of 90 min. Also, for the non-baffled reactor, at the same impeller speed, the temperature of mixture rose very slowly as it took about 30 min to reach 62°C. For the baffled reactor, only about 10 min was required. This finding confirms the hypothesis that the reactor with rapidly-spinning blades also requires baffles to help improve the heat and mass transfer, as well as flow pattern of liquid resulting in rapid temperature rise causing the endothermic reaction to move forward [15]. They work by disrupting the flow pattern and keeping the movement of the top to bottom fluid to promote radially axial circulation of the fluid [18]. In addition, they prevent swirling and vortexing of liquid which results in high shear rate [19] and decrease the relative velocity between the impeller and liquid mixture resulting in enhancement of the degree of turbulence. In fact, from eye

observation through the viewport, for the non-baffled case, most of the liquid mixture appears to be pushed to the side of the reactor and spin freely. As only a small portion of the mixture came into physical contact with the impeller, higher rotational energy was required to bring the overall mixture to the operating temperature compared to the baffled case.

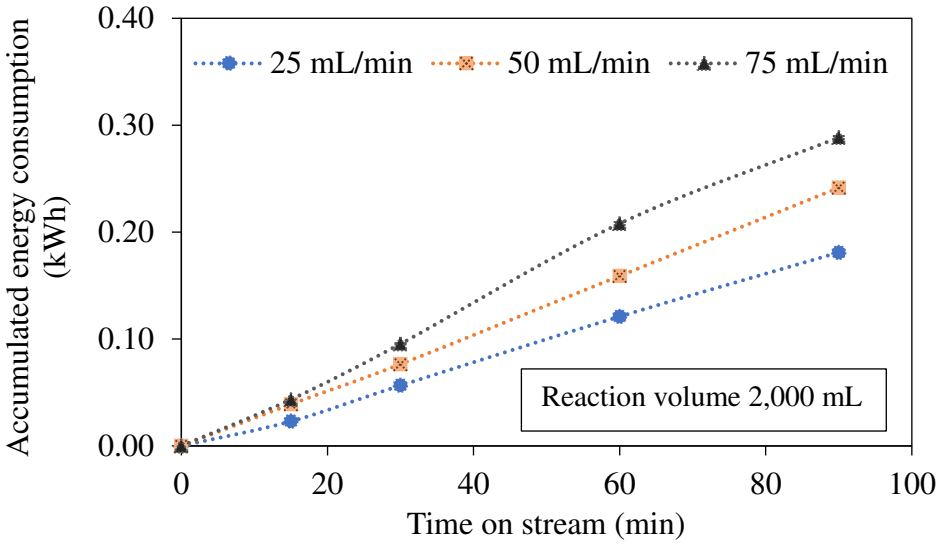
Effects of reaction volume and reactant total flow rate on FAME yield

Fig. 2(a) shows the influence of reaction volume and total feed flow rate on FAME yield at steady state. The flow rate of 50 mL/min appears to provide the highest FAME yield for all mixture volumes studied. At this flow rate, FAME yield was increased when the reaction volume rose from 1,000 to 2,000 mL, and then dropped with a further increase in the reaction volume. Thus, the 2,000 mL volume and the total feed flow rate of 50 mL/min are the optimal process parameters for the designed reactor giving 82.53% steady state FAME yield and increasing to 90.23% after washing.

For volume larger than 2,000 mL, the concentration of micro bubbles from cavitation decreases as well as lower mass and heat transfer, leading to a declined FAME yield. For the effect of total feed flow rate, the FAME yield for all reaction volumes increased with the increase in feed flow rate from 25 to 50 mL/min, but decreased with a higher flow rate of 75 mL/min. This result is in contrast to the study of Chen et al. [20] and Santacesaria et al. [21] as they reported that the increase in flow rate lowered the residence time leading to a lower biodiesel yield. However, the present work controlled the temperature inside the chamber by adjusting the speed of the impeller. When the feed flow rate increased, the mixture temperature decreased, and the impeller must turn faster to maintain the same temperature. It might be concluded that the agitation speed has a greater effect on the biodiesel yield.


25 mL/min
50 mL/min
75 mL/min
90.23%
FAME yield (%)
100
80
60
40
20
0
1,000
1,500
2,000
2,500
3,000
Reaction volume (mL)

(a)


25 mL/min
50 mL/min
75 mL/min
Accumulated energy consumption (kWh)
0.40
0.30
0.20
0.10
0.00
Reaction volume 2,000 mL
0
20
40
60
80
100
Time on stream (min)

(b)

Fig. 2. (a) Effects of reaction volume and total feed flow rate on steady-state FAME yield (refined palm oil, 1 wt% NaOH, 6:1 MeOH:oil molar ratio, 62 - 63°C) , ♦ = after washing and (b) accumulated energy consumption (2,000 mL case)

For the reaction volume of 2,000 mL, the three total feed flow rates of 25, 50 and 75 mL/min correspond to the residence time of 80, 40 and 26.67 min, respectively. As the optimum flow rate was 50 mL/min, the optimum residence time for the studied reactor is 40 min. Darnoko and Cheryan [14] also found an optimum residence time of 60 min to achieve the highest concentration of esters of 85.6% based on a CSTR reactor, with shorter or longer residence time resulting in low yield. The effect of residence time in the present work can be discussed as follows. The longer residence time provides the higher FAME yield, according to the literature that methyl esters content and conversion of oil from transesterification increase with increasing time [14, 22]. In addition, the residence time for continuous transesterification could exhibit wide ranges from seconds to minutes depending on reactor types and flow rate. Long residence time could enhance the hydrolysis of esters causing ester loss and lowering FAME yield [23]. Too much residence time could also lead to the reversible reaction and methanol evaporation, reducing the overall yields [9, 11, 24].

For the accumulated energy consumption shown in Fig. 2(b), higher flow rate requires more energy to heat up additional quantity of reactants entering the reactor. The energy consumption will have an effect on yield efficiency.

An appropriate design of a cylindrical chemical reactor with respect to height and diameter helps increase heat transfer, liquid mixing as well as productivity. Conventionally, the optimum

ratio of the height (*H*) to diameter (*D*) of a cylindrical chemical reactor is unity. The height of the solution mixture in the reactor for the 2,000 mL case is about 11.5 cm (*H*). With the reactor diameter of 15 cm (D), the *H*/*D* ratio is approximately 0.8. The *H*/*D* ratio of unity would correspond to the mixture volume of roughly 2,120 mL. The slight inconsistency between the optimal *H*/*D* ratio of the designed reactor and the theory may indicate that a cylindrical reactor with very high impeller speed may not follow the theory applied for conventional cylindrical chemical reactors with low impeller speed.

Effect of reactant molar ratio on FAME yield

Stoichiometrically for transesterification, 1 mole of triglyceride requires 3 moles of alcohol to generate 3 moles of FAME and 1 mole of glycerol. However, a high amount of alcohol is preferred to push the reaction forward for a very fast reaction rate and enhance the oils conversion. Also, at a lower methanol ratio, the high-viscosity oil needs a higher amount of methanol to be soluble in methanol [25]. In this work, the methanol to refined palm oil molar ratios of 3:1, 6:1 and 9:1 with 1 wt% of NaOH at reaction volume of 2,000 mL and at 62 - 63ºC were investigated and the results are depicted in Fig. 3. The steady-state FAME yield is low for the stoichiometric ratio of 3:1 due to the lowering in miscibility and contacting between molecules of methanol and oil [25]. When increasing the molar ratio to 6:1, the FAME yield increased from 72.69 to 82.53%. Beyond the 6:1 molar ratio, the excess amount of methanol slightly decreased the steady state FAME yield to 78.58%. The cause of the decline in FAME yield could be due to the enhancement of solubility of methanol, FAME and glycerol. A higher amount of methanol also lowered the concentration of oil and decreased the FAME yield. This result corresponds to the report that biodiesel yield can decrease due to excess methanol [23]. Hence, the methanol to oil molar ratio

of 6:1 was an optimum value for further studies. This ratio is also beneficial for yield efficiency as the accumulate energy consumption is minimal at this ratio.

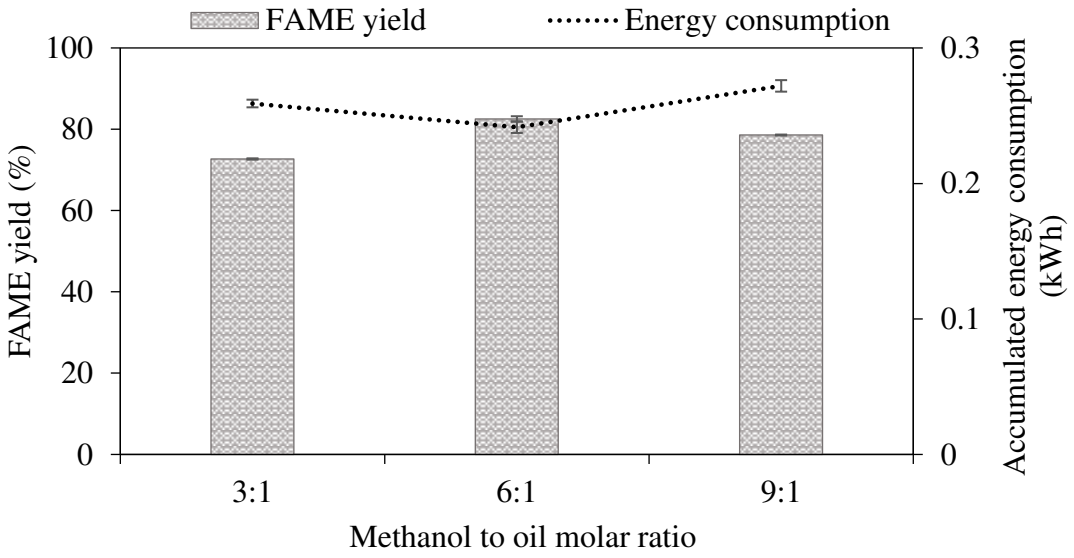


Fig. 3. Effect of reactant molar ratio on steady state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

Effect of catalyst concentration on steady state FAME yield

Based on results in Fig. 4, the steady state FAME yield increased with more catalyst loading, reaching the highest value of 83.61% for 1.25 wt% NaOH. However, the yield increase of only 1.08% by increasing the catalyst concentration from 1 to 1.25 wt% does not justify using the high catalyst loading. Also at 1.25 wt%, emulsion formation was observed, and this phenomenon leads to difficulty in separation [26] including increased production and purification costs. The higher mixture viscosity for the 1.25 wt% case is evident from the substantial increase in the accumulate energy consumption. Therefore, the 1 wt% catalyst concentration is appropriate

for the studied reactor design. It is also beneficial for yield efficiency as the accumulate energy consumption is minimal at this catalyst loading.

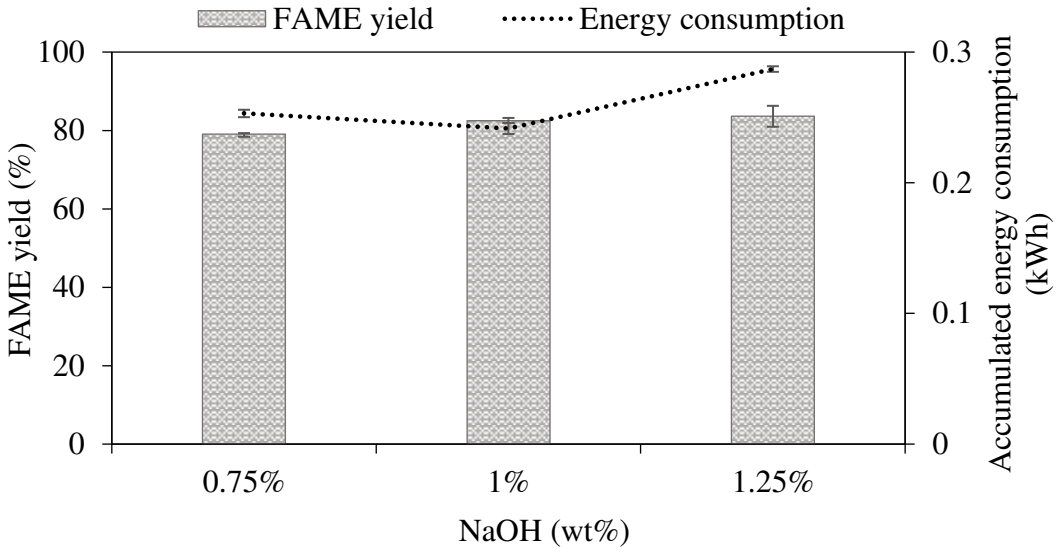


Fig. 4. Effect of catalyst loading on steady state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 62 - 63°C)

Effect of reaction temperature on FAME yield

Reaction temperature affects kinetics and equilibrium. It can increase mass transfer and reduce viscosity of oil. The results shown in Fig. 5 indicate that as the reaction temperature increased from 50 - 62°C, the FAME yield at steady state was enhanced, and that at 65°C, the yield dropped. The maximum steady state FAME yield of 82.53% was obtained at 62°C. At low reaction temperature, the rate of reaction was slow [27]. For excess temperature (65°C) which is higher than the boiling point of methanol (64.7°C), it promotes methanol being in a vapor phase while the oil is still in a liquid phase affecting poor contact between the reactants [26]. . High reaction temperature also affects energy consumption negatively.

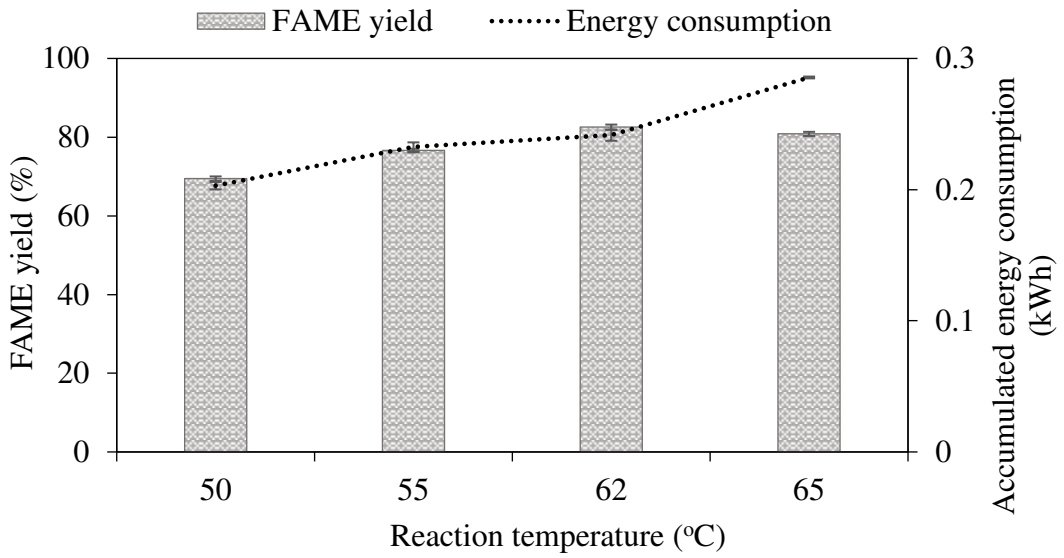


Fig. 5. Effect of reaction temperature on steady state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 1 wt% NaOH)

Effect of reactant discharge position on FAME yield

The influence of reactant discharge position is shown in Fig. 6. The centered position showed better steady-state FAME yield than the against-wall position. At center or near the tip of the impeller positions which delivered highest turbulence [28], the new reactant provided effective mixing. When the discharge position is at the reactor wall, besides not mixing well in every direction, a certain amount of the new reactants would quickly flow out of the discharge port without undergoing transesterification, a phenomenon known as short-circuiting. It is also important to note that the energy consumption was slightly higher for the off-centered case too.

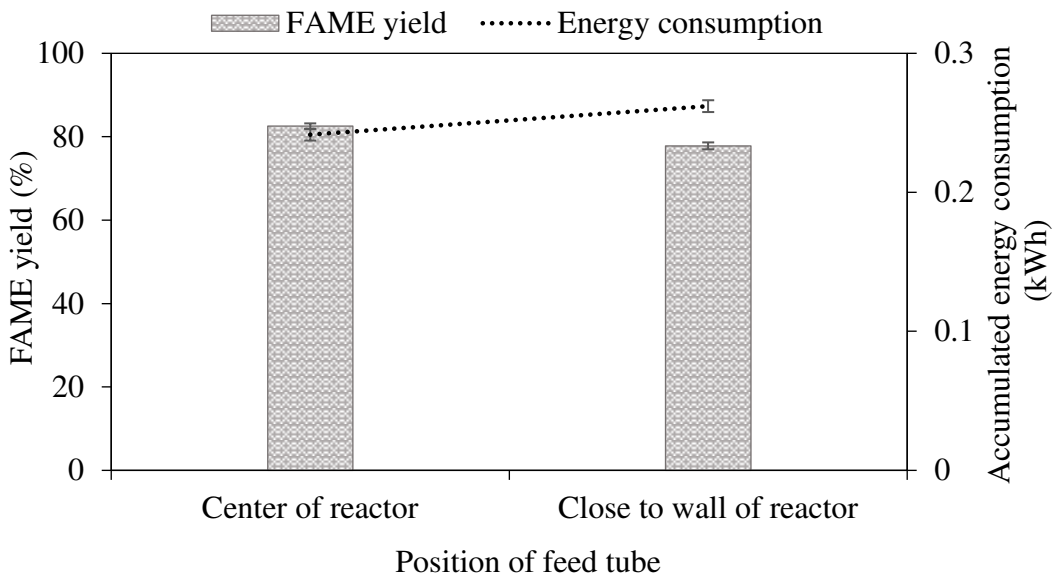


Fig. 6. Effect of reactant discharge position on steady-state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

Effect of various types of vegetable oils on FAME yield

Fig. 7 illustrates the results of transesterification of each oil type. It is seen that palm oil as a feedstock showed the highest steady-state yield of 82.53% (increasing to 90.23% after washing). Corn oil and sunflower oil gave slightly lower FAME yield at steady state, while soybean oil and canola oil gave the lowest methyl esters content. Literature review reveals that fatty acid components of each feedstock do not change notably throughout transesterification while physical and chemical properties of FAME depend on chain length and number of double bonds of feedstocks [29]. Although soybean, sunflower and corn oils contain a similar degree of unsaturated carbon bonds in contrast to palm oil, the steady state FAME yields are different. Thus, FAME yield does not depend on the degree of saturation of the oil. In fact, molecular weight of oils directly relates to carbon chain length [30]. When considering in terms of molecular weight of each feedstock (see Table S1), palm oil which comes with the lowest molecular weight gave the

highest FAME yield while corn oil consisting of the second lowest molecular weight provided the second highest FAME yield. Sunflower oil and canola oil have similar molecular weight, but the FAME yields are contrasting. Soybean oil comes with the highest molecular weight and gave the second lowest FAME yield. This result might be explained that the low molecular weight oil has less powerful steric hindrance and, in some cases, increased reactivity [31] affecting the high conversion of oil. It can be concluded that, based on this study, FAME yield depends on molecular weight (chain length) of feedstocks.

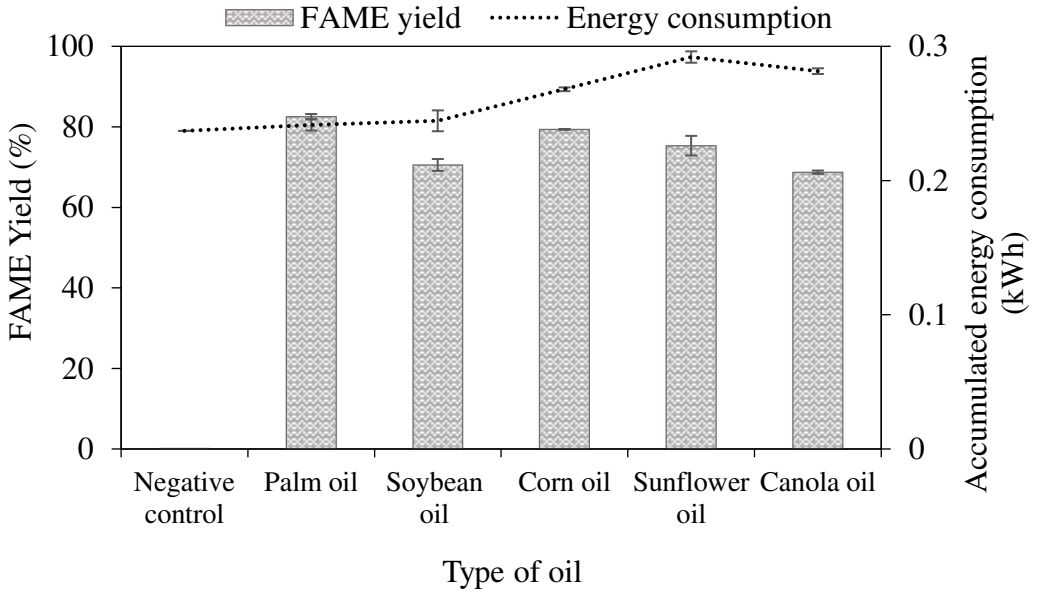


Fig. 7. Effect of various types of vegetable oils on steady state FAME yield (2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

Transesterification of WCO feedstock

As the price of edible oils contributes approximately 80% of biodiesel price [32], biodiesel production cost can be lowered by using WCO instead of refined vegetable oils. The effect of

NaOH concentration on steady-state FAME yield is illustrated in Fig. 8. The FAME yield at steady state increased with increasing NaOH content from 1 to 1.25% decreased with a higher catalyst loading though. The highest steady-state FAME yield was 80.35% (increasing to 87.76% after washing). As expected, low catalyst concentration resulted in low FAME yield as there was insufficient number of active sites to react. On the other hand, too much catalyst (1.5%) increased the saponification with triglycerides resulting in low FAME yield [32] and biodiesel will turn solid, which is unsuitable for actual use. This result corresponds to the study of Maddikeri et al. [33] who studied the intensification reaction of WCO through hydrodynamic cavitation at a catalyst loading of 0.75 - 1.25%. The result showed that too much catalyst concentration did not offer a remarkable increase in FAME yield.

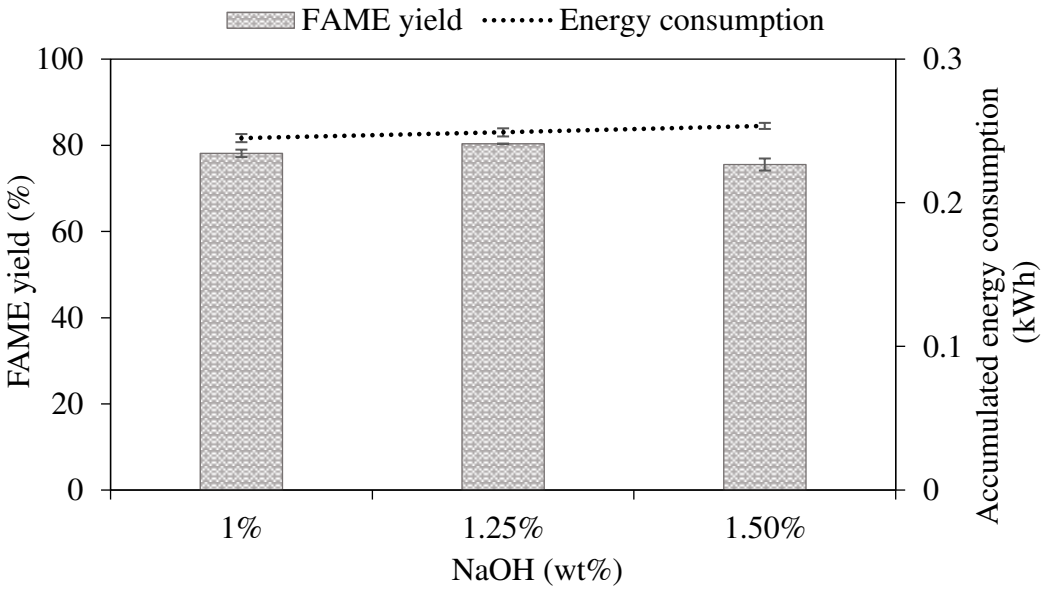
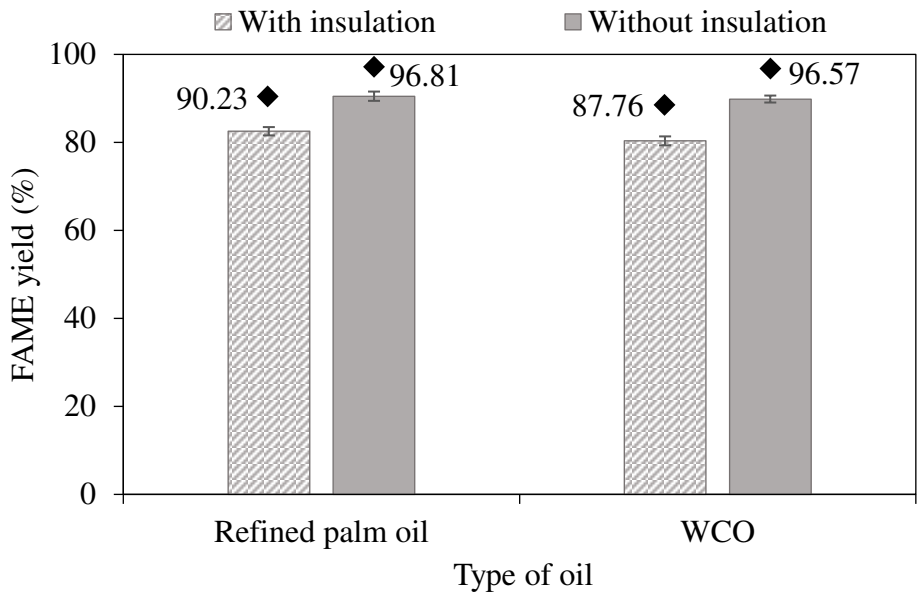


Fig. 8. Effect of catalyst loading on WCO-derived FAME yield at steady state (2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

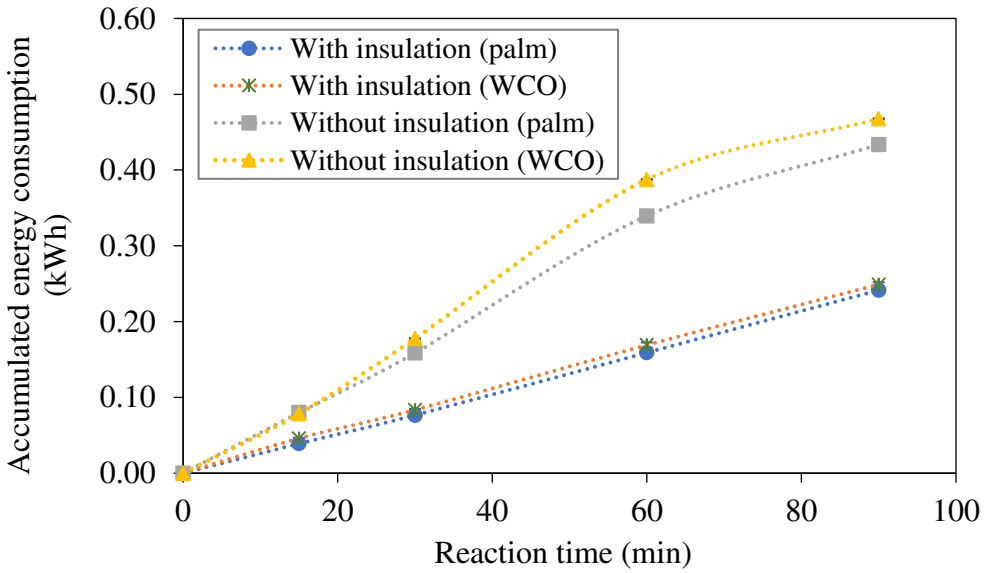
Effect of reactor insulation on steady-state FAME yield

The results are shown in Fig. 9(a). The steady-state FAME yields of 90.5% from refined palm oil and 89.85% from WCO were higher than those of the insulated reactor. After washing, the yields further increased to 96.81 and 96.57% from refined palm oil and WCO, respectively. For the non-insulated reactor, as it continuously loses heat to the environment, in order to keep the bulk temperature between 62 and 63^{o}C, the speed of the impeller must be higher than that of the insulated reactor. This effect is evident from the higher accumulated energy consumption shown in Fig. 9(b). The higher viscosity of WCO than refined palm oil contributed to the higher energy consumption as well. By maintaining the same reaction temperature for both insulated and non-insulated reactor cases, the result signifies the effect of the impeller speed. This suggests that even higher steady-state FAME yield could be achieved by active cooling of the reactor, e.g., water cooling, so that higher impeller speed can be applied while maintaining the same reaction temperature of 62 - 63^{o}C. The high speed of impeller about of 17,900 rpm and calculated Reynolds number estimated to be 19,400 creates fully turbulent operation. Hence, this can be implied that the mixture between oil and methanol are mixed well throughout the experiment [34]. Moreover, due to the fact that transesterification is endothermic reaction in the nature, therefore, the operation without insulation could be facilitated the heat dissipation from the reaction mixture resulting to shift the reaction forward [35].

This finding suggests that the FAME yield of waste cooking oil as feedstock is as good as the yield of FAME based on palm oil. Therefore, the use of waste cooking oil is another promising sustainable alternative for continuous biodiesel production. In addition, in the remote communities, the waste oil from cooking can be collected and used to produce biodiesel. It is one way to reduce waste to the environment, as well as to increase the added value of waste oil.



(a)



(b)

Fig. 9. (a) Effect of insulation on steady-state FAME yield and (b) accumulated energy consumption (2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C), ♦ = after washing

The first order kinetics for transesterification of refined palm oil

The reaction kinetics was evaluated at 50, 55, 62 and 65°C. The kinetics was studied with the residence time between 0 - 40 min. By fitting the experimental data using Eq. (3), a good linear relationship between $\frac{X_A}{(1-X_A)}$ and t indicates that the first order kinetics is suitable for transesterification.

The kinetic rate constant (k) and R^2 are listed in Table S2. The highest rate constant of 0.1204 min^{-1} with $R^2 = 0.9906$ was found at 62°C, confirming that the reaction rate at 62°C is fastest and it follows the first-order kinetics which is in good agreement with the literatures [36].

Activation energy

The activation energy of the studied transesterification obtained from plotting of ln(k) and 1/T as shown in Fig. S1 was 39.41 kJ/mol with the frequency factor of 1.47×10^5 1/min. The Arrhenius equation for the present study can be expressed as:

$$\ln(k) = -\frac{4740.2}{T} + 11.90 \quad (4)$$

In general, the activation energy for homogeneous alkali-catalyzed transesterification should be in the range 33.6 - 84 kJ/mol [37]. The calculated activation energy of the present study is within this range.

Yield efficiency

The yield efficiency of FAME derived from refined palm oil and WCO of selected literatures is reported in Table S3 which summarizes the yield efficiency of each technology reactor. When comparing to values obtained by other researchers using other intensified technologies, the yield efficiency of the present work is higher.

FAME properties

Properties of FAMEs produced from refined palm oil and WCO at the optimum conditions are listed in Table 1. All of the analyzed properties follow the EN 14214 and ASTM D6751 standards.

Table 1 Properties of produced FAMEs

Property	**Synthesized FAME from refined palm oil**	**Synthesized FAME from WCO**	**EN 14214**	**ASTM D6751**
Density (g/cm^3)	0.87	0.88	0.85 – 0.90	0.86 – 0.90
Kinematic viscosity (40^oC, mm^2/s)	4.20	4.19	3.5 – 5.0	1.9 – 6.0
Cloud point (^oC)	12	11	-	-3 – 12
Acid value (mg of KOH/g of oil)	0.39	0.5	$\leq$ 0.5	$\leq$ 0.5
FAME yield (%) (without insulation)	96.81	96.57	$\geq$ 96.5	

Preliminary design of biodiesel production system for small communities

The present work successfully demonstrates the continuous biodiesel production through the upgraded kitchen blender with the production rate of 3 liters an hour (with no purification process). The biodiesels produced from both refined palm oil and WCO meet the world's standards and can be blended with petro-diesel for use in diesel engines. The proposed production system for small communities can be very simple. Instead of large tanks and equipment pieces for a conventional batch process requiring substantial footprint, several of such continuous reactors can be operated in parallel. Each unit, a reactor connected to a kitchen blender, can be placed on a shelf to take advantage of the small height of each unit. Thus, the total area required for transesterification would be very small. For instance, if 30 units were to be operated in parallel, the total area required would be only that of a medium-sized shelf with 3 stories (assuming 10 units on each story) as illustrated in Fig. S2. The production capacity would be as high as 90 L/h, which would be more than sufficient for a small community. Only two pumps would be required, one for oil and the other for MeOH + NaOH, to provide feeds to all units through split valves. The system could easily be expanded by installing more units to increase the production capacity for medium-sized communities or even small enterprises. Another good aspect of running such units in parallel is that if one unit malfunctioned, it could be easily and quickly replaced without affecting the entire production process. In terms of yield efficiency, the present research showed better results, 21.1×10^{-4} g/J for refined palm oil and 19.4×10^{-4} g/J for WCO, than that of commercial biodiesel plants in Thailand of 5.6×10^{-4} g/J [38] and produced biodiesel in Iran of 0.4×10^{-4} g/J [39], signifying that the proposed kitchen blender can be more energy efficient than conventional productions. In terms of capital investment, each unit would cost no more than USD 50. The two fluid pumps with low pumping heads would cost no more than USD 200. The whole production system would cost less than USD 2,000, thus, the capital investment is low. It may also

be possible to gravity drain the two fluids from their tanks, eliminating the use of the two pumps, but the flow rates would not be constant unless the two fluid levels were kept relatively constant during the production. This novel yet very simple, low-cost biodiesel production technology could replace large production plants.

3. Conclusions

The present research successfully demonstrates the operation of the modified high-power fruit blender for continuous transesterification of refined vegetable oils and waste cooking oil for household uses. Results indicated that the optimal conditions were: 2,000 mL reaction volume, 50 mL/min total flow rate, 1% and 1.25% catalyst concentration for refined palm oil and WCO, respectively, 6:1 methanol-to-oil molar ratio and 62 - 63ºC. The highest obtained steady-state FAME yields were 96.81% (for palm oil) and 96.57% (for WCO). All the properties of produced FAMEs meet the EN 14214 and ASTM D6751 standards. The activation energy of the studied transesterification was 39.41 kJ/mol. This simple continuous fruit blender can be operated in a parallel configuration to produce more biodiesel for small community with high yield efficiency and low capital investment.

4. Method

Materials

Various fresh refined vegetable oils and waste cooking oil (WCO) were used as the feedstocks for continuous biodiesel production. Relevant properties of the vegetable oils and WCO

are presented Table S1. The feedstocks: refined palm oil, soybean oil, corn oil and canola oil of Sime Darby Oils Morakot Co., Ltd., Thailand, and refined sunflower oil of Thanakorn Vegetable Oil Products Co., Ltd., Thailand, were purchased from a local supermarket in Bangkok, Thailand. The WCO was provided by a canteen in Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand. All chemicals were of analytical reagent grade and were used as received. 99.8% methanol and 97% sodium hydroxide were supplied from Kemaus. 99.5% n-heptane and > 99.0% methyl heptadecanoate (analytical standard) were obtained from Ajax FineChem and Sigma-Aldrich, respectively.

Equipment details and set up

The high-power fruit blender of 1,200 W, 220 V, 50 Hz, 25,000 rpm maximum (Otto® brand, model: BE127A) was upgraded with a 304 stainless steel chemical reactor. The supplied plastic blending bowl that came with the blender was replaced with the stainless steel rector to ensure long-term durability and safety. The cylindrical-shaped reactor was 19.8 cm in height, 15 cm in diameter and 0.3 cm in thickness. It was insulated with cotton sheets to reduce heat loss to the environment and was installed with 4 baffles of 1.3 cm in width. No modification to the stainless steel impeller shown in Fig. S3 was made; it was the original one supplied with the blender. One side of the reactor had several ports installed with thermocouples and the opposite side was equipped with several discharge ports corresponding to the desired mixture volumes inside the reactor (1,000 – 3,000 mL). The lid of reactor had an inlet port for reactant injection, a quartz viewport to allow visual observation inside the reactor, and a condenser port to condense vaporized methanol back into the reactor as well as to ensure atmospheric-pressure operation inside the reactor at all time. For the reactant injection port, a small stainless steel tube was

connected to it to discharge the reactants at approximately 1.5 cm above the center of the impeller. A diagram of the setup for continuous transesterification is shown in Fig. S4.

Continuous FAME production from refined palm oil

The effect of reaction volume (1,000, 1,500, 2,000, 2,500 and 3,000 mL) was first studied, followed by the effect of reactant total flow rate (25, 50 and 75 mL/min) on FAME yield with the conditions of NaOH loading of 1 wt%, methanol to oil molar ratio of 6:1 and reaction temperature of 62 - 63ºC. After obtaining the optimal parameters of reaction volume and total feed flow rate, the effects of methanol to oil molar ratio (3:1, 6:1 and 9:1), reaction temperature (50 - 65ºC) and concentration of NaOH (0.75, 1 and 1.25 wt%) were evaluated. Also, the effect of reactant discharge position on FAME yield was explored by adjusting the position from the center of the reactor to the wall of the reactor. A control transesterification without the catalyst was also performed.

In all runs, the oil and the catalyst dissolved in methanol were simultaneously loaded into the reactor and the solution was heated to 62 - 63ºC for 15 min by energizing the fruit blender. Methanol with the dissolved catalyst and oil were then fed into the reactor, with each flow rate separately controlled by a peristaltic pump, and the mixture started to flow out through one of the discharge ports left open at the desired reaction volume. A minor variac adjustment was performed periodically to maintain the reaction temperature of 62 - 63ºC. Every studied condition, except for the negative control, was performed in duplicate. The product was sampled at 15, 30, 60, and 90 min. Sampled products were centrifuged for 5 - 7 min to physically separate the FAME layer for further yield analysis. Finally, the products were purified by washing impurities with DI water and heated at temperature of 110ºC to remove remaining water.

To determine the effect of insulation on FAME production, refined palm oil and WCO were used as feedstocks under the optimal conditions with total reactant flow rate of 50 mL/min. The cotton sheets were removed from the chemical reactor and a fan was used to help dissipate heat from the system.

FAME production from various oil feedstocks

The effect of refined vegetable oil types on oil conversion to FAME was evaluated using the best set of process parameters obtained from FAME production from refined palm oil.

FAME production from WCO

When using WCO as a feedstock for transesterification, water content and free fatty acid (FFA) content were important parameters. Under base-catalyzed transesterification, the presence of water leads to hydrolysis reaction of the base catalyst caused by soap formation with triglycerides, free fatty acid, and FAME resulting in reduced FAME yield [32]. Moreover, a neutralized reaction of a base catalyst and FFA would lead to losses of a catalyst [40]. WCO used in biodiesel production should not have the FFA content greater than 2% [41], or the WCO must be pre-treated with the esterification process before being used as a feedstock. To determine the FFA content of the WCO used in the present study, the traditional acid-base titration analysis was employed. The sampled WCO in a hot 2-propanol solution was titrated by potassium hydroxide using phenolphthalein as an indicator [42]. The FFA content in the WCO was found to be 1.21%, so it can be used without an esterification pretreatment. The WCO still needed to be filtered by a fine-mesh sieve to extract food and other residues. The dewatering process was then performed by heating the oil at 110^{o}C for 30 min. Subsequently, the WCO was passed through a 500 μm filter

for final purification. The water concentration of WCO was determined by Karl Fischer coulometric titration method presented below 0.05 wt% following ASTM D6751 standard [43].

Continuous FAME production based on WCO was studied using the optimal conditions of refined palm oil. Because the alkali catalyst was used to neutralize the FFA present in WCO, the catalyst concentrations of 1.0, 1.25 and 1.5 wt% of oil were also studied.

FAME identification

FAME yield was determined following the EN 14103 standard [44], using Shimadzu GC 2010 Plus. This GC system was installed with a flame ionization detector and a DB wax capillary column. FAME yield was evaluated according to Eq. (1):

$$\text{FAME yield (\%)} = \frac{(\sum A) - A_{IS}}{A_{IS}} \text{ x } \frac{C_{IS} \text{ x } V_{IS}}{m} \text{ x } 100 \text{ \%} \quad (1)$$

where $\sum A$ = total peak area, A_{IS} = peak area of methyl heptadecanoate (internal standard), C_{IS} = concentration of methyl heptadecanoate (mg/mL), V_{IS} = volume of methyl heptadecanoate (mL), and m = mass of FAME sample (mg).

FAME yield efficiency

Yield efficiency or energy efficiency was determined to allow power efficiency comparison of different reactor types. It is simply defined as the rate of FAME production divided by the power supply as expressed in Eq. (2) [45]:

$$\text{Yield efficiency } \left(\frac{\text{g}}{\text{J}}\right) = \frac{\text{Rate of FAME production}\left(\frac{\text{g}}{\text{s}}\right)}{\text{Power supply}\left(\frac{\text{J}}{\text{s}}\right)} \quad (2)$$

The properties such as density, kinematic viscosity, acid value and cloud point of the produced FAMEs under optimal conditions of refined palm oil and WCO were determined per the EN 14214 and ASTM D 6751 standards.

Kinetic model

Normally, vegetable oils comprise of 90 – 98 wt% of triglyceride (TG) and a small quantity of diglyceride (DG) and monoglyceride (MG) [46]. Reversible transesterification of vegetable oil and mono-alcohol to produce alky esters and glycerol. Many researchers assume that excess alcohol can shift the reaction forward and that the loss of alcohol is minimized while its concentration remains unchanged. So, the reverse reaction and the intermediate products (e.g., DG and MG) can be ignored [36, 37]. In this study, the alkaline-catalyzed transesterification of refined palm oil was tested through the first order kinetic model. The 1 wt% NaOH loading at 50 - 65^{o}C were the conditions to determine the model.

The first order kinetic model can be simplified from the pseudo-first order model as [45]

$$\frac{X_A}{(1-X_A)} = k\tau \quad (3)$$

where x_A is the palm oil conversion (FAME yield), k is the rate constant, and τ is the residence time.

Arrhenius parameters

The activation energy for transesterification can be determined through the Arrhenius equation, which establishes a relationship among the reaction rate constant (k), reaction temperature (T) and the activation energy (E_a). By plotting $\ln(k)$ vs. $\frac{1}{T}$, the slope and the Y-interception give $-\frac{E_a}{R}$ and $\ln k_0$ (the frequency factor), respectively.

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Author contributions

W.W., V.R., and M.K. carried out the experiments and analyzed the data. D.W. designed the entire project. D.W., K.N., W.K., P.H., and S.A. supervised the project. All authors contributed to the discussion.

Competing interests

There are no competing interests to declare.

Figures

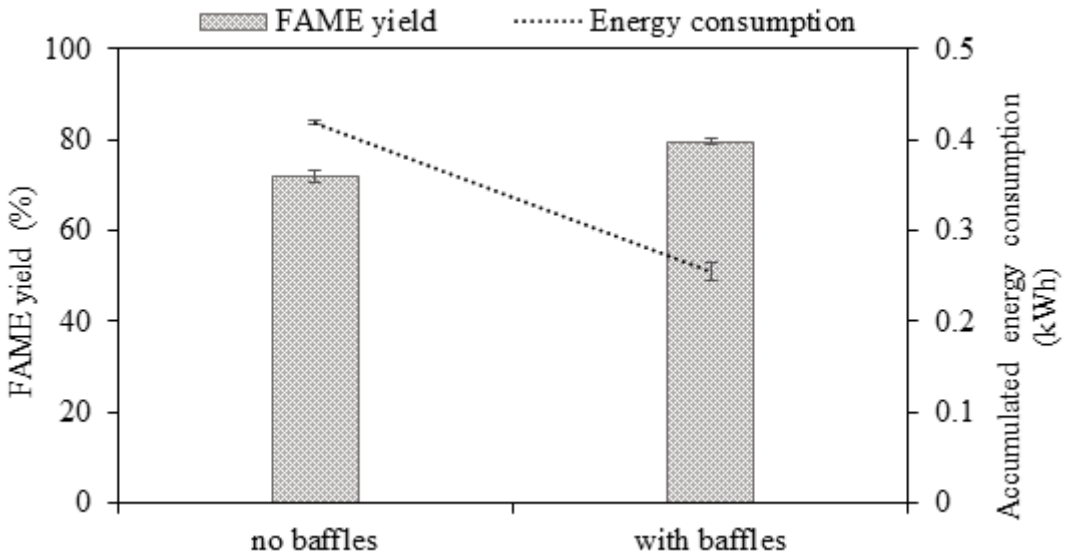
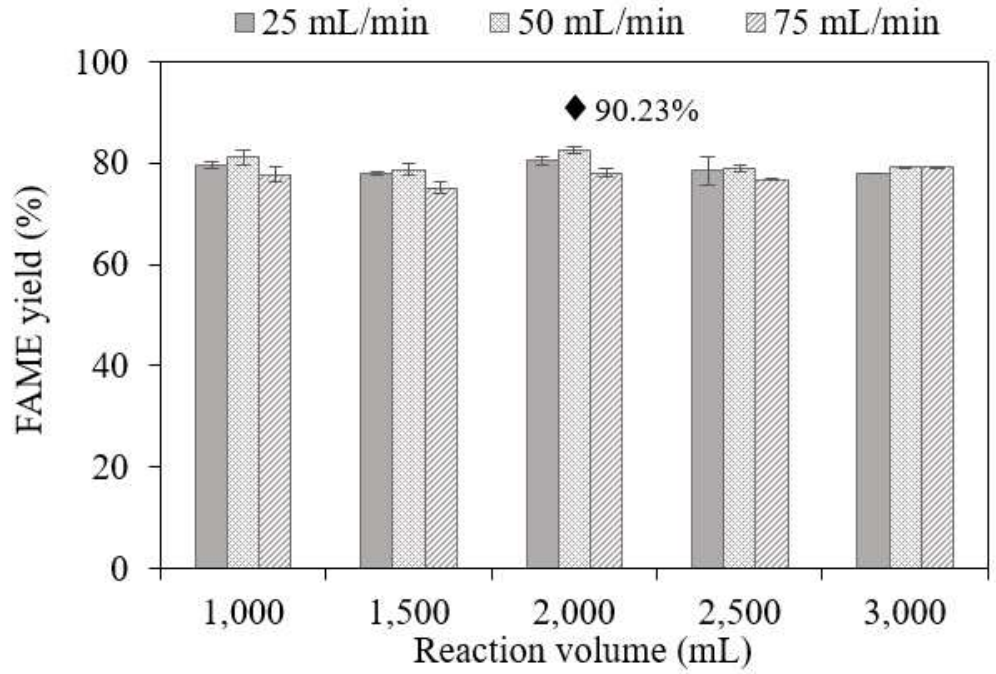
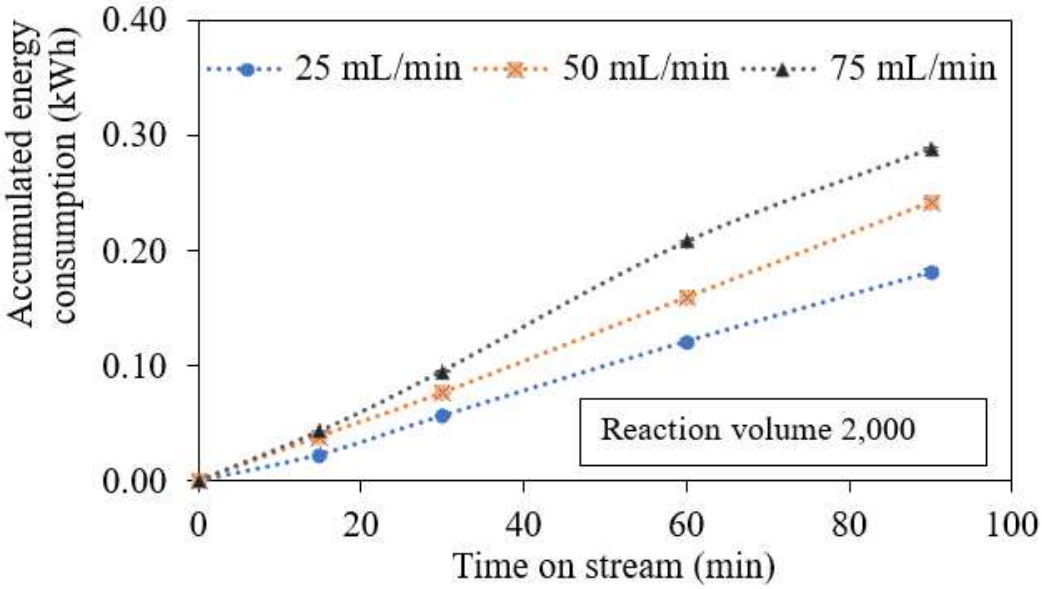


Figure 1

Effect of baffle plates on steady state FAME yield (refined palm oil, 1,000 mL, 25 mL/min, 1 wt% NaOH, 6:1 MeOH:oil molar ratio, 62 - 63°C)



(a)



(b)

Figure 2

(a) Effects of reaction volume and total feed flow rate on steady-state FAME yield (refined palm oil, 1 wt% NaOH, 6:1 MeOH:oil molar ratio, 62 - 63°C) , ▯ = after washing and (b) accumulated energy consumption (2,000 mL case)

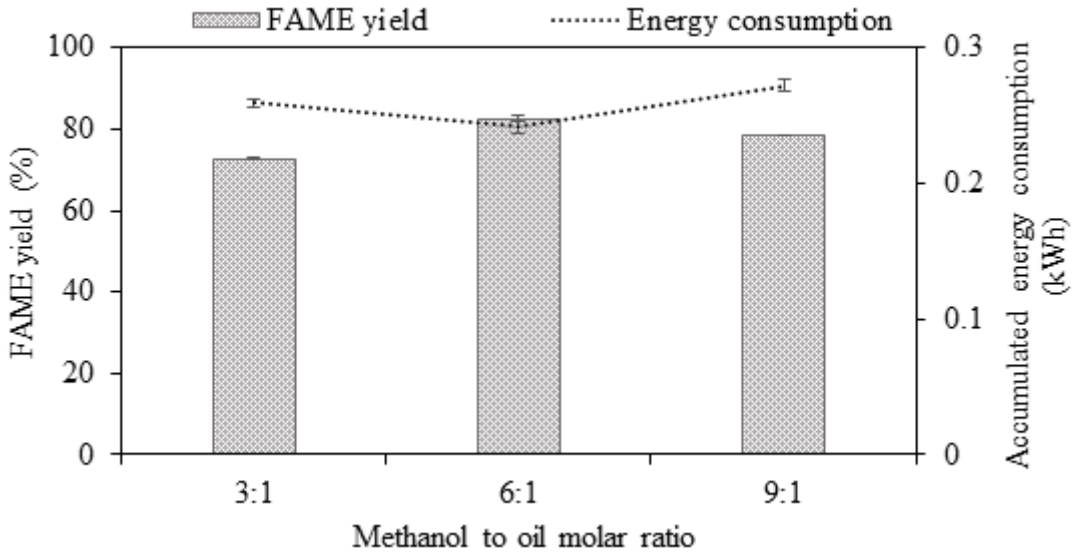


Figure 3

Effect of reactant molar ratio on steady state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

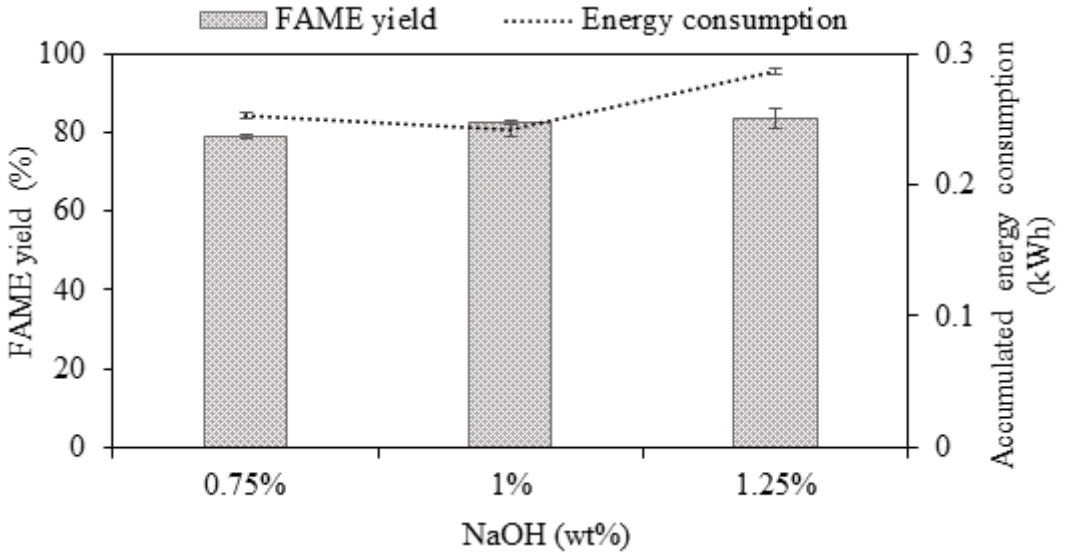


Figure 4

Effect of catalyst loading on steady state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 62 - 63°C)

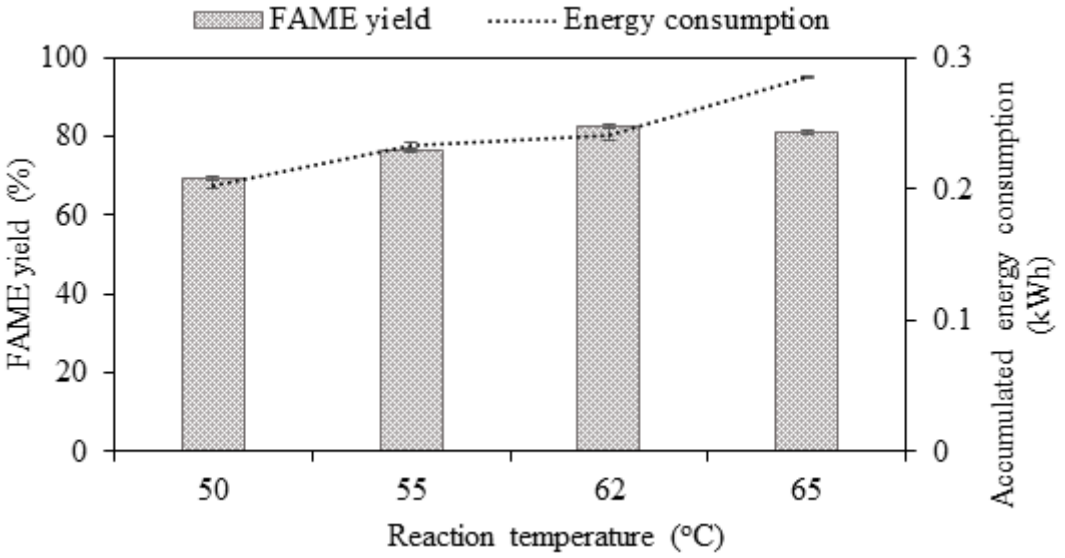


Figure 5

Effect of reaction temperature on steady state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 1 wt% NaOH)

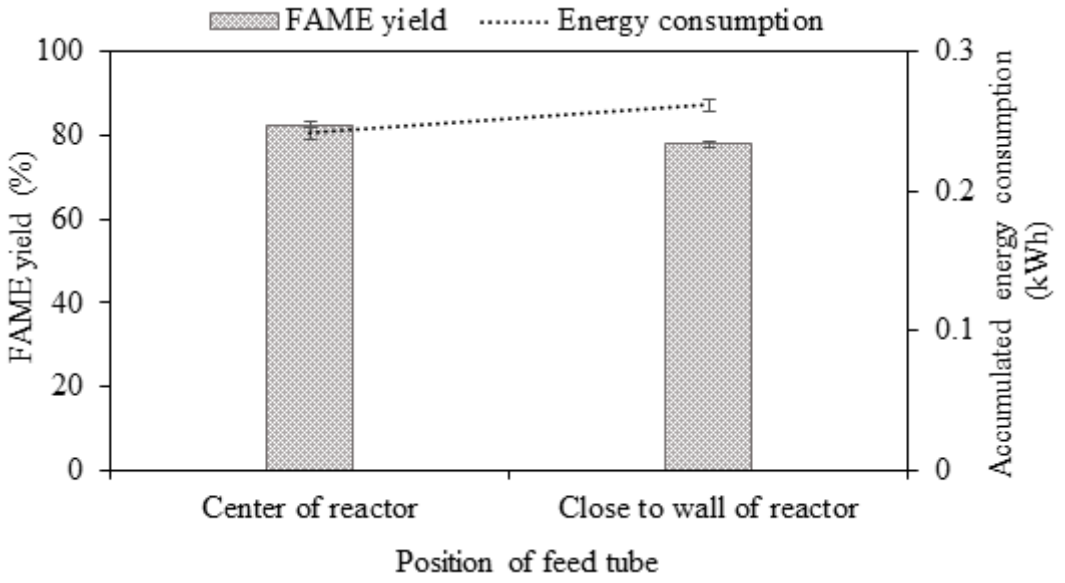


Figure 6

Effect of reactant discharge position on steady-state FAME yield (refined palm oil, 2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

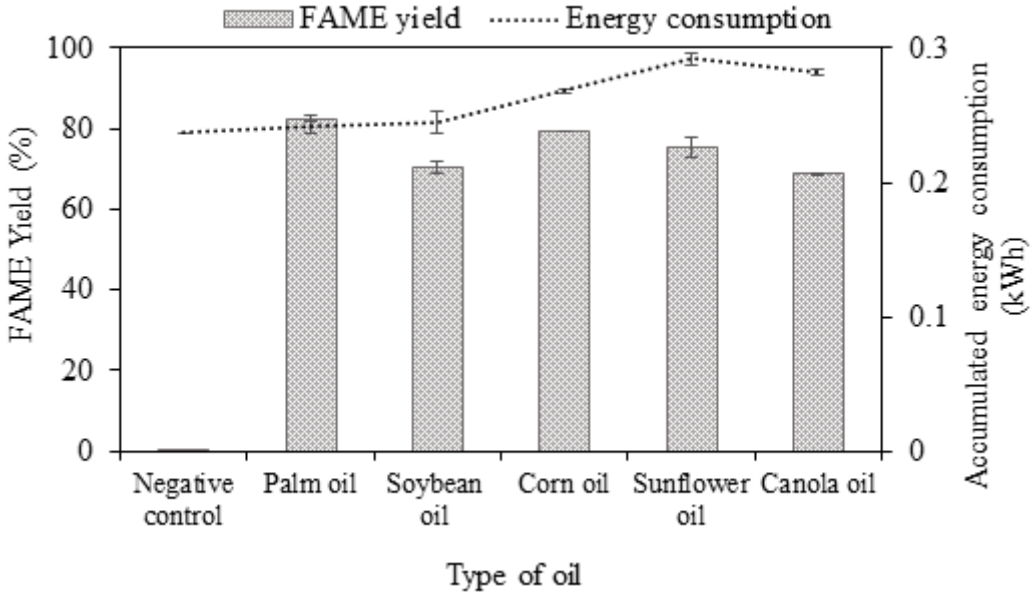


Figure 7

Effect of various types of vegetable oils on steady state FAME yield (2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)

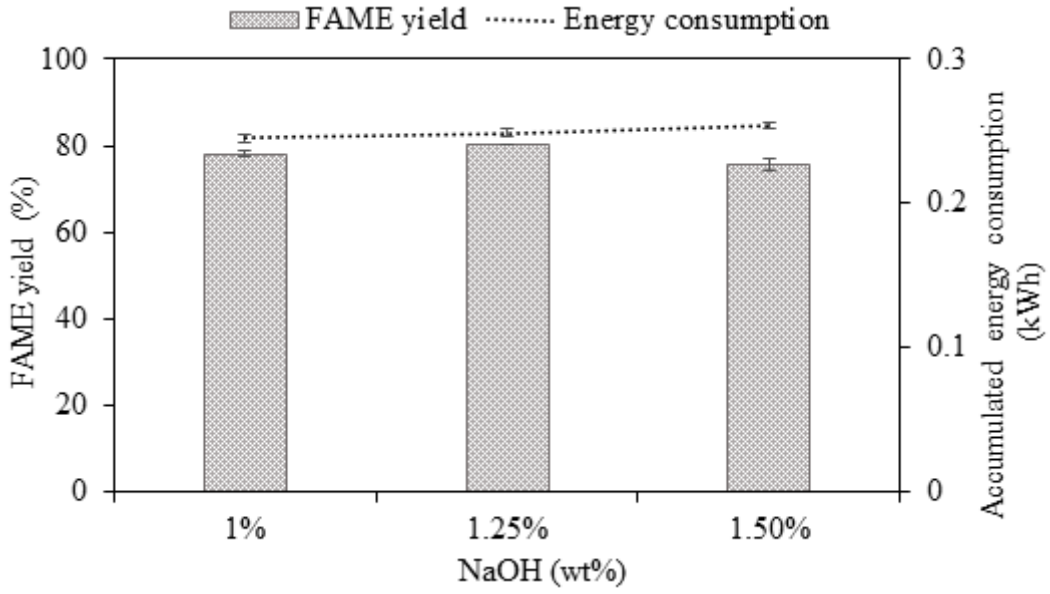
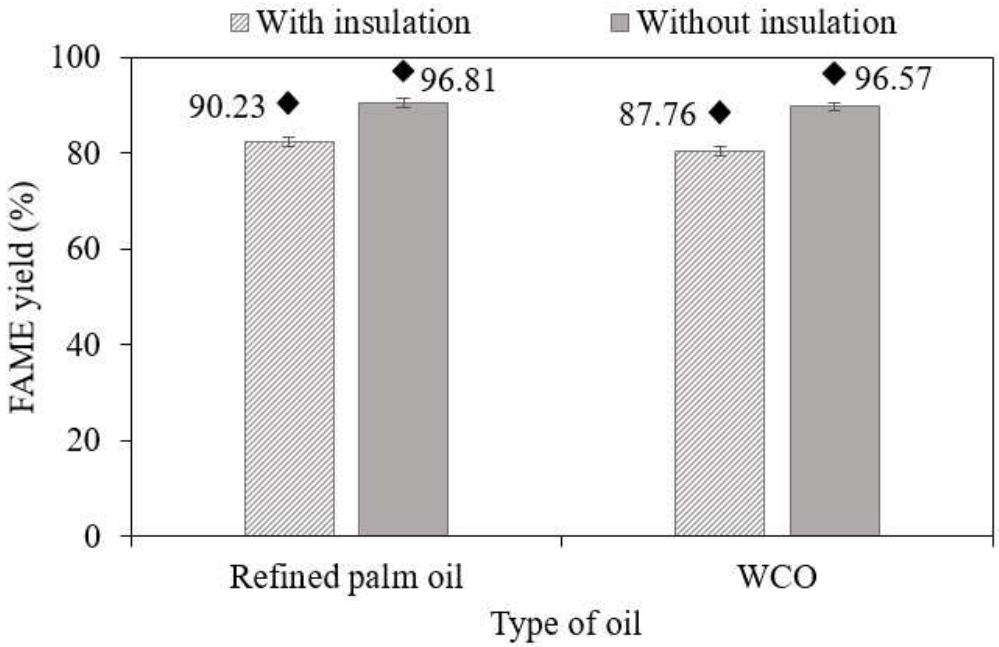
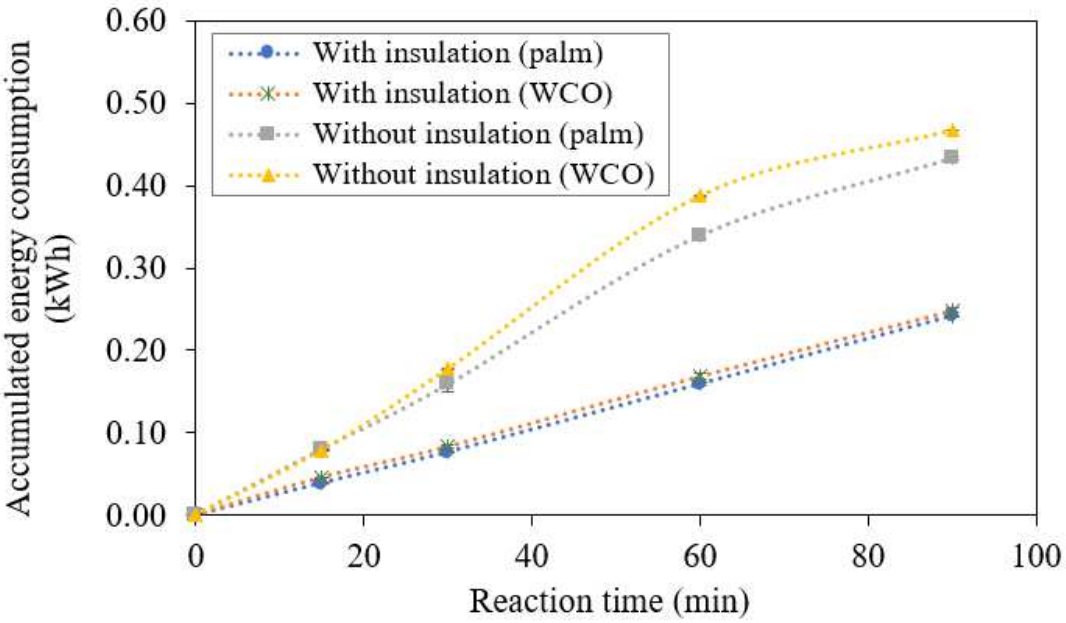


Figure 8

Effect of catalyst loading on WCO-derived FAME yield at steady state (2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C)



(a)



(b)

Figure 9

(a) Effect of insulation on steady-state FAME yield and (b) accumulated energy consumption (2,000 mL, 50 mL/min, 1 wt% NaOH, 62 - 63°C), □ = after washing

Supplementary Files

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