21st International Symposium on Plasma Chemistry (ISPC 21)
Sunday 4 August – Friday 9 August 2013
Cairns Convention Centre, Queensland, Australia

Enhancement of biodiesel production using electrical discharge in liquid with heterogeneous catalyst

Toshimi Nagasawa, Satoshi Kodama, Hidetoshi Sekiguchi

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

Abstract: In this research, pulse electrical discharge in liquid was introduced for the enhancement of biodiesel production rate with heterogeneous catalysts. The experimental result showed the reaction rate was increased and the effectiveness of the discharge was confirmed. Additionally, synergy effect between the discharge and ultrasonic irradiation was observed for enhancing the reaction rate.

Keywords: electrical discharge, liquid, heterogeneous, biodiesel, ultrasound

1. Introduction

As the world energy demand continues to rise while the supply of fossil fuels is limited, research attention is directed towards alternative fuels. Biodiesel, a fatty acid methyl ester (FAME), is one of the alternative fuels and synthesized from triglyceride and methanol, as shown as Fig.1.

The reaction of biodiesel can be catalyzed by alkalis, acids, or enzymes. Homogeneous alkali-catalyzed methyl ester production have fast reaction rate, and this technique is most often used commercially [1]. Nevertheless, the homogeneous alkali catalyst method has some drawbacks such as the requirement of the purification of products.

The use of heterogeneous catalysts has been proposed for solving the problems. Heterogeneous catalyst have many advantages: they are much easier to be separated from liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [2, 3]. Several kinds of solid catalysts such as metal oxides, hydroxides, alkoxides and salts are proposed. These catalysts have different reaction mechanism, for example, CaO behaves as Lewis base and $Ca(OH)_2$ as Brønsted base. However, the reaction rate using heterogeneous catalyst method is low as compared with homogeneous catalyst method because the reaction can only occur in the interfacial region between the methanol, triglyceride and catalyst.

To increase the liquid-liquid-solid contact area, mixing condition is important. In the authors' previous research, the irradiation of ultrasound accelerated the reaction rate of biodiesel production reaction using heterogeneous catalysts. It was confirmed that ultrasonic irradiation produced smaller droplet than conventional agitation and promoted mixing condition, resulting in the increase of liquid-liquid-solid contact area.

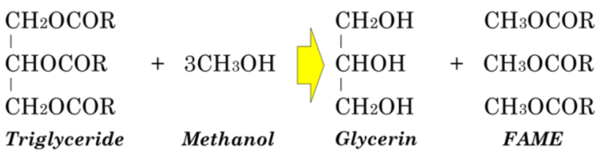

Fig.1. Methyl ester production reaction of biodiesel.

It is reported that pulse electrical discharge in liquid leads to the formation of reactive species [4]. Additionally, pulse electrical discharge in liquid makes shockwaves in liquid, accelerating liquid-liquid-solid mixing condition.

In this research, pulse electrical discharge in liquid and ultrasonic irradiation was introduced for the enhancement of methyl ester production rate. The generation of active species and shockwave by the discharge and ultrasound were expected to enhance the reaction. The main aim of this research was to characterize the effects of pulse electrical discharge in liquid with heterogeneous catalysts. Additionally, synergy effect between pulse electrical discharge and ultrasound in liquid was examined.

2. Experimental

2.1 Materials

In this research, triolein (Kanto chemical co., INC.) was used as a model of triglyceride. Methanol of 99.7% purity (Wako Pure Chemical Industries, Ltd.) was used. CaO of 98% purity (Wako Pure Chemical Industries, Ltd.) was used for Lewis base, and $Ca(OH)_2$ of 96% purity (Kanto chemical co., INC.) for Brønsted base.

2.2 Experimental set-up

Experimental set-up is shown in Fig.2 and magnification of the experimental set-up is shown in Fig.3. Ar or superheated CH_3OH was injected into the mixture of triolein and CH_3OH solution through a needle electrode, to which high voltage pulse was applied by pulse power supply (Nissin pulse electronics co.,LTD.). A grounded plate electrode was placed on the counter side of the needle electrode in the reactor. Ultrasound was irradiated from the top of the reactor by Ultrasonic generator (UH-150S, SMT Corporation).

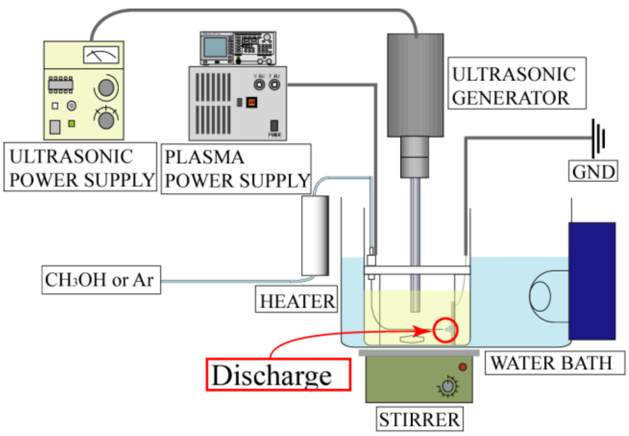

Fig.2. Experimental set-up.

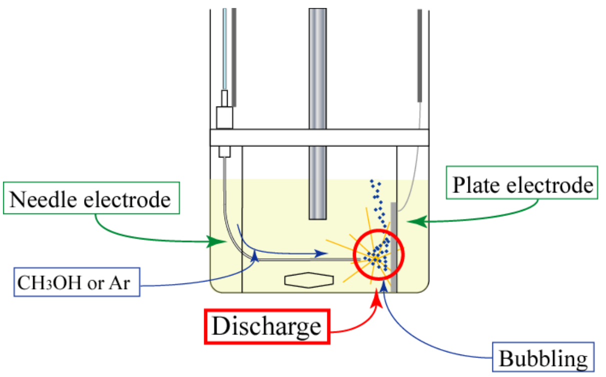

Fig.3. Magnification of the experimental set-up.

2.3 Reaction condition

Reaction conditions are given in Table 1. Methanol flow rate was 12ml/min (as lquid) in the experiment of bubbling methanol. On the other hand, methanol of liquid was supplied periodically in the experiment of bubbling Ar because methanol was consumed by the reaction. Table 2 shows the abbreviations of the experimental conditions. For example, B-(3) expresses the experiment of bubbling Ar with CaO as a catalyst, and irradiated by ultrasound.

2.4 Analysis

HPLC (RI-2031, JASCO) with silica gel column (Finepak Sil-5, JASCO) was used for product analysis. Before the analysis, products were centrifuged for 5min at 1000 rpm by centrifugal separator (CT6E, Hitachi Koki Co., Ltd.) to separate the phases of organics, methanol and solid catalysts.

The yield of oleic acid methyl ester was calculated by following equation:

Table 1 Experimental conditions.

Bubbling gas	CH_3OH	Ar
Reaction time[min]	180	180
Temperature [°C]	60±3	60±3
Triolein amount [ml]	30	30
Initial volume of Methanol [ml]	5	15
Catalyst	CaO	CaO, $Ca(OH)_2$
Catalyst amount [g]	1.57	1.57
Applied voltage [kV]	2.96~4.8	2.88~4.48
high voltage pulse [μs]	20	20

Table 2 Abbreviations of the experimental conditions.

Bubbling CH_3OH with CaO	Bubbling Ar with CaO	Bubbling Ar with $Ca(OH)_2$
A	**B**	**C**

Only catalyst	Catalyst +discharge	Catalyst +ultrasound	Catalyst+discharge +ultrasound
(1)	**(2)**	**(3)**	**(4)**

$$\text{Yield of oleic acid methyl ester [\%]} = \frac{\text{Amount of Oleic acid methyl ester [mol]) / 3}}{\text{Initial amount of triolein [mol]}} \times 100$$

3. Result and discussion

3.1 Experiment A (CH_3OH bubbling with CaO)

Fig.4 shows the time courses of yield of product (oleic acid methyl ester) in the experiment A. As noted in Fig.2, the reaction rate of A-(2) was increased compared with A-(1). It shows the enhancement of the reaction rate by the discharge, expecting that the discharge is effective for promoting biodiesel production with heterogeneous catalysts. However, when experiment of A-(4) was carried out, the discharge with ultrasound had negative effect in the reaction. The color of solution after the experiment revealed black, implying the discharge decomposed biodiesel.

Fig.5 shows photographs of discharge in the reaction: photograph (a) is early stage of the reaction and photograph (b) is later stage. The behaviors of the discharge changed during reaction time: light emission color turned green into white, and interval of discharge and discharge sound changed. Mostly the same changes were observed in other experiments.

3.2 Experiment B (Ar bubbling with CaO)

Fig.6 shows the time courses of the yield in the experiment B. Similarly to the experiment A, the reaction rate of B-(2) was increased as compared with B-(1). However, the reaction rate of B-(4) was fastest in the four conditions, indicating the synergy effect between discharge and ultrasound. This may be because that Ar gas and ultrasound in the experiment B-(4) made the discharge more stable compared with the experiment A-(4).

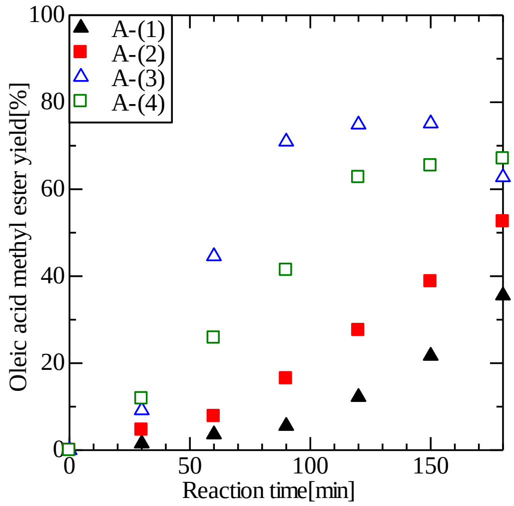

Fig.4. The time courses of the yield of oleic acid methyl ester in the experiment A.

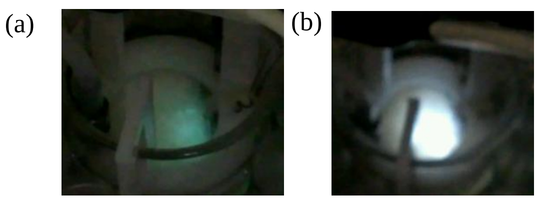

Fig.5. Appearance of discharge in (a) early stage of the reaction and (b) later stage of the reaction.

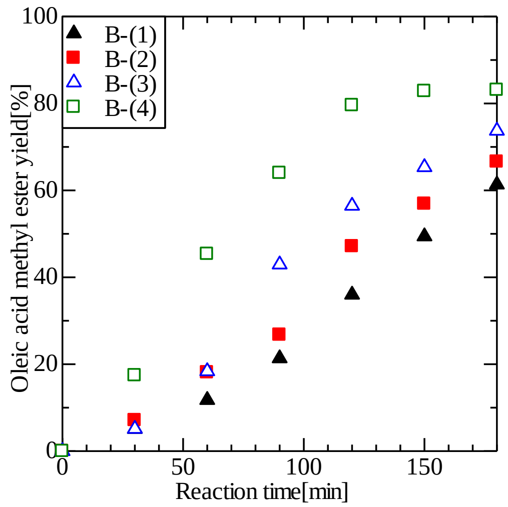

Fig.6. The time courses of the yield of oleic acid methyl ester in the experiment B.

3.3 Experiment C (Ar bubbling with $Ca(OH)_2$)

Fig.7 shows the time courses of the yield in the experiment C. The reaction rate of C-(2) was increased compared with C-(1) and C-(3). It is interesting that the reaction rate of C-(2) is faster than C-(3). It may be because $Ca(OH)_2$ is dehydrated into CaO by locally high temperature caused by the discharge. However, the reaction rate of C-(4) was decreased as compared with C-(2) because the discharge was initially unstable in C-(4).

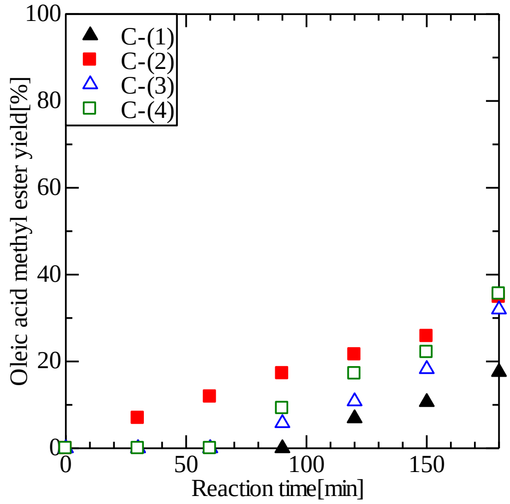

Fig.7. The time courses of the yield of oleic acid methyl ester in the experiment C.

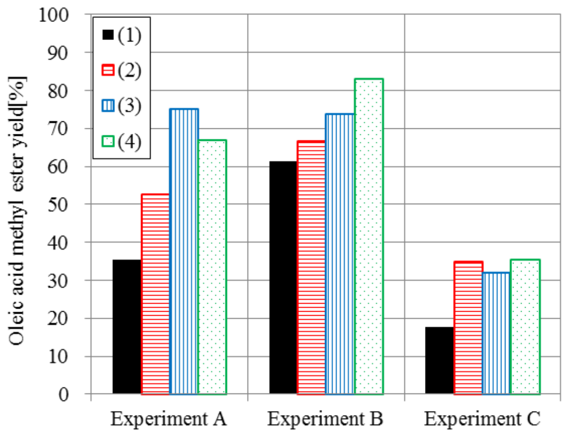

Fig.8. Comparison of the maximum yield of oleic acid methyl ester.

3.4 Comparison of the yield of all experiments

The yields of all the experiments are summarized in Fig.8. Effectiveness of electric discharge in liquid and ultrasound was confirmed clearly. However, synergy effect between electric discharge and ultrasound was confirmed only in the experiment B.

3.5 Effect of electric discharge in liquid

As mentioned above, the effectiveness of electric discharge in liquid was confirmed. This phenomenon was deemed of contributions to the following three regions around the electric discharge.

First, the discharge affected the catalysts surface. The discharge generated shock wave, making catalyst size smaller and reaction surface area of catalyst larger. In addition, it was expected that the shock wave accelerated desorption of products, thus triolein could be easily absorbed on catalyst. Furthermore, it was expected that the discharge reformed catalyst: as mentioned in section 3.3.

Second, the discharge affected the solution. The shock wave of the discharge made droplet of oil smaller, increasing reaction surface area.

Last, the discharge affected the reaction field. It is considered that the discharge produced active species, causing the acceleration of the reaction rate directly. In addition, it was expected that the discharge made reaction field locally high temperature, resulting in the increase in the reaction rate. The further researches will confirm these effects.

3.6 Synergy effect between pulse electrical discharge in liquid and ultrasound

Synergy effect was not confirmed in the experiment A, however it was confirmed in the experiment B. It may be because using Ar as bubbling gas made the discharge stable and breakdown voltage was decreased, reducing the decomposition of biodiesel into carbon.

4. Conclusions

In this research, pulse electrical discharge in liquid and ultrasound was introduced for the enhancement of methyl ester production reaction. It was confirmed that the discharge accelerated the reaction rate of biodiesel with heterogeneous catalyst. It is expected that pulse electrical discharge in liquid influences the surface of catalyst, solution and reaction field. The combination of the discharge and ultrasound was also effective for enhancing biodiesel production.

5. References

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