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論　文　名	「A New Production Method for Green Biodiesel Fuel (BDF) and Effects of Gamma-ray Irradiation and Ultrafine Bubble on BDF Stability (グリーンバイオディゼル燃料の新規製造法と BDF の安定性に対するガンマ線照射および超微細気泡の効果)」
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論文要旨

Currently, the awareness of environmental issues and the energy crisis related to fossil fuels has prompted research for alternatives to fossil fuel. Compared to petrol diesel, biodiesel fuel (BDF) has following advantages: renewable, biodegradable, non-corrosive and non-toxic, aromatics and sulfur free, higher cetane number, and lower carbon dioxide emissions.

Compared with the conventional mechanical stirring method for BDF production, the co-solvent method is an effective, environmentally friendly method, which consumes lower energy, fewer amounts of reagents, and achieves a higher yield of FAMEs. Following tetrahydrofuran, acetone has been used as the co-solvent for the transesterification. However, solvents with a high amount in the BDF production can affect to environment and human health. Therefore, it is an urgent necessity to reduce the amount of solvent for BDF production using the co-solvent method and develop a new technology. Isopropanol (IPA) is considered a potential co-solvent because it can be dissolved all compounds related

to transesterification including oil, methanol (MeOH), potassium hydroxide (KOH), glycerol and FAMEs. Additionally, IPA has a higher boiling point (82 °C) than acetone (56 °C). IPA can solve the limitation of low recovery of acetone after the production process of BDF. Therefore, IPA was selected to study as a new solvent for co-solvent method of BDF production.

Nowadays, more than 95% of feedstocks used for the production of BDF are derived from edible oils such as canola oil, rapeseed oil in Europe, soybean oil in the United States, palm oil in Southeast Asia**.** However, the cultivation of these feedstocks competes for agricultural land with the growth of crops for human foodstuffs and increase the green house gas emissions by indirect land use change (iLUC). Therefore, many non-edible oils have been sought as alternative feedstocks for BDF production. Generally, non-edible oils contain a lot of unsaturated fatty acid moieties and have a high content of free fatty acids (FFAs), which causes unexpected properties of BDFs produced, such as high iodine value, poor oxidation stability and unsuitable viscosity. Researchers have been interested on finding technologies to improve oxidation of BDF produced from non-edible oils.

Gamma-ray has widely applications on food irradiation. It can cause some changes of physicochemical properties of irradiated foods. However, it has not many investigations on effect of gamma-ray irradiation on improvement of BDF quality.

Ultrafine bubble (UFB), which has a bubble diameter of less than 1 μm, has attracted much attention due to its unique stability in the gas – liquid phase. The UFBs have long stability in aqueous phase than normal gas bubbles because of their electrical charged surface property, which prevents them from pulling together to form a larger bubble that might dissolve in liquid. Although the potential of UFBs has been reported in various applications for water treatment, agriculture, fisheries, engineering and health science, limited research has been conducted on application for oil or BDF. Thus, the behavior of

UFB hydrogen on protection of oxidization of oil or BDF remains an open topic.

From the above descriptions, this thesis is conducted with two purposes. The first purpose is to develop new production process for high-quality green BDFs production from plant oil. The new co-solvent of IPA was discovered instead of acetone. The properties of resulting BDF are compared with the EN 14214/JIS K2390 quality criteria. The second purpose is to study the effects of γ-ray irradiation and UFB hydrogen on unsaturated FAMEs and BDF. In order to address these purposes, the work is described as following chapters.

Chapter 1 provides general information of BDF, feedstocks, production methods and oxidation stability of BDF. In this chapter, the purposes of the current thesis also are clarified.

Chapter 2 describes a new method for biodiesel production from canola oil using isopropanol as a co-solvent. Acetone and fatty acid methyl esters (FAME) have been used as co-solvents for BDF production. In this report, we investigated the transesterification kinetics by varying IPA amount and the optimum conditions for BDF production with 10 wt% IPA. In the IPA amount of 5–25 wt%, the transesterification proceeded in a heterogeneous condition (FAME and glycerol (GL) phases) as the GL phase was formed and separated from the FAME phase. The transesterification rate increased with increase of IPA amount and the correlation coefficient (r) between the rate constant and IPA amount was 0.97 ($P < 0.05$). The optimal conditions of transesterification for biodiesel production from canola oil with 10 wt% IPA were as follows: 1.0 wt% KOH, MeOH/oil molar ratio of 6:1, and a reaction temperature of 30 °C. The quality of biodiesel satisfied the JIS K2390 and EN 14214 standards. Transesterification using 10 wt% IPA co-solvent could facilitate the phase separation after the reaction and the amount of waste was reduced. The recovery of IPA from FAME phase was >96%, hence IPA could be reused. These results indicated

that IPA was a superior co-solvent for the BDF production from plant oil feedstocks.

As mentioned above, γ-rays can cause some changes of physicochemical properties of irradiated foods. In ***Chapter 3***, degradation of fatty acid methyl esters by gamma-ray irradiation was described and discussed.

There is a few information on the effect of γ-ray irradiation on the structure of fatty acid methyl ester (FAME). In this study, we examined the radiolysis of FAMEs, such as methyl stearate (C18:0), methyl oleate (MO, C18:1), methyl linoleate (MLa, C18:2), methyl linolenate (MLn, C18:3), and methyl α-eleostearate (MESA, C18:3, purity 70.9 wt/wt%). In hexane, the degradation percentages in the air condition, were higher than those in nitrogen atmosphere because of the formation of free radicals during the γ-ray irradiation. The degradation percentage of FAMEs were affected positively by the irradiation dose of γ-ray and the initial FAME concentration. The degradation percentages were higher in methanol than those in hexane. The degradation percentages of FAMEs increased with an increase in the number of double bonds in their molecular structures (r^2 = 0.98–1.0) ($P<0.05$). However, since MESA has three conjugated double bonds, its degradation percentage was more rapid. The radiolysis products of FAMEs using γ-ray irradiation were detected using capillary gas chromatography – tandem mass spectrometry. The results of the radiolysis product of FAMEs indicated that the degradation proceeded by two processes: direct ionization by energetic photons (in which hydrocarbons and low molecular weight FAMEs are produced) and indirect irradiation by hydroxyl radicals generated from methanol or trace water in hexane (in which aldehydes and alkenes were produced).

In ***Chapter 4***, effect of UFB hydrogen on BDF was described and discussed. In this study, the investigations on oxidative stability of biodiesel were conducted by Rancimat method, which is regulated on biodiesel standards. Analysis methods of HPLC, NMR, IR

and Wijs titration (for iodine value) were used to evaluate the effects on the oxidation products, the FAME content and the unsaturation degree of BDF. The amount of volatile products formed from UFB hydrogen BDF was smaller than that of controlled sample (non-UFB hydrogen). The results IR spectra also presented the smaller amount of oxidation products were formed when the BDF mixed with UFB hydrogen. The ester contents of UFB hydrogen BDF declined 2.3 times slower than that of controlled sample in the oxidation time of 48 h. Meanwhile, in 48 h, the iodine values of UFB hydrogen BDF and controlled one degraded 65% and 84.9%, respectively. In conclusion, combing these results along with the data of 1H-NMR spectrum, the study elucidated that UFB hydrogen can delay the oxidization process in BDF.

In ***Chapter 5***, the obtained results were summarized, and the future study was discussed for developing the method of production BDF on a large scale and applying new technologies to improve the oxidative stability of BDF.

審査結果の要旨

地球温暖化の主な原因とされている化石燃料に代わる環境調和型燃料として、バイオディゼル燃料（BDF）が強く期待されている。カーボンニュートラルと見なされる植物バイオマス由来の油脂を安定的に得るためには、食用油の生産に必須の農地との競合を生じない非食用の植物油脂の利用が期待されている。しかし非食性油脂は不飽和脂肪酸を多量に含み、BDF の品質劣化や酸化劣化のためディゼル油に要求される製造基準を満たす高品質の BDF 生産が達成できない現状にある。本論文においては、非食性油脂の BDF の原料としての欠点を改善するための方策として、新たにイソプロピルアルコール（IPA）を共溶媒としてより効率的な製造法を検討し、さらに水中での安定性に優れたナノバブルに着目し、ナノバブルに封入した水素ガスの抗酸化性の評価を行い、以下の成果を得ている。

（1）従来のアセトンや脂肪酸メチルエステルに代わる共溶媒として反応後の回収再利用が容易で副反応の少ない IPA の利用による反応の効率化を発想し、カノーラ油を原料として触媒としてのメタノール､KOHの量比,温度などを最適化し99.5%以上の転換効率を達成し、国内外の製造基準に適合する BDF の製造法を確立した

（2）東南アジア由来の非食用油由来の BDF の品質低下の原因となっている二重結合を含む脂肪酸メチルエステルのγ線照射による分解除去を発想し、^{60}Coγ線照射による生成物をガスクロマトグラフィー質量分析法（GC-MS）で分析することにより、二重結合が起点となり放射線分解が生じることを明らかにし、その機構について考察した。

（3）水素ガスのナノバブルを、カノーラ油から製造した BDF に分散させ、BDF の酸化安定性について製造基準の規格で規定されている Rancimat 法を用いて検討した。BDF の酸化生成物、脂肪酸メチルエステル含量、不飽和度への影響を評価することにより、水素ガスナノバブル分散させることで BDF の酸化プロセスを遅らせ、BDF の品質保持が可能であることを見出した。

以上の研究結果は東南アジア地域に産する非食用の植物油脂からの BDF 製造技術の実用化に必須の要素技術の確立に直接寄与するものである。これらの成果はアジア地域からの低炭素社会の実現を発信するための基礎となり、今後の展開を大いに期待させるものである。また、申請者が自立して研究活動を行うに必要な能力と学識を有することを証したものである。