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*Research Article*

# BDF Synthesis using Clamshell as Ecofriendly Catalyst

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**Abstract:**
*BDF (Bio-diesel Fuel) is regarded as a kind of SAF (Sustainable Aviation Fuel) that can be used for diesel engine. The basic method of producing BDF is based on transesterification reaction where vegetable oil reacts with methanol under conditions of proper catalyst and temperature. So far, catalysts such as NaOH, KOH, CaO and $H_2SO_4$ have been suggested for BDF synthesis. Though higher BDF yield ratio up to 95% was reached, after treatment of using large quantity of water to wash the remained catalyst out of the produced BDF caused some environmental problems. For example, to produce 900L BDF, usually 60L water is needed. In order to deal with this problem, we have successfully employed eggshell as the ecofriendly catalyst to produce BDF under microwave irradiation. In this case, even water-washing is not applied to BDF-producing process, BDF yield ratio could reach 99.5%. In this paper, we aim to make suggestions of using clamshell to synthesize BDF. Firstly, calm shell is milled and prepared as catalyst. Secondly, it is characterized. Thirdly microwave irradiation based BDF synthesis are conducted under a certain of experimental conditions. Fourthly, The BDF yield ratio is measured. Finally, the physical properties such as density and viscosity are invested. It is found that the BDF ratio could reach 87.98% and the specific gravity was 0.895.*

**Keywords:** *BDF synthesis, Clamshell, Catalyst, Microwave irradiation*

## 1. Introduction

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 [1], a decrease for the seventh consecutive year since 2014. However, the Japanese government has set a goal of reducing $CO_2$ emissions by 46% [2] from the fiscal 2013 level (1.32 billion tons) by the year 2030, it is necessary to develop new alternative green energies to deal with above-mentioned problems. Biodiesel fuel 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.

So far, we have used ultrasound to synthesize BDF, and the BDF yield ratio reached 78.18% with reaction time of 40 min [3]. However, one of the final goals of our research is to achieve a BDF yield ratio of 95% or higher with shorter reaction time, therefore some new methods of BDF producing have been investigated and tested.

Recently, applying microwaves to BDF synthesis is regarded as a new method to increase BDF yield ratio was suggested. Unlike conventional heating methods, microwaves can heat the inside and outside of a heated object almost uniformly by a phenomenon called dielectric heating [4]. Expected benefits include significantly shortened reaction

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times, low-cost processes, and power savings [5]. In their previous research [6], Ikenaga et al. reported that a microwave BDF synthesis using lead oxide as a catalyst achieved a BDF yield ratio of about 90% using homogeneous catalytic method. Homogeneous catalytic reactions using alkali hydroxide are the mainstream for biodiesel production. This is because the reaction can be carried out under relatively mild conditions of about 333K [7]. However, this method requires rinsing off the added catalyst, which results in the discharge of a large amount of alkaline wastewater, so neutralization and other wastewater treatment are indispensable. 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 [8]. In order to handle BDF water-washing problem, researcher like Kawashima et al. achieved a BDF yield of 90% in their study of BDF by using solid catalyst of activated calcium oxide [9]. Based on those research reports, during our last year's study of synthesizing BDF, eggshells as catalyst was firstly employed for BDF production under condition of microwave irradiation and it was confirmed that maximum BDF yield ratio was 99.5% [10] and reaction time was within 10 min. Encouraged by this achievement, in this paper, we try to make suggestions of using clamshell instead of eggshell to synthesize BDF under microwave irradiation. It is found that the main components of clamshell and eggshell are calcium carbonate ($CaCO_3$) and both of them have alkaline property, which means that clamshell is possible to be used as solid catalyst for BDF synthesis. Besides, every year clamshell is discarded as waste material in Japan, and how to effectively utilize clamshell is a challenging problem.

During our research, firstly, clamshell is milled and prepared as catalyst. Secondly, it is characterized by SEM and X-ray diffraction analyser. Thirdly microwave irradiation based BDF synthesis are conducted under a certain of experimental conditions. Fourthly, The BDF yield ratio is measured. Finally, the physical properties such as density and viscosity are invested. It is found that the BDF ratio could reach 87.98% with reaction time of 10 min while viscosity for synthesized BDF at 20℃ was around 56 mPa·S.

## 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 also regarded as BDF.

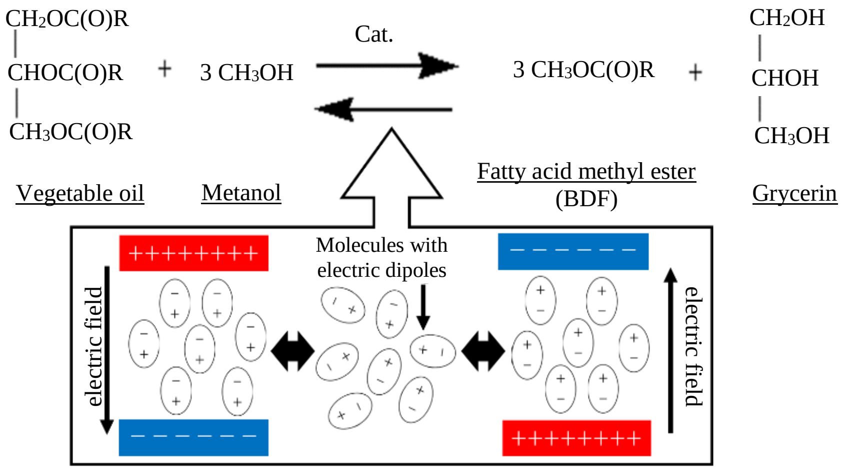


**Fig. 1.** Synthetic principle of BDF.

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 are affected by the microwave-induced molecular rotation, which increases the degradation rate and accelerates the ester exchange reaction.

**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 |

## 3. Experiment

*3.1 Catalyst Preparation*

In this research, clamshell is used as solid catalysts. The main component of clamshell is calcium carbonate ($CaCO_3$). However, in order to use them as alkaline catalysts, clamshell must be dried at 378 K for 2 hours and then calcined at 1173 K for 2 hours to produce calcium oxide (CaO). The chemical equation for calcium oxide is shown in Equation 1.

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

The prepared catalysts are observed on the surface using a scanning electron microscope (SEM, JEOL Ltd. JSM-IT100). Finally, a powder X-ray diffraction (XRD) analyzer (Rigaku Corporation Smart Lab) is used to investigate the changes in the crystal skeleton structure of the clamshell. 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 stirrer (AS-ONE HS-50E-B). Next, the solid catalyst is placed in a test tube, and the ester exchange reaction is carried out in a microwave chemical reaction apparatus (Biotage's Initiator+) (Fig. 3).

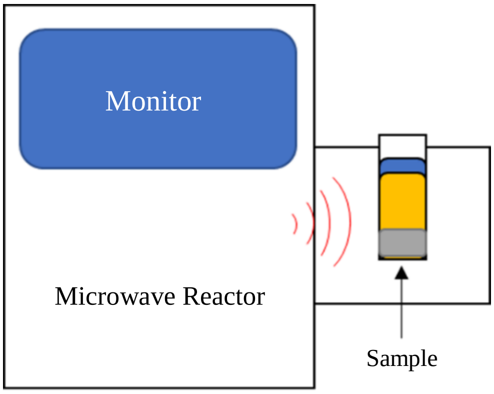


**Fig. 2.** Schematic of Microwave BDF synthetic system.

**Fig. 3.** Initiator+.

The experimental condition for BDF is shown in Table 2. 4ml of vegetable oil and 1 ml of methanal were mixed together in a test tube and then emulsified by using ultrasonic irradiation for form emulsified reactants. The emulsified reactants with 1g of prepared clamshell were set to the microwave reactor (Initiatpor+). Other reacting conditions such as temperature and reacting time were set to 90℃ and 10 min, respectively. For comparison, prepared eggshell as catalyst was used for another BDF synthesis experiment.

**Table 2:** BDF synthesis conditions

| Tem. (℃) | Time (min) | Vegetable oil (ml) | Methanal (ml) | Catalyst (g) | Oil type | Type of catalyst | Tube size (ml) |
|---|---|---|---|---|---|---|---|
| 90 | 10 | 4 | 1 | 1 | rapeseed | eggshell<br>clamshell | 2-5 |

*3.3 BDF Yield Ratio Measurement*

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 methyl were detected, from which the BDF synthesis ratio 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 |

*3.4 Measurement of Viscosity and Specific Gravity*

In order to investigate the quality of the synthesized BDF, viscosity and specific gravity are measured by a viscosity measuring instrument and a hydrometer, respectively. For viscosity measurement, the relationship between viscosity and temperature was investigated while for comparison, rapeseed oil's viscosity was measured too.

## 4. Results and Discussion

*4.1 Results obtained from SEM*

Surface state of clamshell by SEM is shown in Fig. 4. There are many small holes on the surface of the clamshell that might play important roles in absorbing reactants and quicken BDF synthesis reaction. Element components of clamshell is shown in Fig. 5. Main element components are Ca, O and C were detected and the mass percentage of Ca, O and C are 52.14%, 44.12% and 3.74%, respectively. With those data, it was confirmed that the main material of the prepared clamshell is CaO that is kind of basic catalyst. Since CaO had already been employed as a effective solid catalyst for BDF synthesis under ultrasonic irradiation [11], and the BDF yield ratio could reach 90%, it is a natural thing to use the prepared clamshell as a eco-friendly catalyst for BDF synthesis.

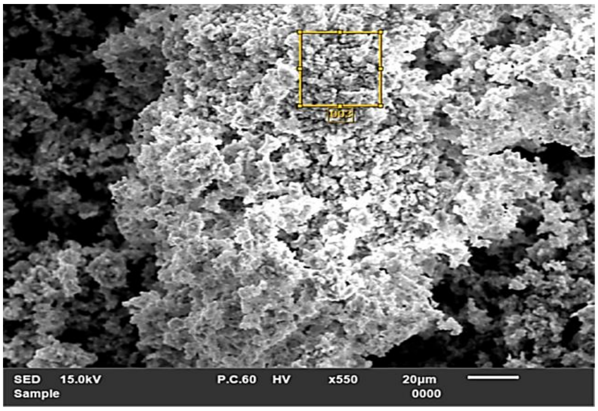


**Fig. 4.** Surface state of clamshell by SEM.

*4.2 Results obtained from XRD*

Crystal skeleton structure of clamshell by XRD is shown in Fig. 6. At diffraction angle of 37.35°, the strongest intensity was obtained. Besides, at other diffraction angles such as 33.5°, 54.4°, 66°and 68°, relatively stronger intensity peaks were observed too. To characterize the prepared clamshell, database of solid materials' crystal skeleton structures was carefully investigated. As shown in Fig. 7, which is the typical XRD result of lime, by comparing Fig. 6 with Fig. 7, it was found that both the clamshell and the lime almost have the same crystal skeleton structure, which indicates that the prepared clamshell is kind of lime.

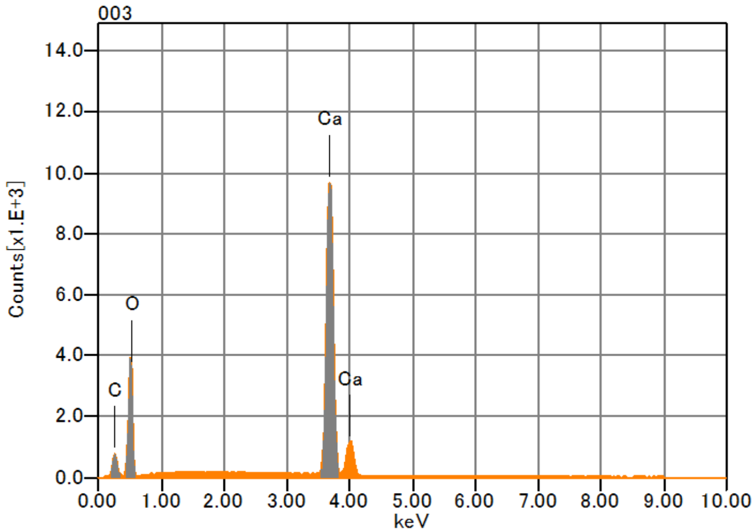


**Fig. 5.** Element components of clamshell.

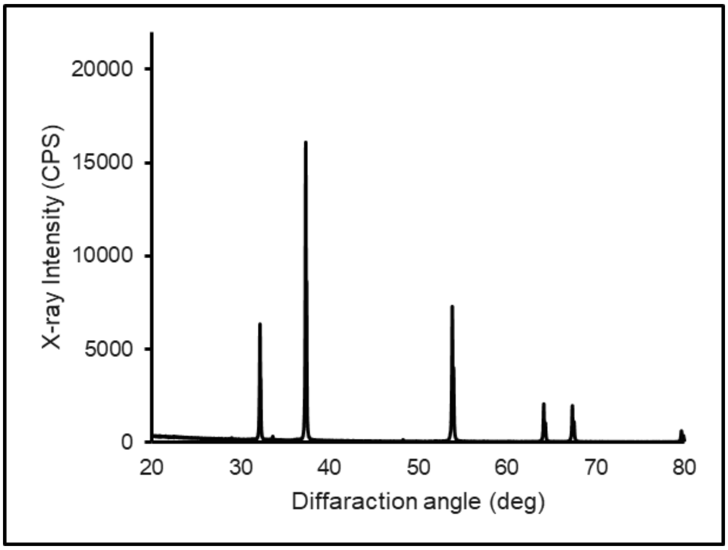


**Fig. 6.** Crystal skeleton structure of clamshell by XRD.

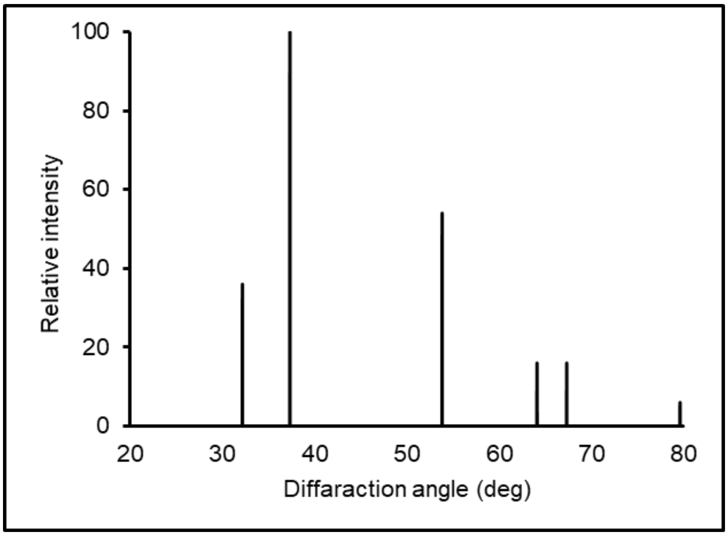


**Fig. 7.** Crystal skeleton structure of Lime by XRD

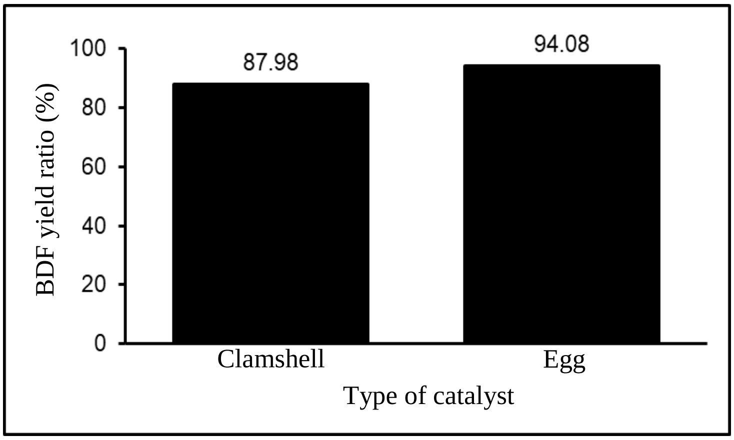


**Fig. 8.** BDF yield ratio.

*4.3 BDF Yield Ratio*

BDF yield ratios by using egg and clamshell are shown in Fig. 8. In case of clamshell, BDF yield ratio was 87.89% while in case of egg, BDF yield ratio was 94.08%, which demonstrated that both clamshell and egg as eco-friendly catalyst could effectively facilitate BDF synthesis reaction. However, the difference of the BDF yield ratio between eggshell and clamshell can be explained as follows: Firstly, as shown in Fig. 9 where element components of eggshell is demonstrated, it was confirmed that apart from Ca, O and C, Mg was also detected for the eggshell and the existence of Mg may enhance BDF yield ratio. Secondly, by comparing the surface observation photos of eggshell and clamshell, it is found that the surface area eggshell is larger than that of clamshell. Finally, the crystal skeleton structures of eggshell and clamshell are slightly different. All these facts would lead to the different BDF yield ratios for eggshell and clamshell.

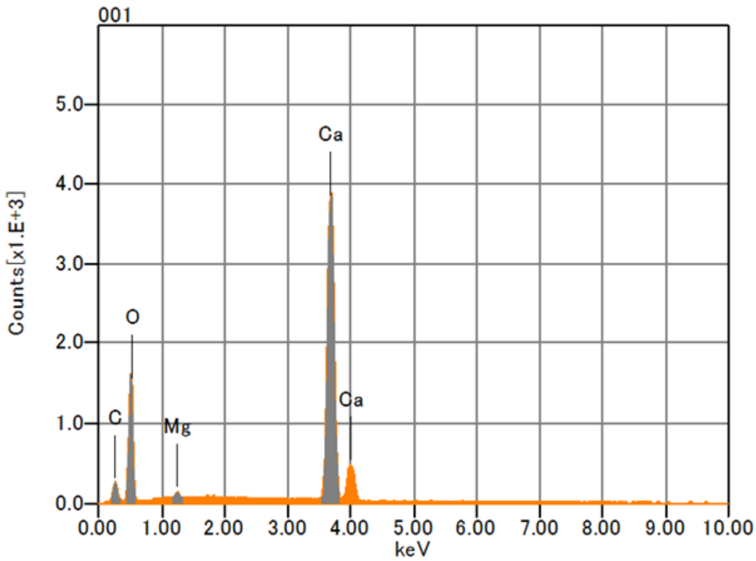


**Fig. 9.** Element components of eggshell.

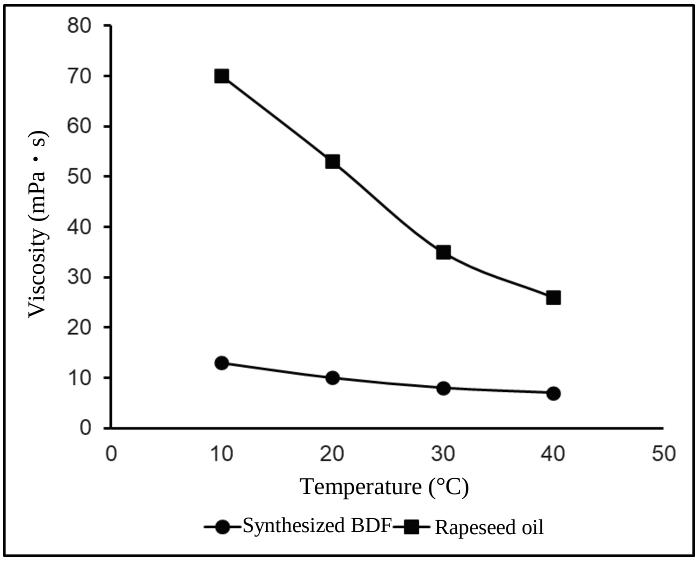


**Fig. 10.** BDF viscosity changes.

**Table 4:** Specific gravity of BDF

| Standard BDF | Synthesized BDF |
|---|---|
| 0.86-0.90 | 0.895 |

*4.4 Viscosity and Specific Gravity*

Viscosity changes for synthesized BDF and rapeseed oil under different temperature are shown in Fig. 10. With the increased temperature, viscosities for both synthesized BDF and rapeseed oil decreased gradually. However, compared with rapeseed, viscosity of BDF decreased from 70 to 14 mPa・S, which means BDF synthesis can drastically decrease the viscosity of the vegetable oil and make itself a potential fuel for diesel engine. The viscosity for synthesized BDF at 20℃ was around 56 mPa・S. In order to investigate whether the viscosity of the synthesized BDF meets that of the standard BDF based on JIS (Japan Industry Standard) or not, the measured viscosity at 40℃ was converted into kinematic viscosity and compared with that of the standard BDF. It was confirmed that the kinematic viscosity of synthesized BDF was 7.81 $m^2/s$ which is larger over the proper range of kinematic viscosity of standard stand (3.5-5.1 $m^2/s$). It is thought that this BDF synthesis reaction was not completed because the BDF yield ratio was 87.98% (Fig. 8) and unreacted rapeseed oil may increase the kinematic viscosity.

Specific gravity of BDF both standard BDF and synthesized BDF is shown in Table 4. Since specific gravity of synthesized BDF was 0.895 that satisfied that of standard BDF (0.86-0.90), it could be said the synthesized BDF is possible to be used for diesel engine in terms of specific gravity.

## 5. Conclusion

In this study, clamshell as basic catalyst was applied to BDF synthesis. After a serial of experiments on preparation of clamshell, catalyst characterization, BDF synthesis and BDF yield ratio measurement and viscosity and specific gravity measurement, conclusions are obtained as follows:

(1) Prepared clamshell is a kind of eco-friendly basic catalyst;

(2) By using prepared clamshell as catalyst, BDF yield ratio was 87.98%

(3) Viscosity and specific gravity for synthesized BDF were measured. By comparing the measured values with those of standard BDF, it was confirmed that BDF synthesis reaction was not completed fully under the current experimental condition.

Improving the catalyst characteristics and other reaction conditions to continuously enhance BDF yield ratio is our future subject.


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## References


[1] National Institute for Environmental Studies. Greenhouse gas emissions in FY2020 [Internet]. 2020 [cited 2021 Dec 10]. Available from: https://www.env.go.jp/content/900518252.pdf. (In Japanese)

[2] Kantei. Global warming prevention headquarters, NDC in Japan [Internet]. 2021 [cited 2021 Oct 22]. Available from: https://www.kantei.go.jp/jp/singi/ondanka/kaisai/dai48/pdf/ndc_kouken.pdf. (In Japanese)

[3] Zhu N, Kuo M, Han CH. Biodiesel fuel(BDF) synthesis by using ion exchange resin based on ultrasonic irradiation and its application. IOP Conf Ser: Mater Sci Eng. 2020;886:012004.

[4] Oshima K. Mechanism and applications of microwave heating. Journal of the Japan Society of Colour Material. 1971;44(1):27-35. (In Japanese)

[5] Fukushima H. Microwave processing and applications to future automobile. R&D Review of Toyota CRDL. 2015;46(3):75-92

[6] Ikenaga K, Inoue T, Hamada A. Investigation of metal oxides for microwave preparation of bio diesel fuel. The 26th Annual Conference of Japan Society of Material Cycles and Waste Management; 2015 Sep 2-5; Kyushu University, Japan. p. 285-286. (In Japanese)

[7] YanoT, Koda J. Minimization of washed wastewater volume in the refining process of biodiesel fuel. Proceedings of the Conference on Waste and Resources Recycling; 2013; Japan. p.387 (In Japanese)

[8] Kouzu M, Umemoto M, Kasuno T, Tajika M, Aihara Y, Sugimoto Y, et al. Biodiesel production from soybean oil using calcium oxide as a heterogeneous catalyst. J Jpn Inst Energy. 2006;85(2):135-141. (In Japanese)

[9] Kawashima A, Yamamoto H, Tetsuya K. Development research of bio-diesel production process by using activated calcium oxide. Proceedings of the Annual Conference of the Japan Institute of Energy; 2004; Japan. p. 182-183. (In Japanese)

[10] Kumeyama H, Zhu N. Synthesis of BDF based on microwave irradiation and its application. J Res Appl Mech Eng. 2023;11(1):1-12.

[11] Suzuki W, Nakaya Y, Sinzaki R, Li W, Zhu N. BDF synthesis based on tube flow reactor by using solid catalyst. Proceedings of the 6th TSME International Conference on Mechanical Engineering; 2015 Dec 16-18; Phetchaburi, Thailand.