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Research Article

Synthesis of BDF Based on Microwave Irradiation and Its Application

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Abstract:
BDF (Bio-diesel Fuel) is expected to be an alternative fuel to diesel oil through methyl esterification. Currently, the alkaline catalyst such as sodium hydroxide is widely used to produce BDF. However, problems of complicated manufacturing process and large quantity of water needed for aftertreatment are faced. Therefore, the objective of this study is to propose a microwave irradiation method for synthesizing BDF based on the eggshells solid catalysts, by which BDF aftertreatment is not needed and water can be saved. In the experiment, firstly, eggshells were prepared to solid catalysts and characterized by SEM and X-ray Diffractometer. Secondly, BDF was synthesized by microwave irradiation and BDF yield ratios under several experimental conditions were quantitatively analysed by GCMS. Finally, exhaust gas concentration of using diesel oil and BDF as fuels for a wagon with a diesel engine was measured. As a result, it was found that BDF yield ratio under microwaves radiation could reached 99.58% and CO2 emission was lower for BDF than for diesel oil while NOx emission was lower for diesel oil than for BDF.

Keywords: *BDF, Microwave, Solid catalyst, BDF yield ratio, Eggshell*

1. Introduction

The world's energy consumption is increasing year by year. As energy consumption increases, the demand for fossil fuels such as oil, coal, and natural gas is expected to increase. In recent years, the depletion of fossil fuels and global warming caused by CO_2 emitted from the use of fossil fuels has become an issue. Japan's CO_2 emissions in 2020 are 1.05 billion tons, a decrease for the seventh consecutive year since 2014 [1]. However, the Japanese government has set a goal of reducing CO_2 emissions by 46% from the fiscal 2013 level (1.32 billion tons) by the year 2030 [2], it is necessary to develop new alternative green energies to deal with above-mentioned problems. Biodiesel fuel (BDF) is attracting attention as a promising alternative fuel because it leads to measures to reduce CO_2 emissions and has been demonstrated to be practical for diesel engines.

The method of BDF synthesis is kind of ester exchange reaction (methyl esterification) where vegetable oil and low-grade alcohol are reactants heated and stirred with the condition of catalyst, and after some reacting time, for example two hours, the BDF (fatty acid methyl esters) and the by-product of glycerin (Glycerin). Are obtained under condition of 60℃ and1atmospheric pressure. So far, many methods of BDF synthesis have been reported. The conventional method is to use the so called homogeneous catalytic reaction where sodium hydroxide is used as catalyst and a heater and a stirrer are necessary. Homogeneous catalytic reactions using alkali hydroxide are the mainstream for

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biodiesel production. This is because the reaction can be carried out under relatively mild conditions of about 333K [3]. However, this method requires rinsing off the remained catalyst inside BDF, which results in the discharge of a large amount of alkaline wastewater, so neutralization and other wastewater treatment are indispensable. Taking the NPO INE Oasa, which produces BDF in Oasa, Kitahiroshima-cho, Hiroshima Prefecture, as an example [4], two volumes of tap water are added to approximately 10 volumes of crude BDF for washing, and this washing process is performed three times. In other words, to obtain 90 L of BDF from 100 L of waste cooking oil in one BDF production process, 60 L of water is discharged. The chemical oxygen demand of the washed wastewater is extremely high at 50,000 ppm, making it difficult to discharge the water directly into the sewage system. In addition, soap is a by-product of the water washing process, which obscures the interface during the oil-water separation operation, resulting in a lower yield ratio [5]. As an alternative method to deal with this problem, solid catalyst has been suggested. Kawashima and his colleagues have achieved 90% yield in their research on BDF using solid catalysts of activated calcium oxide [6].

In the previous year, the authors have used ultrasound irradiation and zeolite as catalyst to synthesize BDF without using the external heater and the BDF yield ratio reached 78.18% [7]. Compared with the conventional method, ultrasound irradiation method means that the compact BDF synthesis is made possible.

However, one of the final goals of our research was to achieve a BDF yield ratio of 95% or higher. For this reason, the authors try to apply microwaves and solid catalyst to BDF synthesis as a new method to increase yield ratio. Unlike conventional heating methods, microwaves can heat a subject from inside to outside almost uniformly based on a phenomenon called dielectric heating [8]. Expected benefits include significantly shortened reaction times, low-cost processes, and power savings [9]. In theirs research, Ikenaga et al. reported that a microwave BDF synthesis using lead oxide as a catalyst achieved a BDF yield ratio of about 90% [10] using homogeneous catalytic method.

Also, in this research, in selecting various heterogeneous catalysts, we focused on eggshells because we wanted to use environmentally friendly materials as catalysts. Eggshells are mainly composed of calcium carbonate, which can be converted to calcium oxide by a chemical reaction when sintered at high temperatures. However, the amount of eggshells disposed of and the means to recover them are issues to be addressed when using eggshells for catalysts. Approximately 2,574,000 tons of chicken eggs were produced in 2021 [11], and eggshells account for about 10% of the total weight, which means that about 260,000 tons of eggshells are disposed of every year. Although some major food manufacturers recycle 100% of the eggshells produced during processing into soil conditioners and calcium-fortified food additives [12], eggshells from households and restaurants are disposed of as they are. Therefore, if a means of recovering eggshells is established in the future, it should be possible to supply enough eggshells to be used as catalyst for BDF.

Hence, the objective of this study is to propose a microwave irradiation method for synthesizing BDF based on the eggshell solid catalysts, by which BDF aftertreatment is not needed and water can be saved. In the experiment, the first step is the preparation of egg catalyst. Next, BDF is synthesized by microwave irradiation and the yield ratio of BDF is analyzed. Finally, combustion and running experiments will be conducted to investigate the power and exhaust gas characteristics of BDF.

2. BDF Synthesis Principle

The chemical reaction equation of the BDF synthesis principle is shown in Fig. 1. Vegetable oils such as rapeseed oil and soybean oil are mixed with low-grade alcohols such as ethanol and methanol, and an alkali catalyst are mixed together at first stage. Lower alcohols generally refer to alcohols with a carbon number of 5 or less, and are characterized by their tendency to dissolve in water. Subsequently, microwave irradiation is applied, and ester exchange takes place to produce fatty acid methyl esters (FAME) and glycerin (Glycerin). The resulting fatty acid methyl ester (FAME) is regarded as BDF. In addition, since ester exchange is a reversible reaction, usually care must be taken to increase the concentrations of ethanol and methanol more than the ideal molar ratio of ethanol or methanol to vegetable oil.

In the microwave-assisted BDF synthesis method, microwaves with a frequency of 2.45 GHz interact with a reaction mixture containing vegetable oil, alcohol, and catalyst to produce triglycerides (BDF). Triglycerides composing of three polar C=0 groups and rotatable C-C and C-O bonds, together with the low-grade alcohols are affected by the microwave-induced molecular rotation and friction, which increase the temperature of the reactants and the degradation rate and accelerates the ester exchange reaction [13].

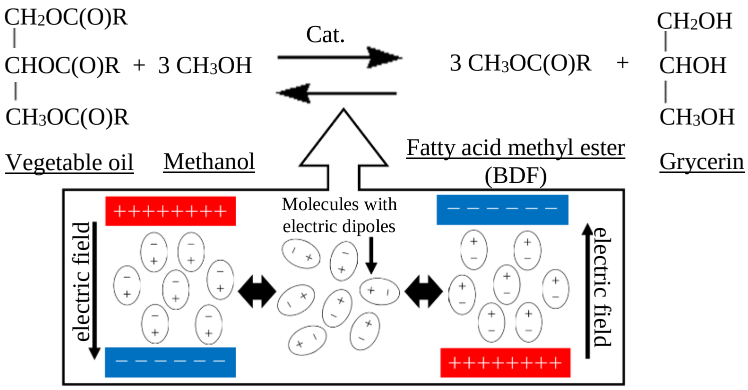

Fig. 1. Synthetic principle of BDF

3. Experiment

3.1 Catalyst Preparation

In this research, eggs are used as solid catalysts. The main component of eggs is calcium carbonate (CaCO3). However, it is necessary to produce calcium oxide (CaO) for use as an alkaline catalyst. The chemical formula for calcium oxide is shown in Equation 1.

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

In the preparation method, the eggshell membrane is first removed and washed with pure water. Then, drying is performed at 105°C for 2 hours, and finally baking is performed at 900°C for 2 hours.

Table 1: XRD measurement conditions.

Type of measurement	2θ-θ
Measurement angle (deg)	20-80
X-ray output (kV)	40
Detector	D/teX Ultra
Filter	Cu K-beta

The prepared catalysts are observed on the surface using a scanning electron microscope (JEOL Ltd. JSM-IT100). Finally, a powder X-ray diffraction analyzer (Rigaku Corporation Smart lab) is used to investigate the changes in the crystal skeleton structure of the eggshell. The XRD measurement conditions are shown in Table 1.

3.2 BDF Synthesis Experiment

A schematic of the microwave BDF synthesis system is shown in Fig. 2. In the microwave-assisted BDF synthesis experiment, vegetable oil and methanol are placed in a test tube and emulsified using a ultrasonic reactor (AS-ONE HS-50E-B). Next, the solid catalyst is added to the emulsified reactants inside the test tube, and then the test tube is put inside a microwave chemical reaction apparatus (Biotage's Initiator+) (Fig. 3) to carry out the ester exchange reaction.

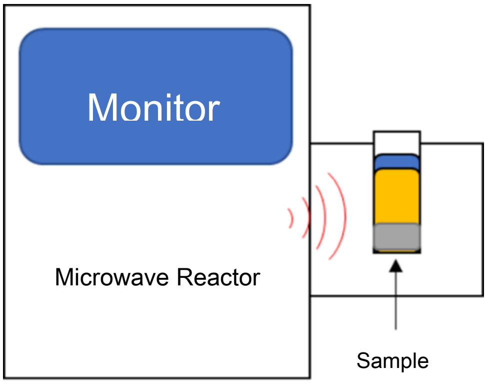

Fig. 2. Schematic of Microwave BDF synthetic system

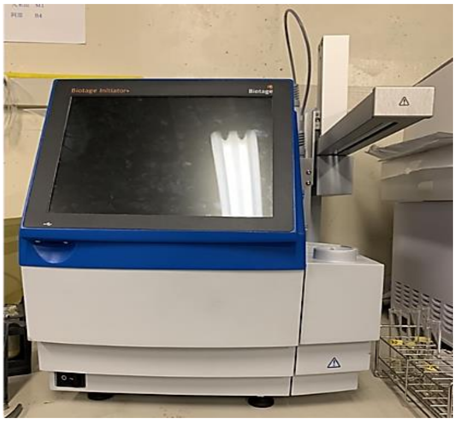

Fig. 3. Initiator+

Table 2: BDF synthesis conditions.

Reaction parameters	Time (min)	Temperature (℃)	Vegetable oil (ml)	Methanol (ml)	Catalyst (g)	Oil type
Effect of Time	2～10 (Every 2 min)	130	4	1	1	Cole seed
Effect of Temperature	10	70～170 (Every 20 ℃)	4	1	1	Cole seed
Effect of Oil type	10	90	4	1	1	Cole seed Jatropha
Effect of Methanol	10	130	4	0.5～2.5 (Every 0.5ml)	1	Cole seed

According to our previous study, the synthesis of BDF process is expected to be affected by various parameters such as temperature and reaction time, oil type, catalyst and methanol content, hence a series of experimental conditions was prepared to synthesize BDF. The conditions set are shown in Table 2. For reacting time, in the preliminary experiment, it was found that 10 min was enough to complete BDF synthesis. In this study, it is certain for the authors to find out any possibility to shorten the reacting time, hence BDF synthesis was conducted from 2-10 minute. For the reaction temperature, it is said that with higher temperature, the reaction will be conducted completely, hence temperature range of 70-170℃ was set. For the effect of methanol, since ideal molar ratio of the methanol quantity is 1ml, with more methanol, it is expected that the BDF synthesis reaction as ester exchange reaction will be conducted fully, hence the range of methanol quantity of 0.5-2.5 ml was prepared.

In regard with the BDF yield ratio measurement, GCMS (Shimadzu GCMS QP2020) is employed to measure the yield of BDF. In the measurement, a standard sample and BDF were quantitatively analyzed. As the analysis time progressed, various BDF fatty acid methyls were detected, from which the BDF synthesis rate was calculated from the peak areas of the standard sample and BDF. The measurement conditions are shown in Table 3.

Table 3: GCMS conditions.

Column Length (m)	30m
Column I.D. (mm)	0.25mm
Column Flow Rate (ml/min)	1.8ml/min
Carrier gas pressure (kPa)	100.2
Injector temperature (℃)	250℃
Detector temperature (℃)	250℃
Standard sample	Methyl Heptadecanoate

3.3 Thermal Efficiency Measurement

Schematic of the combustion experiment is shown in Fig. 4 and Fig. 5. Combustion experiments are conducted using a general-purpose diesel engine. Combustion experiments were conducted using three types of fuels: 100% BDF, 100% diesel oil, and 50% BDF 50% diesel oil. BDF used for this combustion experiment was offered by Fukuroi Seiso Company. Different electric power served as different load for the engine. For each load, the electric power, fuel consumption and exhaust gas concentration was measured by the Watt checker, the Flowmeter and the Exhaust-gas analyzer (HODAKA), respectively.

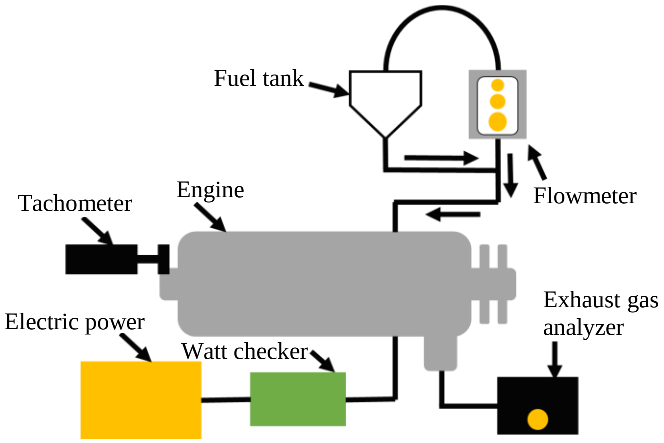

Fig. 4. Schematic of combustion experiment

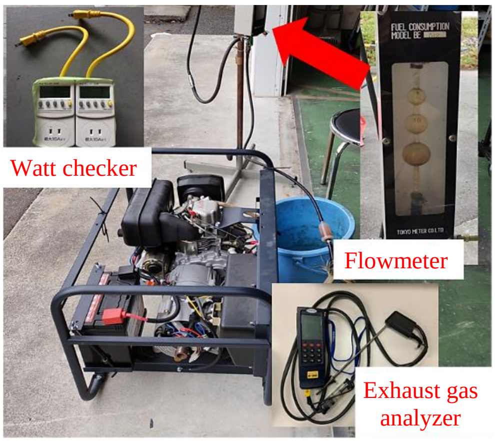

Fig. 5. Details of combustion experiment

3.4 Exhaust Gas Measurement

Schematic of the road driving experiment is shown in Fig. 6 and Fig. 7. In the road test, a car (Toyota Succeed wagon) is used to measure exhaust emissions while driving on the road by the same Exhaust-gas analyzer (HODAKA) used before. 100% diesel oil and 100% BDF offered by Fukuroi Seiso Company were compared.

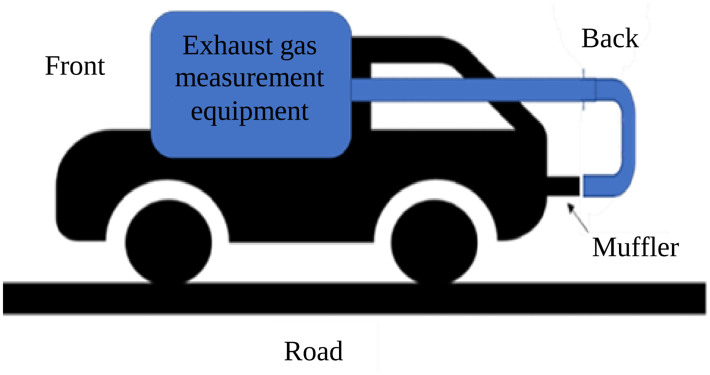

Fig. 6. Schematic of road driving experiment

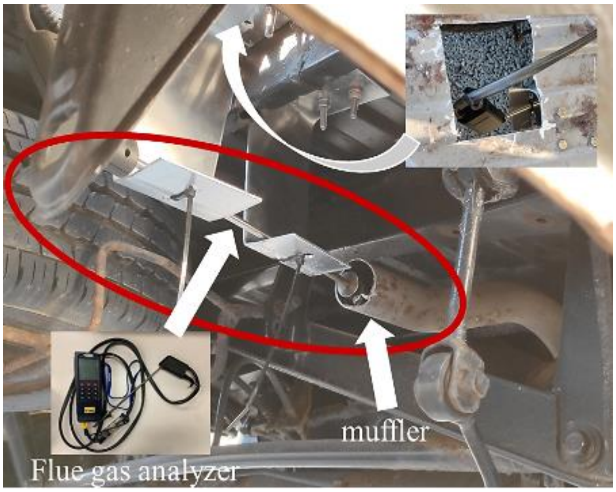

Fig. 7. Details of road driving experiment

4. Results and Discussion

4.1 SEM and XRD Results

Figure 8 shows the results of elemental analysis by SEM. Calcium and oxygen were strongly detected in SEM, confirming that calcium carbonate, the main component of eggshells, was converted to calcium oxide. Next, Fig. 9 shows the results of crystal skeletal structure analysis by XRD. This crystal skeleton structure is consistent with the Lime peak shown in Fig. 10 obtained from XRD database. Therefore, it was confirmed that the prepared eggshell is a type of calcium oxide called Lime.

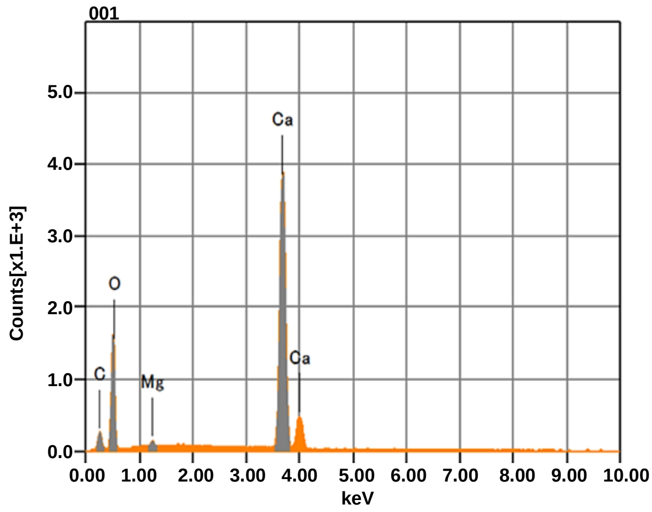

Fig. 8. Results of Elemental Analysis

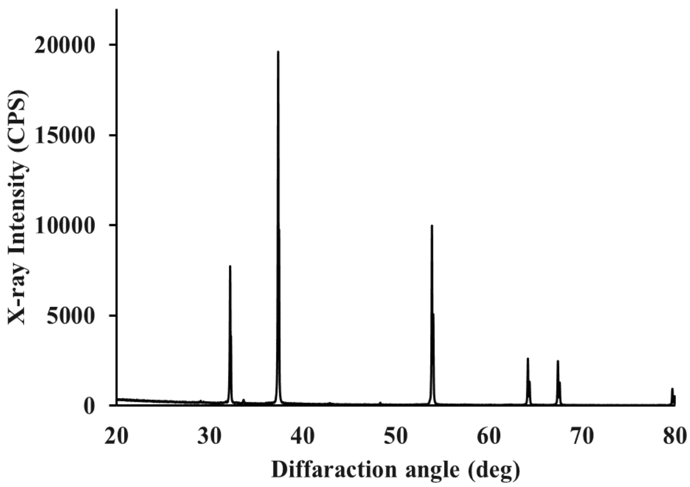

Fig. 9. Crystal structure of eggshell

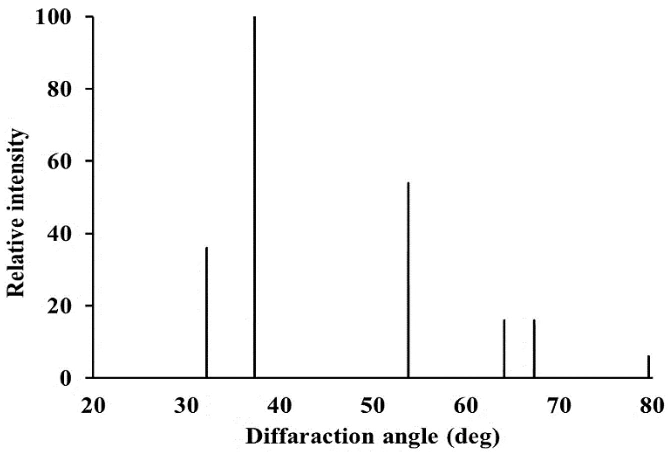

Fig. 10. Relative peak of Lime

4.2 BDF Yield Ratio

4.2.1 Effects of Time

The result of BFD yield ratio related to the reacting time is shown in Fig. 11. The highest BDF yield at 2 minutes was 95.30%. However, for 4-10 minutes' reaction, BDF yield ration decreased. The reason for the decrease is likely to be the phenomenon of the reversible reaction occurred. As explained before, BDF synthesis is the esterification which is reversible. It appeared that under this experimental condition for 2 min's reaction, the fatty acid methyl esters (BDF) and glycerin that just reached the reaction limit, then if the reacting time became longer, the synthesized BDF may have decomposed to vegetable oil and methanol.

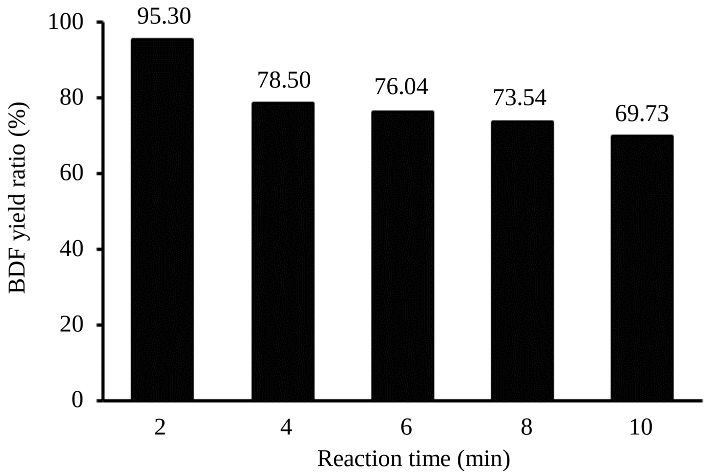

Fig. 11. Effect of time on BDF yield ratio

4.2.2 Effects of Temperature

The results of the BDF yield ratio measurements at each 20°C are shown in Fig. 12. The highest BDF yield ratio was obtained at 90°C, reaching 94.08%. On the other hand, the higher temperature range after 110°C resulted in lower BDF yield ratios. Generally speaking, chemical reaction with higher temperature will easily be conducted.

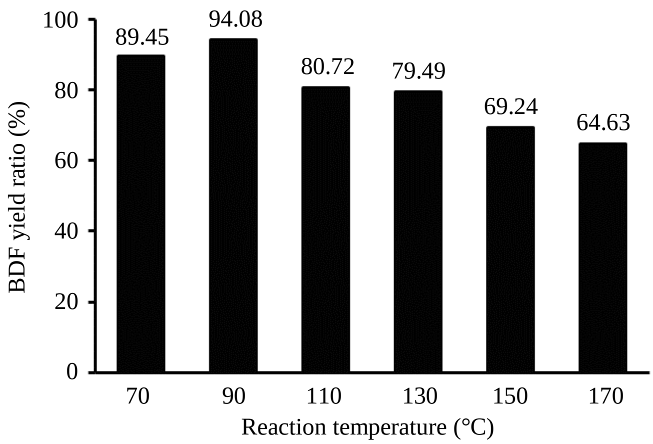

Fig. 12. Effect of temperature on BDF yield ratio

However, in case of microwave-based heating, vegetable oil and methanol' dielectric loss coefficients played important role when heated. Therefore, their temperature rising ratios are different too. Besides, dielectric loss coefficient is affected by the temperature. With these complicated reasons, it is not simple to make a conclusion that the higher temperature could lead to the higher BDF yield ratio. It is believed that there should exist the most suitable temperature condition for BDF synthesis to get higher BDF yield ratio.

4.2.3 Effect of Different Types of Vegetable Oils Methanol Content

BDF synthesis experiments with different types of vegetable oils (Fig. 13) were compared with two types of vegetable oils: rapeseed oil and jatropha oil. The results showed that the maximum BDF yield ratio was 94.08% for rapeseed oil and 70.70% for jatropha oil, with rapeseed oil having a 23.38% higher BDF yield. The kinematic viscosity of jatropha oil at 40°C is 37.81mm^2/s while that of rapeseed oil is 28.57mm^2/s [14]. Therefore, the intermolecular reaction rate was slowed down, which may have affected the BDF yield. In addition, post-synthesis jatropha BDF contains a large amount of impurities, which may also have a negative impact.

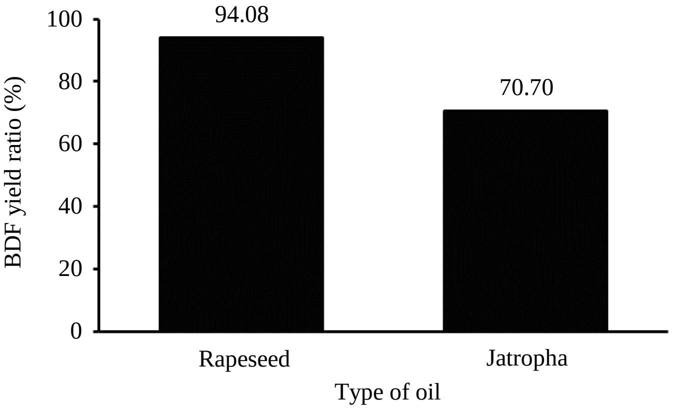

Fig. 13. Effect of time on BDF yield ratio

4.2.4 Effects of Amount of Methanol

In Figure 14, the BDF yield ratios were compared by increasing the amount of methanol by 0.5 ml one by on in the range of 0.5 to 2.5 ml. As the amount of methanol was 0.5ml, BDF yield ratio reached 85.11%. However, during the range of 1-2.5ml, BDF yield ratio decreased as the amount of methanol increased, which is contradictory to the common sense from the point view of chemical equilibrium. It is considered that BDF yield ratio based on microwave is not only influenced by the amount of methanol when other conditions are fixed, but also by the mixing state of the vegetable oil with methanol and catalyst. That is the reason why ultrasound irradiation was firstly employed to emulsify the vegetable oil and methanol. Actually, it was observed that when the amount increased, the mixing state of the reactant was not good enough, which lead to the decrease of BDF yield ratio.

In order to improve BDF yield ratio, the authors tried to use two-step method, which means the uncompleted product will be irradiated by microwave again, for 1.5-2.5 ml samples since the BDF yield ratio was as low as 50-60%. As shown in Fig. 14, The BDF yield ratio was up to 99.59%, which indicated a significant improvement in BDF yield. It is surmised that in two-step method, extra unreacted amount of methanol remained at first-step accelerated the esterification reaction at the second-step reaction.

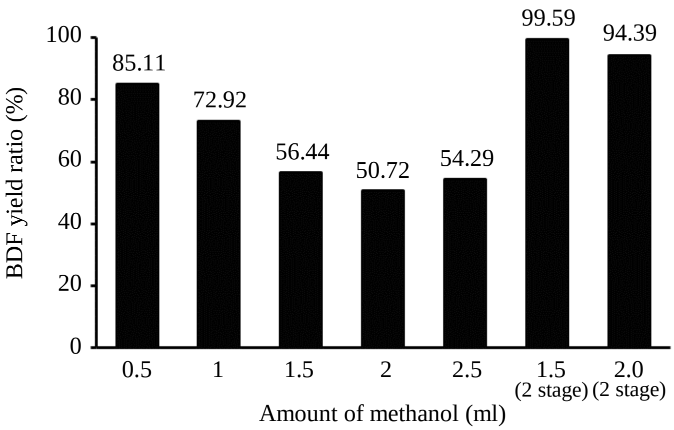

Fig. 14. Effect of time on BDF yield ratio

4.3 Thermal Efficiency

The results of the combustion experiment are shown in Fig. 15. Since the thermal efficiencies of the three fuels are almost the same, for example around 20% when load is 1500E, BDF can be used as a fuel for diesel engines.

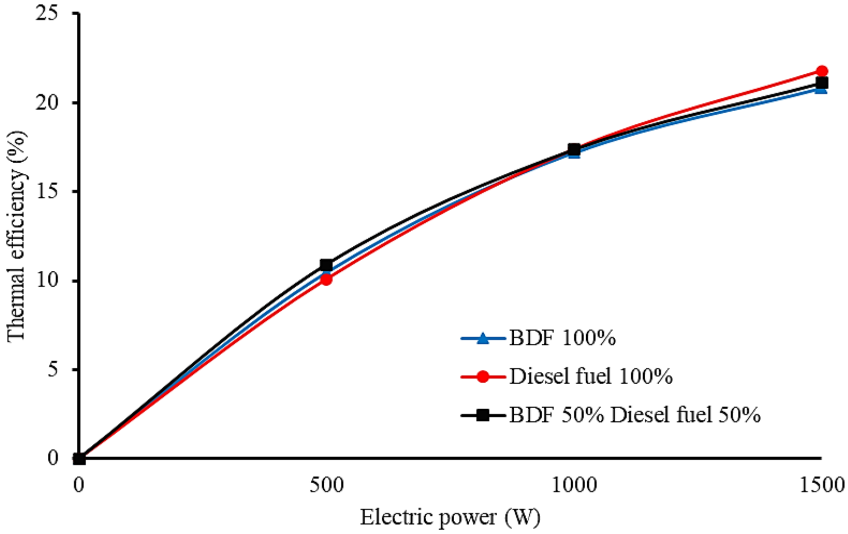

Fig. 15. Results of thermal efficiency.

4.4 Exhaust Gas Concentration

The exhaust gas measurement results are shown in Fig. 16 and Fig. 17. CO_2 concentration was lower for BDF in the range of 10-50 km/h, with a maximum difference of 1.8% at 10 km/h. Since the CO_2 in BDF is derived from naturally occurring oil, the CO_2 emitted from this combustion is considered to be equivalent to the CO_2 released into the air as plants die or decompose. On the other hand, NOx concentrations did not show significant differences.

BDF contains more oxygen than diesel oil and easily combines with nitrogen during combustion, we had assumed that the overall NOx concentration would be higher than that of diesel oil, but in fact there was no significant change.

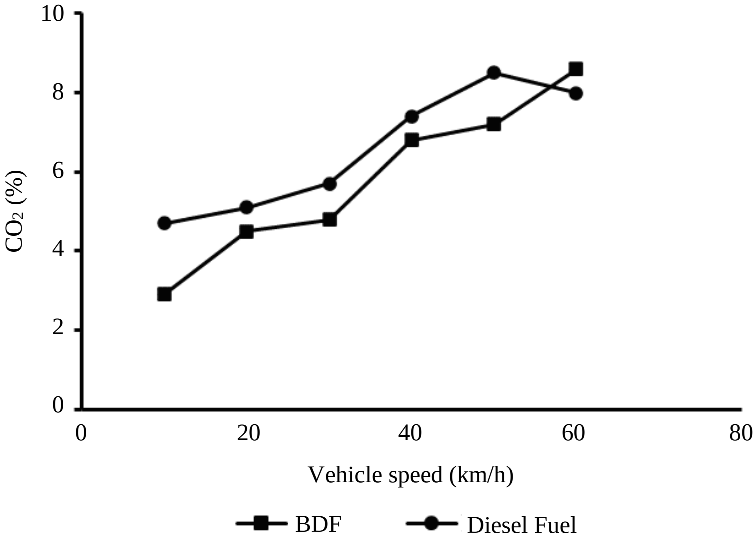

Fig. 16. CO_2 concentration

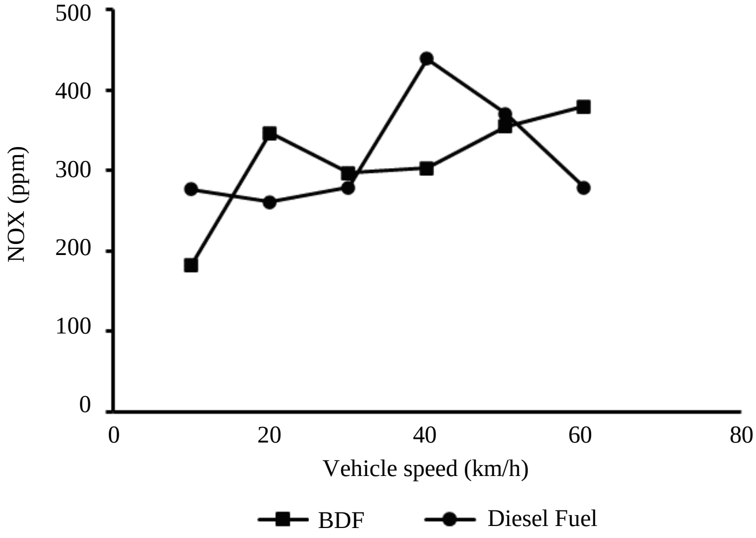

Fig. 17. NOX concentration

Table 4: Conditions that exceed 90% BDF yield ratio.

	Time (min)	**Temperature (℃)**	**Vegetable oil (ml)**	**Methanol (ml)**	**Catalyst (g)**	**Oil type**
Sample1	2	130	4	1	1	Cole seed
Sample2	10	90	4	1	1	Cole seed
Sample3	10	130	4	1.5 (Two-stage)	1	Cole seed

5. Conclusion

1) The eggshell crystals are a type of calcium oxide called lime.
2) Experimental conditions for BDF synthesis ratio exceeding 90% are listed in Table.4.
3) The thermal efficiency of BDF is almost the same as that of light oil, and from the viewpoint of thermal efficiency, BDF can be used as an alternative fuel to light oil.
4) CO_2 emissions of BDF were lower than those of diesel oil by a maximum of 1.8%, but NOX emissions did not show a significant change in emissions between diesel oil and BDF.

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