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論　文　名	Biodiesel production from virgin and waste cooking oils by the ultrasonic irradiation and the co-solvent methods on pilot plant and laboratory scales
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論文要旨

Due to the limited fossil fuels, the rapidly increasing fuel demand, the fluctuations of the petroleum price, the increasing pollution of the environment, and the threat of global warming, it has become necessary to find alternative clean and renewable energy resources. Biofuels, wind, and solar energies are ones among the favorable alternatives to fossil fuels as sources of energy. A liquid fuel consisting of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, known as “biodiesel”, is a promising potential alternative to diesel fuel. The cetane number, viscosity, gross heat of combustion and phase changes of the biodiesel are similar to those of petroleum diesel fuel. Furthermore, biodiesel fuel has many advantages over petroleum diesel fuel, as it produces less smoke and particles when it is burnt. In addition, it results in lower carbon monoxide release, and has lower emissions of hydrocarbons and no emissions of sulfur. Most importantly, it is derived from renewable resources and is easily biodegradable.

Biodiesel produced from virgin vegetable oils costs much more than petro-diesel; this is a major barrier to the commercialization of biodiesel in the market. The high cost of biodiesel is mainly due to the cost of raw materials, especially virgin vegetable oils. Therefore, it is necessary to find ways to minimize the production cost of biodiesel. In this context, methods that can reduce the costs of raw materials as well as the energy consumption are of special concern. The use of waste cooking oils (WCO), which are much cheaper than virgin oils, is one of the most attractive options to reduce the raw material cost.

Over the past two decades, applications of sonochemistry have been widely developed in many areas of chemical technologies. Ultrasound energy is well known as a useful tool to make fine emulsions

from immiscible liquids. Utilizing the characteristics of the ultrasound, the transesterification reaction between vegetable oil and alcohol can reach equilibrium in a short reaction time with a high yield of alkyl esters even at low temperatures.

In this thesis, the application studies of innovative methods for biodiesel production were performed on pilot plant and laboratory scales. The main factors affecting on the yield of product were examined in details for each method. In addition, from the experimental data, mechanism of the transesterification reaction was elucidated and compared with the conventional methods to show the advantages of the ultrasonic irradiation and co-solvent methods. The results obtained from this study will be summarized over all as follows.

The thesis consists of five chapters.

Chapter 1, entitled as “Overview and background of research field”, gives basic concepts of biofuels and trends of production and utilization of biofuels over the world. Then, the overviews of biodiesel and ultrasonic sonochemistry including the background of biodiesel, conventional methods for biodiesel production, and ultrasound and its application are reported. Finally, the purpose and organization of the thesis are presented.

Chapter 2, entitled as “Ultrasound-assisted production of biodiesel fuel from vegetable oils in a pilot scale circulation process”, describes the transesterification of canola oil with methanol performed in the presence of KOH catalyst by a circulation process at ambient temperature. In this process, the reaction was accelerated by ultrasonic irradiation of low frequency (20 kHz) with an input power of 1 kW. The influences of various parameters on the transesterification reaction, including the amount of catalyst, the molar ratio of methanol to oil and the reaction time, were investigated. The time profiles of triglycerides (TG) and fatty acid methyl esters (FAME) were followed to find optimal conditions. In addition, the concentrations of monoglycerides (MG) and diglycerides (DG), intermediates were also examined to elucidate mechanism of the transesterification. Under optimal conditions found in this study, the conversion of TG to FAME was greater than 99% within the reaction time of 50 min. Crude FAME was purified by washing with tap water and drying at 70^{o}C under reduced pressure. The FAME obtained from this study even with low energy and low material consumption satisfies the biodiesel-fuel standards, JIS K2390 (Japan) and EN 14214 (EU).

Chapter 3 is entitled as “A two-step ultrasound assisted production of biodiesel fuel from waste cooking oils: A practical and economical approach to produce high quality biodiesel fuel”. Promising potential of ultrasound-assisted transesterification is demonstrated in Chapter 2 to give the high quality of FAME in the circulation process when a high quality material, virgin canola oil, was used. However, it was quite difficult to scale up the circulation system to hundreds or thousands of liters. Furthermore, the cost of biodiesel product is high due to the use of virgin canola oil. The objective of this chapter is the modification of the reaction system adapting for a large scale, and the use of an inexpensive raw materials. In this context, the transesterification reaction of WCO with methanol in the presence of KOH catalyst was performed in a continuous ultrasonic reactor with a two-step process. For the first-step, the transesterification was carried out with the molar ratio of methanol to WCO of 2.5:1, *i.e.* less methanol fed than the theoretical stoichiometric ratio, and less amount of catalyst than the conventional method. The yield of FAME was about 81%. A yield of FAME around 99% was attained in the second step with the molar ratio of methanol to initial WCO of 1.5:1, and the amount of catalyst 0.3 wt.%. The FAME yield was extremely high even at the short residence time of the reactants in the ultrasonic reactor (less than 60 s for the two steps) at ambient temperature. The recovery of biodiesel fuel from WCO is more than 93 wt.%, and electricity consumption for one liter biodiesel is 72 W h. The quality of the final biodiesel product fro WCO meets the standards JIS K2390 and EN 14214 for biodiesel fuel.

Chapter 4, entitled as “Co-solvent method: A new green chemistry for preparation of biodiesel”, describes a new method without any agitations or physical forces, that is a co-solvent method. The homogeneous reaction system for production of biodiesel can be developed by adding organic solvents into the reaction mixture of oil and methanol with KOH catalyst. Among these organic solvents, acetone is the best solvents for the transesterification. By adding acetone at room temperature (15–20^{o}C), the yield of FAME can be more than 95% within 10 min of reaction time. The advantages of this process compared with the conventional mechanical stirring method are presented as follows: Acceleration of reaction rate of transesterification without heating; increase in the speed of the separation of glycerin from the reaction mixture; reduction of the amount of catalyst and methanol, and no retardation in the homogeneous reaction by coexistent water. In addition, the kinetic data show that the retardation of transesterification is not due to the back reaction but due to the isolation of methanol and sodium hydroxide catalyst from the reaction field with precipitated glycerin produced at the later stage of the reaction.

Chapter 5, entitled as “Conclusion”, summaries the results and findings described in Chapters 2-4, and gives the future perspectives of the ultrasonic irradiation or co-solvent methods and utilization of glycerin.

From the results obtained in this thesis, we can confirm that the ultrasonic irradiation and the co-solvent method are the potential candidates for biodiesel production on industrial scales. Based on the experimental data, we can scale up the pilot plant into the big scale for the industrial production.

審査結果の要旨

本論文は、地球温暖化問題に対する解決策として利用拡大が図られているバイオ燃料の一つであるバイオディーゼル燃料の製造技術の開発を目的とした研究の成果をまとめたものであり、次のような成果を得ている。

１） 製造容量１００L 規模のパイロットプラントで、内容積１L 未満の反応器に周波数２０kHz の超音波を照射することにより、植物油とメタノールを反応物、水酸化カリウムを触媒とするエステル交換反応系において常温条件下で効率的に高純度の脂肪酸メチルエステル（FAME)、すなわちバイオディーゼル燃料、を製造できることを明らかにしている。

２） 本技術は反応時に昇温を必要としないため、従来法に比較してエネルギーコストが低く、加えて低反応物量、低触媒量で交換反応を進められる。未使用植物油を原料にエステル交換反応させ、従来法によるグリセリン分離・FAME 精製処理を行うだけでバイオディーゼル燃料の国内規格 JIS2390 および欧州規格 EN14214 を満たす品質が得られることを実証している。

３） より効率的に FAME を製造する技術として２段階反応法を採用し、廃食用油を原料にした実製造において原料油：メタノール＝１：４、触媒量１．０重量%で、常温条件下超音波照射１分以内でエステル交換反応が終了し、JIS および EN 規格を満たすバイオディーゼル燃料を製造できることを実証している。全工程に要するエネルギー使用量は燃料製造１L あたり７２kWh という低エネルギー消費の製造法を確立している。

４） 実験室規模での実験研究により、エステル交換反応を有機溶媒共存下で行う共溶媒法を検

討し、穏やかな攪拌操作により常温条件下１時間以内で反応を完了できること、反応条件およびグリセリンの分離時間短縮の両面から判断して溶媒としてアセトンが最適であること、を明らかにしている。また、このエステル交換反応において従来考えられてきた逆反応が、極めて遅いか存在しないという反応機構上の新しい知見も明らかにしている。

以上の諸成果は、バイオディーゼル燃料製造において超音波照射法および共溶媒法のもつ物理・化学的特徴およびそれぞれの特徴をもたらす作用機序を明らかにするとともに、超音波照射法については実製造技術としての製造条件を確立し、共溶媒法については基礎的な知見および製造技術としての潜在的な優位性を明らかにしたものであり、低コストで高品質バイオ燃料を製造するという世界的要請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。