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論　文　名	「New production process of high-quality biodiesel fuel from biomass with highly effective co-solvent method」 （高効率共溶媒法によるバイオマスからの高品質バイオディーゼル燃料の新規生産プロセス）
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論文要旨

In the context of increasing energy demand and exhausting fossil fuels, biodiesel fuel (BDF) is an important alternative, non-toxic, and eco-friendly fuel for transport and industry. However, the existing problem of BDFs is that they cannot compete with petroleum diesel because of their high costs which are mainly caused by the input raw materials and production methods. To solve this problem, many input feedstocks and new techniques have been developed.

Compared with the conventional mechanical stirring method for BDF production, the co-solvent method is an effective, environmentally friendly method, which consumes less energy, fewer amounts of reagents, and achieves a higher yield of fatty acid methyl esters (FAMEs). Following tetrahydrofuran, acetone has been used as a co-solvent for the transesterification. However, solvents with a high amount in the BDF production process can affect the 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.

Presently, BDFs are mostly produced from edible oils, such as soybean oil, canola oil, and palm oil. Nevertheless, the cultivation of these feedstocks competes for agricultural land with the growth of crops for human foodstuffs and increases of

green-house gas emissions by indirect land-use changes (ILUC). Therefore, many non-edible oils have been sought as alternative feedstocks for BDF production.

Jatropha curcas oil, recently, has been considered as one of promising potential non-edible oil sources for BDF production in Southeast Asia, Central and South America, India and Africa because of its properties and compositions. However, *Jatropha curcas* plants can be damaged by low-temperature conditions (<20°C/frost) and give low seed yield if affected by high temperature and heavy rain during the flowering period. The choice of feedstocks depends on properties, compositions and stable oil/fat yield. Therefore, it is necessary to find some other potential raw materials for BDF production, such as rubber seed oil, *Vernicia montana* Lour. oil, candlenut oil, cottonseed oil and castor oil.

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 (> 120g I_2/100g), poor oxidation stability (< 8 h at 110°C) and unsuitable viscosity (out of range 3.5–5mm^2/s at 40°C). Gamma-ray irradiation is one of superior techniques for food preservation and reduces unsaturated FAMEs due to producing free radicals. However, effect of γ-ray irradiation on unsaturated FAMEs containing three double bonds, such as methyl linolenate and its isomers, has not been investigated.

Hence, my research described in this thesis has been conducted with two purposes. The first purpose is to develop a new production process of high-quality BDFs from *Vernicia montana* Lour. oil and rubber seed oil using the co-solvent method. Especially, for BDF production from rubber seed oil with high content of FFAs, a two step-co solvent method was developed. Throughout these processes, a new co-solvent of FAMEs was discovered instead of acetone. The properties of resulting BDFs are compared with the EN 14214/JIS K2390 quality criteria. The second purpose is to study the effect of γ-ray irradiation on unsaturated FAMEs. In order to address these purposes, the work is described as in the following chapters.

Chapter 1 provides general introductions of BDF, input materials, production methods, and the effect of γ-ray irradiation on FAMEs. In this chapter, the purposes of the current thesis also are clarified.

Chapter 2 describes production of BDF from *Vernicia montana* Lour. oil using a co-solvent method, and subsequently the stability of the resulting BDF during storage. *Vernicia montana* Lour. oil is a non-edible oil with 34% oil content in seeds and 0.75% FFAs content. The seed yield has been estimated to be 10 tons/ha/year. Using the co-solvent method for BDF production from *Vernicia montana* Lour. oil, a BDF conversion efficiency of 99% was achieved in 30 min. The optimum conditions for BDF production were: methanol/oil molar ratio of 6:1; 1% (wt/wt) KOH; 20% (wt/wt) acetone as a co-solvent; and a reaction temperature of 40°C. The resulting BDF satisfied the EN 14214/JIS K2390 quality criteria regarding its FAME, water, MG, DG, TG, free glycerol and total glycerol contents, as well as its acid value and density. Notably, the BDF produced from *Vernicia montana* Lour. oil showed good stability to air at temperatures ≤ 30°C for 1 month, with similar stability properties to the BDF produced from rapeseed oil. However, the BDF from *Vernicia montana* Lour. oil contained a high amount of unsaturated methyl ester derived from α-eleostearic acid moieties (C18:3, 80%), which caused unexpected properties, such as high viscosity (7.7mm^2/s) and high iodine value (158.5g I_2/100g). Therefore, it is necessary to improve these properties to make it available in the marketplace.

Chapter 3 is devoted to BDF production from rubber seed oil (RSO) with a high content of FFAs using a two-step co-solvent method. RSO is a high potential feedstock for production of BDF in South East Asia, where 77% of the world's natural rubber is produced and rubber tree seeds (*Hevea brasiliensis*) are presently disposed of as waste biomass from latex production. Utilization of RSO as a feedstock for BDF production could not only lower the price of BDF but also contribute to solving the environmental problem caused by a huge amount of rubber seeds wasted every year. However, the high content of FFAs in RSO (35.6%) is a challenge for producing a high quality BDF because soap can be formed when using alkaline catalyst to produce BDF.

Using acetonitrile as a co-solvent in an initial esterification, a FFAs level of 2% was achieved in the crude RSO under optimum conditions as follows: a methanol/FFAs molar ratio of 5:1, 1.5% sulfuric acid, and 30% acetonitrile at 60°C. FAMEs produced in the first step was used as a co-solvent for the subsequent transesterification of the oil. This reaction was completed in 30 min under optimum conditions as follows: a

methanol/oil molar ratio of 4.5:1 and 1% KOH at 40°C. The quality of BDF produced satisfied the EN 14214/JIS K2390 standards. These results suggest that FAMEs act as the co-solvents in BDF production as acetone is usually applied. The co-solvent method using the co-solvents of FAMEs is both environmentally and economically friendly.

The application of the co-solvent method to produce BDFs from *Vernicia montana* Lour. oil and RSO led to a reduction of energy consumption as a result of considerable reductions in the reaction time and reaction temperature compared with other conventional methods.

Chapter 4 presents the results of γ-ray irradiation applied to BDF produced from *Vernicia montana* Lour. oil containing 80% α-eleostearic acid moieties (C18:3) to improve the physicochemical properties discussed in Chapter 2. The γ-ray irradiation is widely used for food irradiation to inhibit microbial growth, thereby increasing the shelf-life of foods. However, γ-rays can cause some changes of physicochemical properties, such as reducing viscosity, oxidation stability in oily and starchy foods because molecular changes occur in irradiated foods.

Four kinds of FAMEs, methyl stearate (C18:0), methyl oleate (C18:1), methyl linolenate (C18:3) and methyl α-eleostearate (C18:3, purity 80%) were used for γ-ray irradiation. The experiments were conducted in two solvents (hexane and methanol), and the irradiation dose was in the range of 5–15 kGy. In hexane solutions with the dose of 10 kGy, methyl stearate showed the lowest degradation percentage (8%), followed by methyl oleate (15%) and methyl linolenate (18%). Methyl α-eleostearate showed the highest degradation percentage (58%). Similarly, the degradation percentages of methyl oleate, methyl linolenate and methyl α-eleostearate in methanol solutions were 18, 21, 62%, respectively. These results indicated that the degradation percentage depends on the chemical structure of the molecules; the number of double bonds and their conjugated form.

The degradation processes were elucidated from radiolytic products using gas-chromatography/mass spectrometry (GC/MS). The results indicated that the degradation involved two processes: direct ionization by energetic photons that produces hydrocarbons and low molecular weight FAMEs, and indirect irradiation by hydroxyl radicals generated from methanol or trace of water that produces aldehyde and

lower molecular weight FAMEs containing aldehyde group.

In summary, by γ-ray irradiation of 15 kGy, the BDF produced from *Vernicia montana* Lour. oil can be effectively converted into alternate components with 60% efficiency, and furthermore, the degradation percentage depends on the irradiation dose. These results suggested that it is possible that the physicochemical properties of BDF can be adjusted to satisfy the requirements of the quality criteria for BDFs by controlling irradiation doses. However, further investigation of the effect of irradiation on BDFs needs to be conducted to evaluate comprehensively the improvement of BDF properties.

In ***Chapter 5***, the main conclusions of this thesis were drawn.

審査結果の要旨

地球温暖化に最も影響する温室効果ガスとして問題視されている CO_2 の主要な排出源となっている化石燃料に代わる環境調和型燃料として、バイオディーゼル燃料（BDF）が強く期待されている。カーボンニュートラルの考えが適応できる植物バイオマス由来の油脂は BDF の原料として期待されているが製造コスト、食用油との農地の競合など、実用化に向けての課題が多い。本研究は農業生産と競合することなく荒れ地の緑地化にも貢献できる東南アジア産の *Vernicia montana* Lour.（カントンアブラギリ）と現在利用されずに廃棄されているゴムノキの種実油を原料とし、製造コストの低減に役立つ共溶媒法を基礎に新たな製造法を開発するとともに BDF 成分の放射線分解反応についても検討した。

(1) *Vernicia montana* Lour.からの抽出油にアセトンを共溶媒として用い、国内外の製造基準に適合する BDF の製造法を確立した。また 30℃保存で最低 1 ヶ月は品質劣化に問題がないこと、また製品に含まれるα-エレオステアリン酸メチルセステル(C18:3, 80%)が品質に大きく影響することを詳細な分析により明らかにした。

(2) 未利用のゴムノキの種実油に初めて着目し、さらに高品質の BDF 製造の妨げとされた遊離脂肪酸(35.6%)の影響を低減するために申請者は共溶媒法を利用した二段階のメチルエステル化反応を考案し、共溶媒としてアセトニトリルを用いて遊離脂肪酸のメチルエステル化することにより、油中の遊離脂肪酸濃度の 2%までの低減化に成功した。さらに生成した脂肪酸メチルエステル(FAMEs)を共溶媒として活用することにより、欧

州や我が国の品質基準に適合する BDF の製造方法を確立した。

(3) 上記 BDF に含まれる FAMEs から異なる脂肪酸メチルエステル（C18:0)、(C18:1)、（C18:3)を選び、^{60}Co ガンマ線照射による分解挙動を調べ、これらの放射線分解により油の粘度調節や FAMEs 組成改変などの品質調整プロセスの可能性が示唆された。さらに不飽和脂肪酸エステルの共役二重結合が放射線分解の効率に影響する新たな分解機構の可能性が初めて見いだされた。

以上の研究結果は東南アジア地域において実用化可能な BDF 製造技術の発展の端緒となり得る有用な知見を与えており、また不飽和脂肪酸エステルの放射線化学においても今後の研究の発展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に必要な能力と学識を有することを証したものである。