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論　文　名	「Biodiesel fuel production from triolein and fatty acids with alcohols under ultrasonic irradiation condition」 （超音波照射下でのアルコールとトリオレインおよび脂肪酸からのバイオディーゼル燃料の製造）
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論文要旨

The environmental impact of fossil fuels is well known nowadays, since the fossil fuels contribute to global warming by transferring previously sequestered carbon molecules into the atmosphere as carbon dioxide, a greenhouse gas, which is major source of air pollution through other combustion products found in an exhaust. Biodiesel fuel offers a solution to the air pollution problems. It has been claimed that biodiesel fuel does not contribute to an inhibition of global warming, because like petroleum, the exhausted gases from biodiesel fuel contains carbon dioxide. However, plants remove carbon dioxide from the atmosphere during photosynthesis, so that a net production of CO_2 is arguably zero. The levels of other pollutants are generally lower with biodiesel fuel than with petroleum. The fuelstocks for biofuels are produced by domestic agriculture, which means that biodiesel fuel production is conducted domestically as well. Biodiesel fuel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animals fats. Chemically, it is defined as the alkyl esters of long chain fatty acids derived from renewable lipid sources (triglycerides). It is environmentally biodegradable, and produces significantly less the amount of carbon monoxide, sulfur dioxide, hydrocarbons, particulates and air toxic emissions than those of diesel. Fatty acids alkyl esters (FAAE) can be used as biodiesel fuel or can be used as an additive or extender to diesel fuel.

This thesis was conducted with three purposes. The first one was the transesterification of triolein under

the ultrasonic irradiation condition. The influences of the molar ratio of alcohol/triolein, base-catalyst concentration and test temperature were studied to elucidate the optimum condition for the transesterification of triolein. The second one was to evaluate the effects of the alcohols with a long chain and secondary alcohols on the transesterification of triolein under the ultrasonic irradiation condition. The third one was to evaluate the transesterification of fatty acids by using various acid catalysts and molar ratios and the role of acid catalyst under the ultrasonic irradiation condition.

In chapter 1, the introduction of the biodiesel fuel and sonochemistry was described on the advantages and disadvantages of the biodiesel fuel, the specification of the biodiesel fuel, the overview of the biodiesel fuel production technology, and the characteristics of ultrasound.

In chapter 2, the transesterification reaction of triolein (triglyceride) and methanol was investigated as functions of molar ratio (methanol/triolein) and KOH (as catalyst) concentration at 25 ^{o}C under a stirring condition. This is a preliminary experiment to compare with the results obtained under an ultrasonic irradiation condition and to make an effect of ultrasound clear by obtaining a methyl ester conversion under a stirring condition. The optimum condition was found at the molar ratio of 6:1 (methanol /triolein) and 1.5%wt KOH catalyst concentration. However, it was found that the time to reach the maximum methyl ester conversion was so long, that the other methods need to be conducted to overcome that. Furthermore, it was also found that the maximum methyl ester conversion decreased with an increase in KOH concentration more than 1.5 %wt, above which the gel- formation as a form of soap was considered to take place. Therefore, it was concluded that this formation led to the decrease in the methyl ester conversion.

In chapter 3, it was systematically investigated on the effects of ultrasonic irradiation, molar ratio (alcohol to triolein), catalyst concentration and test temperature on the transesterification of triolein with a short chain alcohol (methanol and ethanol) and base catalysts such as KOH and NaOH to find out the optimum condition of the transesterification and to elucidate a fundamental insight into transesterification of triolein under ultrasonic irradiation condition.

By comparing the results obtained under the ultrasonic irradiation condition with those under the stirring condition, it was found that (1) the time to reach the maximum methyl and ethyl esters with KOH and NaOH was significantly short, (2) the maximum ester conversion tended to have a higher value and (3) the catalytic concentration to get the maximum ester conversion was small. In addition, it was also decided that the optimum condition under the

ultrasonic irradiation condition was as follows: molar ratio (methanol to triolein) 6:1, catalytic concentration of 1%wt and reaction time 30 min. As a result, it may be concluded that the ultrasonic irradiation method provides a possibility for producing the cheap alternative biodiesel fuel.

From the test temperature dependence of the transesterification of triolein with methanol and a base catalyst (NaOH and KOH) under the ultrasonic irradiation condition, it was found that the maximum methyl ester conversion increased with increasing temperature. Furthermore, the apparent activation energy (ΔG) was estimated from relationships between the rate and the reciprocal of temperature as follows: ΔG at high temperatures (more than 20°C) is 0.18 ~ 0.22 kJ/mol for NaOH and KOH, and ΔG at a lower temperature (less than 20°C) is 2.4 ~ 2.7 kJ/mol for NaOH and KOH. The latter value shows that the transesterification reaction was the diffusion controlled reaction.

In chapter 4, the transesterification of triolein under the ultrasonic has been conducted is to elucidate the effects of the kind of catalyst and the type of alcohol under low-frequency ultrasonic irradiation conditions (40 kHz). It was found that the ester conversion was very low at sulfuric acid catalyst at 25 °C and no conversion was observed at acetic acid catalyst. In addition, it was found that the ester conversion depended upon the kind of alcohols; as the number of carbon in alcohol increased, the reaction rate decreased, which means that the structural effect of the alcohol affected the transesterification reaction. Furthermore, the secondary alcohols such as 2-propanol, 2-butanol, 2-hexanol, and 2-octanol showed little ester conversion. It was presumed that the steric hindrance of alcohol strongly affected the transesterification of triolein.

In chapter 5, we tried to elucidate the transesterification of FFAs for the parameters under the ultrasonic irradiation and stirring conditions by using acid catalyst, but not base catalyst. The optimum condition for the production of ethyl ester under the ultrasonic irradiation condition was as follows: molar ratio of ethanol to oleic acid 3:1, H_2SO_4 concentration of 5%wt and irradiation time 2 hour at 60°C. Therefore, it was found that the transesterification of the fatty acids was very difficult compared to that of triolein.

On the basis of the results obtained, we decided the optimum condition on the transesterification of triolein to get the maximum ester conversion. We also found that as ultrasound accelerates the transesterification reaction, the ultrasonic irradiation method is one of the best methods to produce the biodiesel fuel with the highest ester conversion. In addition, we elucidated the roles of catalyst, alcohol, test temperature and fatty acids et al in the

transesterification of triolein.
Finally, the conclusions of this thesis were summarized in **chapter 6**.

審査結果の要旨

本論文は、用いられた食用油の組成は複雑で組成の違いで BDF の収率が異なることで、BDF 収率の最適条件が明確にされておらず、さらに、BDF 収率がアルコール種、アルコール濃度、触媒種、反応時間等々にどのように影響されるかを定量的、総合的に検討されていないことから、種々のアルキル鎖のトリグリセリドの混合物である植物油のモデル化合物として、アルキル鎖長１７で二重結合が１つあるオレイン酸（トライオレイン）を選び、トランスエステル化反応について総合的に検討した結果、以下のことが明らかとなった。

(1) アルカリ触媒を用いたトライオレインのトランスエステル化反応および酸触媒を用いた脂肪酸のエステル化反応に対して、超音波は機械攪拌条件下の結果と比較して顕著な促進作用があった。

(2) 1 級アルコールであるメタノールとエタノールは他のアルコール種に比べて BDF 収率が最大となることがわかった。さらに、メタノールを用いて、BDF 収率の最適条件を明らかにした。

(3) 1 級アルコールにおいて、カーボン数がエタノールより大きいアルコールでは BDF 収率が減少することが分かった。これはカーボン数が大きくなるに従い、トライオレインとアルコールとの溶解性が増加するにもかかわらず、BDF 収率が減少することから、アルコールの構造的な効果（長鎖）が BDF 収率に影響したものと推測した。

(4) 立体障害の大きい 2 級アルコールと脂肪酸のトランスエステル化反応は機械撹拌及び超音波条件下では殆ど進行しないことが分かった。それゆえに、トランスエステル化反応はアルコールの立体構造に大きく影響され、超音波は反応を直接促進するのではないことが明らかになった。

(5) 触媒種に関して、アルカリ触媒（NaOH, KOH）が弱酸性触媒（CH_3COOH）あるいは酸性触媒（H_2SO_4）よりトランスエステル化反応に最も有効であることがわかった。

本研究は、BDF の製造に関して、トライオレインのトランスエステル化反応について総合的に検討し、超音波照射下におけるトライオレインからの、BDF 収率の最適条件を明らかにするとともに、BDF 収率に及ぼすアルコール種、触媒種および脂肪酸の影響を詳細に調べ、明確にしており、新たな BDF 製造の発展および BDF 収率の最適化に貢献するところ大である。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。

本委員会は、本論文の審査および最終試験の結果から、博士（工学）の学位を授与することを適当と認める。