


Asia-Pacific Journal of Science and Technology
<https://www.tci-thaijo.org/index.php/APST/index>

Published by the Research and Graduate Studies,
Khon Kaen University, Thailand

Biodiesel oil production from waste cooking oil by using the pilot plant-scale solar reactor for the local community in Thailand

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Received 6 March 2022

Revised 9 July 2022

Accepted 20 July 2022

Abstract

In this study, waste cooking oil (WCO) was used as a raw material to produce biodiesel oil using the pilot plant-scale solar reactor for the local community in Thailand. The obtained biodiesel oil sample was purified, analyzed, and characterized by several techniques such as Proton nuclear magnetic resonance spectroscopy (¹H-NMR), Gas Chromatography (GC), and Fourier-transform infrared spectroscopy (FT-IR). The experimental results revealed that the pilot plant-scale solar reactor for the local community could produce the percentage yield of biodiesel oil from WCO up to 86.25±1.58%. In addition, the purity of biodiesel product in terms of the fatty acid methylester %FAME content was more than 97% confirmed by the ¹H-NMR and GC analysis technique under the optimum reaction conditions of methanol to oil molar ratio of 6:1, NaOH loading amount of 0.5 wt.% compared with the weight of oil, reaction temperature about 60 ± 5°C, and the reaction time of 1 h. The fuel properties of the synthesized biodiesel oil were within the standard for liquid biofuel. Furthermore, the laboratory testing and field testing of the produced biodiesel oil against the small diesel engine indicated that biodiesel oil derived from a pilot plant-scale solar reactor has excellent quality and efficiency comparable to the conventional diesel oil of B10 and B20 with considerable differences of less than 5%. All experimental results concluded that the pilot plant-scale solar reactor was another possible alternative to produce liquid biofuel for practical use with a small agricultural diesel engine in the rural area of Thailand.

Keywords: Biodiesel oil production, Waste cooking oil, Pilot scale-solar reactor, Liquid biofuel

1. Introduction

Biodiesel oil is one of the most popular renewable energy sources to use as a liquid biofuel, also applied either by blending against conventional diesel oil or being used without mixing in several diesel engines. Biodiesel oil advantages include biodegradability, complete combustibility, reduced emission of greenhouse gases and delicate particulate matter (PM2.5), excellent lubricity, and production from renewable resources and waste cooking oil [1-4]. In addition, the European Biomass Industry Association reported the use of biodiesel oil of 1 kg could

reduce the amount of CO₂ up to 3 kg [5]. For these sufficient reasons, biodiesel oil is widely used worldwide, and it had recent years, the trend increasing significantly. As a result, biodiesel oil is substituted for conventional diesel oil, especially in the agriculture sector [2,4,5].

Biodiesel oil is generally known as the fatty acid of the ester compound dependent on the type of alcohol used as a reagent, such as fatty acid methyl ester (FAME) used in methanol or fatty acid ethyl ester (FAEE) used in ethanol. Usually, the transesterification reaction is employed to produce biodiesel oil because it is a simple technology and the most commercial technology [4-7]. The homogeneous and heterogeneous catalysts both the type of acid and base are traditionally applied to activate the reaction [2,7]. Additionally, this reaction has several factors that directly affect the production process: alcohol to oil molar ratio, type of alcohol, reaction temperature and time, amount of catalyst loading, and kind of raw material oil source [7,8]. These key factors are presented by many published reports of extensive research under experimental conditions in a laboratory setting. Moreover, the kinetics of the transesterification reaction for biodiesel oil production is also considered and reported [8-11]. However, the successful application of knowledge in biodiesel oil production from laboratory experiments to actual production, especially a community-scale biodiesel oil production process, is one of the challenges and engaging in the sustainable development of alternative and renewable energy sources.

Focus on Thailand, biodiesel oil is generally used as an alternative and renewable liquid biofuel both with and without blending conventional diesel oil. In the report from Thailand Alternative Energy Development Plan (AEDP 2015-2036) presented by the Department of Renewable Energy Development and Energy Efficiency, the Ministry of Energy found a seriously promoted utilization of biodiesel oil in the transportation and industrial sector [12]. Biodiesel oil blended against conventional diesel oil equal to 20 percent (denoted as B20) is found to be sold by the available gas station. In addition, biodiesel oil production is also promoted on the community enterprises-scale to universally used with agricultural machinery in the farm sector. This consistent policy can decrease the cost of the farm output and directly affect better environments and reduce dependence on energy from imports [13]. Notwithstanding, the critical factor to carefully consider in the community enterprises-scale biodiesel oil production process is the reactor with a relatively high price, generally about 100,000-200,000 baht, depending on the size, design, and function.

Much research involved the study of the reactor for biodiesel oil production with various scales such as laboratory-scale, pilot-scale, community-scale, and industrial-scale. According to several research reports, it is found that batch production of biodiesel oil is efficient and suitable for local communities due to the simplicity of the technology and cost-effectiveness [14,15]. Therefore, our work research aimed to develop and test the biodiesel oil production process from waste cooking oil (WCO) with the pilot plant-scale solar reactor for the local community. The physicochemical properties of the obtained biodiesel oil product were analyzed, evaluated, and compared with European Standard (EN)-14214 and American Society for Testing Materials (ASTM)-D6751 standards for liquid biofuel. Finally, the produced biodiesel oil was applied with small agricultural diesel engines traditionally used for plowing to compare the efficiency against conventional diesel oil.

2. Materials and methods

2.1 Chemical Materials

In this work, WCO was used as raw material which got from the local market in Sakon Nakhon Province, Thailand. The collected WCO was filtered to separate food waste particles and impurities. It was then carefully stored in sealed plastic drums to prepare for further use in the biodiesel oil production process. The physicochemical properties of WCO as a raw material for biodiesel oil production are shown in Table 1. Methanol (CH₃OH) as a reagent which was a commercial grade with a purity of 95%, was purchased from LAB SCIENCE AND SERVICE Co., Ltd. The NaOH commercial grade was obtained from S-C SCIENCE Co., Ltd, which was employed as an economic catalyst in the transesterification reaction for biodiesel oil production. The Thin Layer Chromatography (TLC) plate (Silica Gel 60 F254) bought from Merck, Darmstadt, Germany, was used for adequately monitoring the transesterification reaction progress. The mixture developing solvent for the specific TLC technique, namely petroleum ether, diethyl ether, and glacial acetic acid with an analytical reagent grade, was purchased from ANAPURE Co., Ltd, and QR&C Co., Ltd. The conventional diesel oil of B10 and B20 (blending biodiesel oil 10% and 20% with traditional diesel oil, respectively) was purchased from the available gas station in Sakon Nakhon province to compare the performance of the engine testing.

Table 1 Physicochemical properties of WCO as a raw material for biodiesel oil production.

Parameter	Unit	WCO ^a
Acid number	mg KOH/g	1.88
Free fatty acid (FFAs)	wt%	0.94
Density @15°C	kg/m ³	954
Kinematic viscosity @40°C	cSt	30.54
Water content	wt%	0.044
Oxidation Stability	H	4.20
Pour point	°C	10
Cloud point	°C	14
Copper strip corrosion	Number	No. 2

^aAll of the results in Table 1 were averaged from the repeats analytical 3 times and the standard deviation was within 3%.

2.2 Biodiesel oil production with the pilot plant-scale solar reactor

The pilot plant-scale solar reactor to produce biodiesel oil products for the local community was designed and constructed for batch operation procedure with a working volume of 40 L from the absolute size of 50 L or approximately 80% of the total volume (the considerable volume of WCO combined with methanol). The pilot plant-scale solar reactor for biodiesel oil production was shown in Figure 1, which referenced the previous report work of Inthachai et al. [16], who invented and tested a prototype solar reactor of a size of 5 L to generate biodiesel oil efficiently. The pilot plant-scale solar reactor consists of four crucial parts: 1) raw material oil (WCO) preheating tank, 2) a reaction tank set with a motor and an impeller for stirring the mixture, 3) a solar cell set for generating electricity, and 4) a set of an electric current and temperature control.

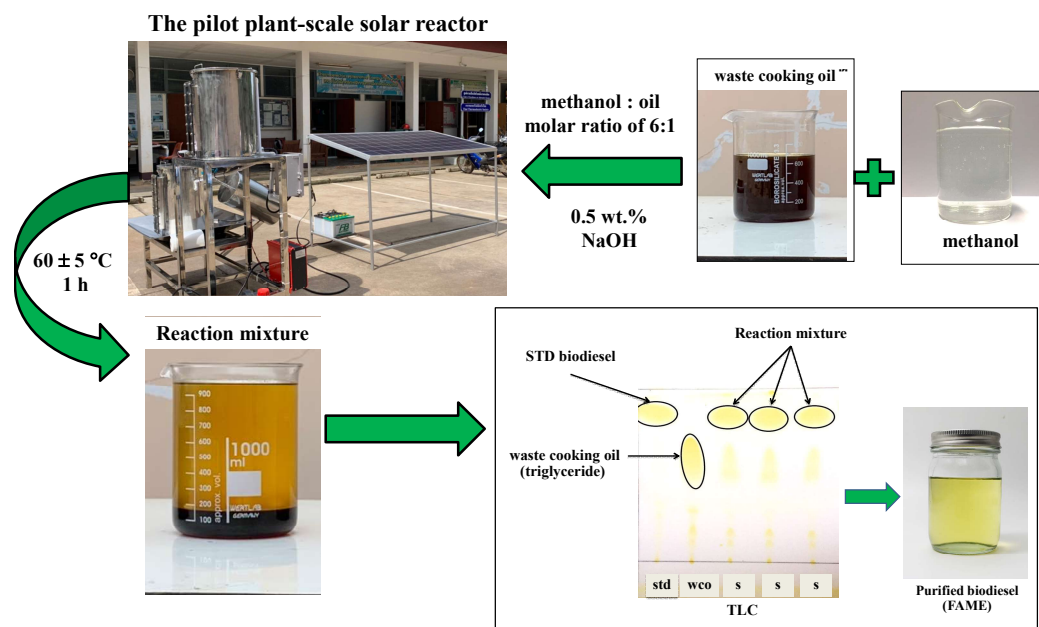


Figure 1 The process diagram of biodiesel production from WCO uses the pilot plant-scale solar reactor for the local community.

The critical overview of the biodiesel oil production procedure with the pilot plant-scale solar reactor is presented in Figure 1. The biodiesel oil production procedure started by preheating the WCO, which was filtered carefully to separate food waste particles and the impurity approximately amount of 30 L within the raw material oil preheating tank at the temperature of $80 \pm 5^\circ\text{C}$ and the considerable time of 1 h. At the same time, methanol and NaOH were carefully mixed within a reaction tank set followed the optimum reaction conditions of methanol to oil molar ratio of 6:1 and NaOH loading amount of 0.5 wt% compared with the weight of oil, based on data from the research of Inthachai et al. [16]. After reaching the set time, the heat of the WCO was stopped and waited until the WCO temperature dropped to about $65 \pm 3^\circ\text{C}$, then slowly allowed the WCO to mix with the methanol and NaOH solution in the reaction tank set. This transesterification reaction was set at a reaction time of 1 h and controlled at a mild temperature of approximately $60 \pm 5^\circ\text{C}$. During biodiesel production, the stirring speed was maintained at 300 rounds per minute (rpm). The TLC method was applied in preliminary testing to monitor the

progress of the reaction based on the reports of Supamathanon et al. [17], Phewphong et al. [18], and Roschat et al. [19].

After the reaction was completed, the reaction mixture was cooled to room temperature and stopped stirring until the biodiesel oil and glycerol were wholly separated. Then biodiesel oil was separated and washed with hot water at 60-70°C several times to eliminate impurities such as sodium ions, excess methanol, and soap. In the final process, the obtained biodiesel oil was dried at 100°C to remove residual water and excessive moisture. The resultant biodiesel oil was carefully collected in the sealed tank for then the analysis of biodiesel oil properties and the engine test.

2.3 Analysis and fuel properties characteristic test of biodiesel oil product

The percentage yield of the biodiesel oil product obtained from the WCO proceeded with the pilot plant-scale solar reactor was correctly calculated with the use following Equation (1):

$$\text{The yield of biodiesel oil product (\%)} = \frac{\text{The volume of biodiesel oil product}}{\text{The volume of WCO as a raw material}} \times 100 \quad (1)$$

%FAME content was evaluated by the Proton nuclear magnetic resonance spectroscopy (¹H-NMR) technique on a Brüker Ascend™ 600 MHz spectrometer and gas chromatography technique (GC-2010, Shimadzu) following the European standard EN-14214 method for testing biodiesel oil product [20-24]. In addition, the Fourier-transform infrared spectroscopy (FT-IR) technique with the Perkin-Elmer RXI spectrometer was applied to identify the functional group of the WCO (triglyceride), which was changed to biodiesel oil product (FAME). The physicochemical properties of the produced biodiesel oil were evaluated and tested as described by EN-14214 and ASTM-D6751 standards for quality specification of biodiesel oil automotive fuels with 100% purity, including kinematic viscosity, methyl ester content, density, flash point, cloud point, pour point, total acid number, oxidation stability, total contamination, water content, and copper strip corrosion [25,26].

Furthermore, The Kubota RT100, an ignition small agricultural diesel engine with compression four-stroke and single-cylinder, was applied for the performance of engines test using the resultant final biodiesel oil versus conventional diesel oil of B10 and B20 following the method from the research of Inthachai et al. [16]. The pollution gases consisting of the hydrocarbon (HC), CO, CO₂, and NO₂ from engine combustion using the biodiesel oil product and conventional diesel oil were evaluated with the Flue Gas Analyzer (EMS Model 5003). Finally, the biodiesel oil derived from the WCO and proceeded with the pilot plant-scale solar reactor was tested with practical use by plowing and pumping water at the productive farmland in the rural area of Sakon Nakhon province, Thailand.

3. Results and discussion

3.1 Analysis and quality evaluation of biodiesel oil product

The pilot plant-scale solar reactor with a production capacity per day of about 50-60 liters was employed to synthesize the biodiesel oil product from WCO as a raw material. The results of an analysis and quality evaluation of biodiesel oil products consist of the yield of biodiesel oil production and the purity of biodiesel oil which was significantly dependent on the specific percentage of FAME content. The percentage yield of biodiesel oil production could be directly calculated by the ratio between the volumes of final biodiesel oil product against the volumes of WCO as a material source. The experiment results on the use of a pilot plant-scale solar reactor for biodiesel oil production showed that the yield of biodiesel oil products was achieved at 86.25±1.58%. In contrast, approximately 13.75±0.37% was a glycerol by-product. The obtained data in this work should be noted that the repeat experiments were carried out 5 times to calculate the average and standard deviation values.

The analysis of produced biodiesel oil with the pilot plant-scale solar reactor in terms of %FAME was shown in Figure 2A as a ¹H-NMR spectrum and Figure 2B GC as a chromatogram. From a ¹H-NMR analysis (Figure 2A), the spectrum of WCO as a triglyceride indicated the chemical shift of the signals significant of the chemical structure at about 4.00-4.40 ppm and 5.20-5.40 ppm, which was the glyceridic backbone protons of the triglyceride. However, these chemical shifts of the signals ¹H-NMR were disappeared after the transesterification reaction completed. Due to the glyceridic backbone protons of the triglyceride were transferred to be a small molecule of a new ester compound which could remark chemical shifts of 3.68 ppm as a singlet peak. Similarly, several reports have described and discussed these analysis results of the biodiesel oil product versus raw material oils (triglyceride) with the use of the ¹H-NMR technique, such as Yadav et al. [27], Mathimani et al. [28], and Naureen et al. [29]

FT-IR spectrum of the obtained biodiesel oil as illustrated in Figure 2C was applied to observe the reaction progress and comparison the differentiation of the functional groups in the chemical structure of both WCO (triglyceride) and biodiesel oil product. Both WCO and biodiesel oil were ester compounds which has unique a

chemical functional group namely carbonyl group ($C=O$) as strong stretching vibration at 1745 cm^{-1} . Additionally, the FT-IR spectrum stretching vibration of $-(O=C)-O-C-$ at $1150\text{--}1200\text{ cm}^{-1}$ could identify as a specific characteristic of the ester compound. Furthermore, the other functional group of this ester compound namely $C-H$, $-CH_2-$, and $-CH_3$ displayed peak strong symmetric and asymmetric vibrations at 2922 and 2850 cm^{-1} , the peak bending vibrations at $1470\text{--}1430\text{ cm}^{-1}$, and the peak rocking vibrations at $850\text{--}720\text{ cm}^{-1}$, respectively.

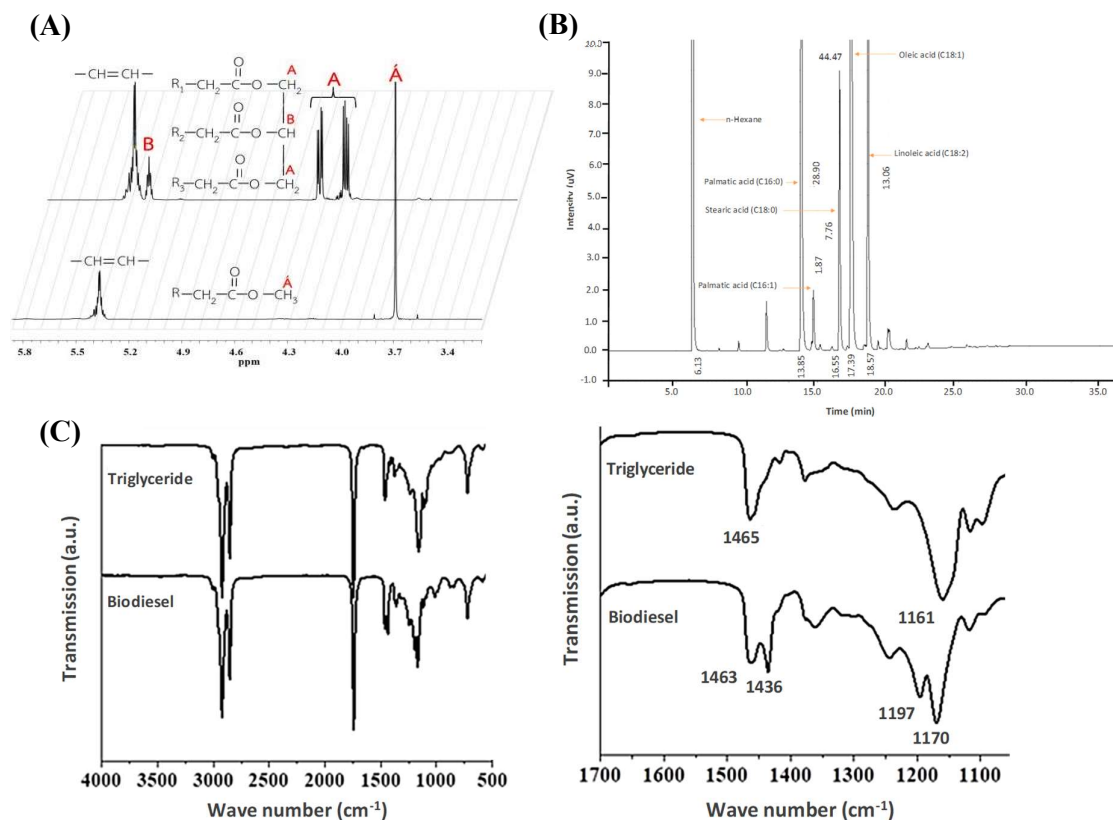


Figure 2 (A) $^1\text{H-NMR}$ spectrum, (B) GC chromatogram, and (C) FT-IR spectrum of the biodiesel oil product obtained from WCO and proceeded with the pilot plant-scale solar reactor.

However, it was noted that there were significant differences in the chemical structure between WCO and biodiesel oil as the peak stretching vibration of $-(O=C)-O-C-$ and the peak bending vibration of $-CH_2-$ and $-CH_3$ groups. The WCO only presented the peak stretching vibration of $-(O=C)-O-C-$ at 1161 cm^{-1} while biodiesel oil displayed two stretching vibration peaks at 1197 and 1170 cm^{-1} . Likewise, WCO showed only bending vibration peaks of $-CH_2-$ and $-CH_3$ groups at 1465 cm^{-1} but biodiesel oil has two peaks at 1463 and 1436 cm^{-1} . This data could explain that the chemical structure of WCO as a triglyceride has structural rigidity caused by the mono-glyceride three molecules bonded together. On the other hand, biodiesel oil was changed from triglyceride molecule to mono-alkyl ester with the methanol reagent to obtain FAME and the FAME molecule which can vibrate freely. These results agree with the reports from Roschat et al. [20,30], Mohamed et al. [27], and Sianipar et al. [31], who used the FT-IR to identify the chemical structure of triglyceride and compared with biodiesel oil.

The gas chromatography technique analysis of the final biodiesel oil product is one of the main parameters to quantify the chemical composition and FAME content. From the GC chromatogram in Figure 2B, the major chemical composition of the fatty acid methyl esters consists of oleic acid methyl ester ($C_{18:1}$) about 44.5%, palmitic acid methyl ester ($C_{16:0}$), linoleic acid methyl ester ($C_{18:2}$), stearic acid methyl ester ($C_{18:0}$), and other compositions approximately 29.9%, 13.9%, 7.8%, and 2.9%, respectively. Calculation of purity of biodiesel oil product in terms of FAME content found that the percentage of FAME content was around 97.24% and agreeable to the %FAME calculated by the $^1\text{H-NMR}$ technique, which was equal to 97.56%.

3.2 The physicochemical properties of the biodiesel oil product

The results of the physicochemical properties of the biodiesel oil product derived from the WCO and proceeded with the pilot plant-scale solar reactor for the local community were presented in Table 2, which was tested at Clean Fuel Technology and Advanced Chemistry Research Laboratory, National Energy Technology Center (ENTEC), the National Science and Technology Development Agency, Thailand. The data in Table 2 displayed that the final biodiesel oil product from the pilot plant-scale solar reactor for the local community was within the standard for bio-auto liquid fuel by both EN-14214 and ASTM-D6751 standards test methods for biodiesel oil. However, the comparison of the fuel properties of the synthesized biodiesel oil product against the conventional diesel oil of B10 and B20 found that biodiesel oil also has a relatively higher value than B10 and B20, especially the kinematic viscosity, density, and flashpoint. This study could explain that biodiesel oil has a long-chain hydrocarbon than conventional diesel oil and consists of an ester functional group in the chemical structure. The chemical structure of biodiesel oil depended on the type of the oil raw material, and it directly affected the quality of the biodiesel oil product. These possible reasons agree with the published report of Ramos et al. [4] and Roschat et al. [20,30]. They have described and discussed the critical factor powerfully affecting the fuel properties of the biodiesel product, specifically its chemical structure. Hence, these studies indicated that the pilot plant-scale solar reactor for the local community could efficiently produce the standardized biodiesel oil from WCO. Additionally, the obtained biodiesel oil could also use efficiently with a small agricultural diesel engine.

Table 2 Fuel properties of the biodiesel oil product synthesized from WCO and proceeded with the pilot plant-scale solar reactor for the local community.

Fuel properties	Standard biodiesel oil	WCO biodiesel oil ^d	Conventional diesel oil B10 ^d	Conventional diesel oil B20 ^d
Methyl ester content evaluated by GC (%) ^a	> 96.5	97.24	-	-
Methyl ester content evaluated by ¹ H-NMR (%) ^b	-	97.56	-	-
Kinematic viscosity @40°C (cSt) ^a	3.5-5.0	4.58	3.34	3.42
Density @15°C (kg/m ³) ^{a,c}	860-900	882	849	858
Acid number (mg KOH/g oil) ^{a,c}	< 0.5	0.28	0.05	0.05
Copper strip corrosion ^{a,c}	No. 1	No. 1	No. 1	No. 1
Oxidation Stability (h) ^a	> 6	> 12	> 20	> 20
Total contamination (ppm) ^a	< 24	20.5	5.67	8.12
Flashpoint (°C) ^a	> 120	187	79	85
Cloud point (°C) ^c	Report	< 6	< -5	< -5
Pour point (°C) ^c	Report	< -5	< -5	< -5

^aEuropean standard (EN-14214) test method, ^bReference to the reports of Naureen et al. [29], ^cAmerican Society for Testing and Material (ASTM-D6751) standard test method, and ^dAll of the results in table 2 were averaged from the repeats analytical 3 times and the standard deviation was within 3%.

3.3 Testing the produced biodiesel oil against the small diesel engine and field testing

The final biodiesel oil derived from a pilot plant-scale solar reactor for the local community was evaluated for efficiency by field testing against the small diesel engine as illustrated in Figure 3 and Figure 4. The result in Figure 3A showed the comparison of the gas emission between conventional diesels oil of B10, B20, and the biodiesel oil product from WCO when the liquid fuel was loaded into the small agricultural diesel engine during an experimental performance at the engine speed about of 2000 rpm. The results for all liquid fuels tested revealed that the biodiesel oil product from WCO produced by the pilot plant-scale solar reactor for the local community tends to emission the gas of HC, CO, CO₂, and NO₂ less than both B10 and B20. This was due to the biodiesel oil having more oxygen atom content in the chemical structure as an ester functional group than conventional diesel oil of B10 and B20 which mixed biodiesel oil with only 10% and 20%, respectively. The oxygen atom content in biodiesel oil avail more complete combustion when injected the oil into the engine and it makes the directly lower gases emission. This possible reason in common was in accordance with the published report of Abed et al. [32,33] and Gad et al. [34].

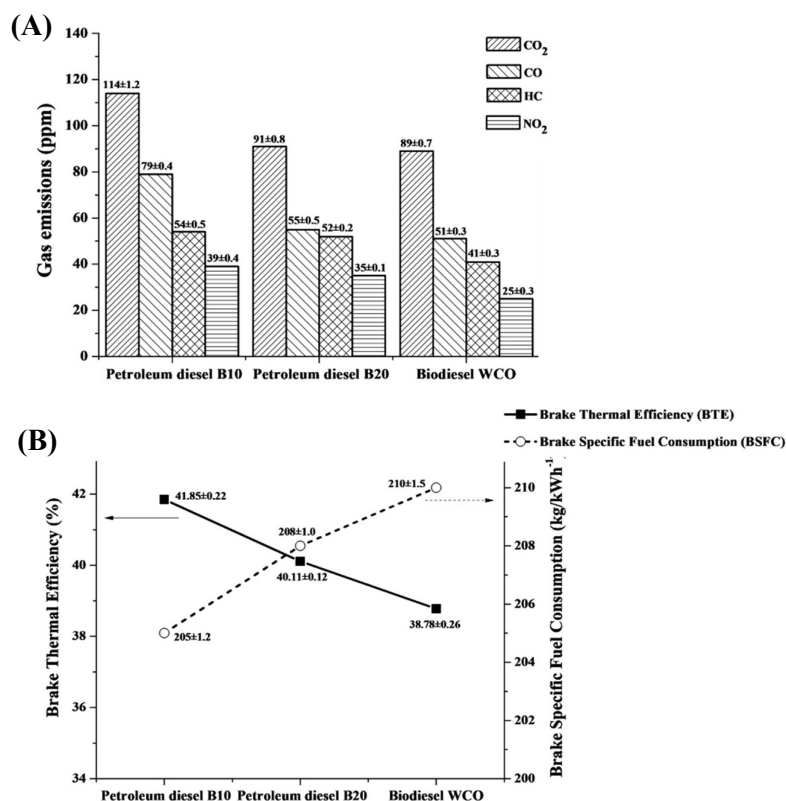


Figure 3 The comparison of the (A) gas emission and (B) testing the performance of engines at the engine speed of 2000 rpm between conventional diesel oil of B10, B20, and the biodiesel oil product from WCO produced by the pilot plant-scale solar reactor for the local community. The results in Figure 3 were averaged from the repeats analytical 3 times, and the standard deviation was within 3%.

Figure 3B presented the percentage of the brake thermal efficiency (BTE) and the brake-specific fuel consumption (BSFC) of the conventional diesel oil of B10, B20, and the obtained biodiesel oil. The percentage value BTE of conventional diesel oil of B10 and B20 has higher than that of the obtained WCO biodiesel oil because of their higher heating values as depicted in Figure 4A. This case explained that the chemical structure of biodiesel oil consisted of the double bond between a carbon atom in the part of the long-chain alkyl group, carbonyl group, and a single bond between an oxygen atom with a carbon atom in the ester functional group, which caused higher viscosity and directly affected the improper droplet being sprayed in the combustion chamber. Therefore, the mass flow rate of biodiesel oil into the engine combustion chamber was unsuitable due to the high viscosity value brought to the BTE value of biodiesel oil lower than that of conventional diesel oil both B10 and B20. This result was agreeable with the data of BSFC value which showed the biodiesel oil was higher than conventional diesel oil of B10 and B20, respectively. The BSFC is a measure of the fuel efficiency of any liquid fuel. Hence, the higher viscosity and density of the biodiesel oil than conventional diesel oil of B10 and B20 have a high oil consumption rate due to the injection of liquid biodiesel oil into the engine combustion chamber higher than conventional diesel oil [35].

Moreover, Figure 4A has demonstrated the comparison of the heating values between conventional diesel oil of B10 and B20 versus the biodiesel oil product from WCO produced by the pilot plant-scale solar reactor for the local community. Biodiesel oil derived from WCO has heating values when combusted lower than conventional diesel oil of B10 and B20 due to a chemical structure containing a double bond and carbonyl group (ester compound). For this reason, the partial energy from combustion was therefore used to break these chemical bonds [30]. Notwithstanding, the field testing of the used biodiesel oil against a small diesel engine for plowing and pumping water at the productive farmland was shown in Figure 4B. The results found that overall engine performance, such as acceleration rate, engine power, and fuel consumption rate, was a few differences (less than 5%) compared to conventional diesel oil of B10 and B20. Consequently, this studies results indicated that the innovation of a pilot plant-scale solar reactor for biodiesel oil production from WCO could produce a high-quality liquid biofuel to apply practically with a small agricultural diesel engine of the local community. The knowledge

from this research was one of the viable ways to self-reliance in the easy production of renewable energy and alternative energy for the people in the rural area to replace conventional diesel oil.

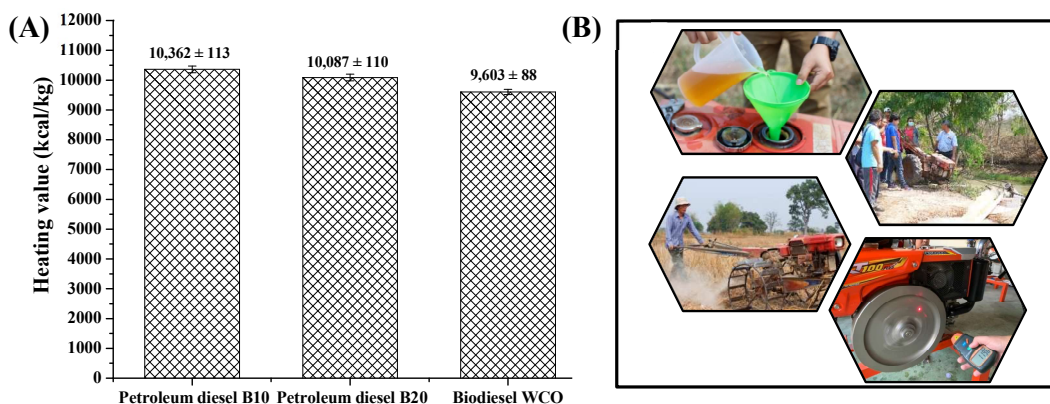


Figure 4 (A) the comparison of the heating values between conventional diesel oil of B10 and B20 versus the biodiesel oil product from WCO produced by the pilot plant-scale solar reactor for the local community and (B) sample pictures of field testing by plowing and pumping water at the productive farmland in the rural area of Sakon Nakhon province, Thailand.

4. Conclusion

The experimental results in this study indicated that the pilot plant-scale solar reactor for the local community has the efficiency and potential of biodiesel oil production from WOC as raw material. The produced biodiesel oil was determined and evaluated by several techniques, both quality properties for liquid biofuel and efficiency, to apply appropriately with a small agricultural diesel engine. The fuel properties of the synthesized biodiesel oil product were met with a specific standard of EN-14214 and ASTM-D6751 testing parameters such as kinematic viscosity, acid number, density, methyl ester content, cloud point, and pour point. In addition, the comparative efficiency of practical use with a small agricultural diesel engine in the rural area of Thailand between conventional diesel oil of B10 and B20 against the synthesized biodiesel oil found that they have similar efficiency values. However, the advantages of the produced biodiesel oil surpassed conventional diesel oil of B10 and B20 represent environmentally friendly, low cost, and economically worthwhile for the people in the local community in possible terms of self-reliance for renewable and alternative energy. Consequently, all of the experimental results in this research work are one of the possible choices to encourage the people in rural areas or developing countries could produce low-priced liquid biofuel with self-reliance.

5. Acknowledgments

This work was supported by scholarship support from the project Capacity Building and Supporting System for Researchers for Community and Social Development (RDG5940004-2S02 under the Thailand Research Fund (TRF) and the National Research Council of Thailand (NRCT) (no. N42A650196). The authors would like to greatly appreciate the Program of Chemistry, Faculty of Science and Technology, and Biomass Energy Research Laboratory under the Center of Excellence on Alternative Energy, Sakon Nakhon Rajabhat University-Thailand, for supporting the equipment and tools required for this project. The authors were also thankful to the National Energy Technology Center (ENTEC)-Thailand for the analysis of the fuel properties of the final biodiesel oil product and the Vidyasirimedhi Institute of Science and Technology-Thailand, for the analysis of the sample by $^1\text{H-NMR}$ technique.

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