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学位授与の日付	2015 年 3 月 31 日
論　　文　　名	Production of biodiesel fuels from Vietnamese *Jatropha curcas* oil and catfish oil by using a co-solvent technology.
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論文要旨

Economic development brings not only huge benefit of human life but also a mountain of problems to be faced with. One of the most tensile ones is shortage of energy, and as a consequence, the fuel price is going up higher and higher. Over excavating of fossil fuel results the running out of traditional energy. In addition, another difficult challenging to our modern society is the climate change, which causes a series of natural disasters and unusual critical weather. Under these conditions, Kyoto Protocol has been established to save our global environment by legal binding limitation of the emissions of greenhouse gases. Therefore, finding a new eco-friendly alternative energy has become essential.

Biodiesel fuel (BDF) is a renewable energy source unlike petroleum-based diesel. One of the main BDF advantages is that it emits few pollutants than petroleum diesel does. No sulfur content in 100% BDF extends the life of catalytic converters for exhaust gas. Another advantage of BDF is that it can also be blended with other energy resources and oil. Besides, BDF can also be used in existing oil heating systems and diesel engines without making any alterations. Furthermore, the lubricating property of BDF may lengthen the lifetime of engines. For these reasons, BDF is believed to be an excellent alternative fuel.

BDF can be produced from various sources, mainly from vegetable oils, waste cooking oil, animal fats and other edible or non-edible oils. Depending upon the climate and soil conditions, different countries are looking for various types of vegetable oils as

substitutes for diesel fuels. For example, soybean oil in the US, rapeseed and sunflower oils in Europe are being considered. Currently, more than 95 % of the world BDF is produced from edible oils which are easily available on large scale from agricultural industry. However, continuous using edible vegetable oils as feedstock for biofuel production are not appropriate due to their high expenses and the heavy pressure on national food security. Therefore, the use of non-edible oil is considered more reasonable and practical as raw materials for BDF production.

The thesis consists of five chapters.

In chapter 1, basic concepts of biofuels, their benefits, type of feedstock, and methods of production are introduced. Then, the overviews of biodiesel, raw materials, catalysts, and methods of production are reported. In this thesis we would like to find the answer to some questions: What is the best raw material for production of BDFs in Vietnam? What is the best production method for production of BDF with high fatty acid methyl ester (FAME) yield and environmentally friendly? BDF production from Vietnamese *Jatropha curcas* oil (JCO) and catfish oil have been studied in this thesis. The reaction conditions for BDF production from JCO and catfish oil with and without solvent were investigated. Also with the aim of optimizing the conditions for BDF production from JCO and catfish oil, a survey of factors affecting the back reaction of transesterification has been conducted.

JCO is one of the best raw materials for producing BDFs due to its inedible property, and thus its production does not compete with food crops. It is relatively inexpensive compared with edible oils of low free fatty acid (FFAs) contents, although JCO has a quite high acid index (Thanh et al., 2012). It was reported that BDF was produced from *Jatropha curcas* seeds and production of BDF from JCO by using solid catalyst. However, the low FAME yield was obtained as 80.2 % and 92.5 %, respectively (Lian et al., 2012; Guo et al., 2013).

Basa catfish is primarily found in the Mekong Delta region of Vietnam. According to Globefish, Vietnam exports approximately 1.35 million tons/y of Basa catfish, equal to 75 % of the global catfish market. Both Tra and Basa fishes can be easily distinguished by silvery belly and an especially high oil content, comprising 25 % of the fish mass. In Vietnam, the amount of oil recovered from seafood processing facilities annually is in the range of 300,000–400,000 tons/y and thus represents an abundant and sustainable resource for the development of BDF production in this country. There are currently few manufacturing institutions capable of researching and developing the technology to produce BDF from fish oil and an overall production process generating high-quality commercial BDF from fish oil meeting international standards.

It is worthy to note that in Vietnam we have another natural oil that is abundant available, too. This is rubber seed oil which is extracted from rubber seed’s kernels; it can be served as a potential feedstock for BDF production.

In chapter 2, BDF was successfully produced from Vietnamese JCO with high content of FFAs in two stages. The results showed that in the first stage, the acid-catalyzed esterification process was carried out with the optimal conditions as follows; a methanol-to-FFAs molar ratio of 6:1, 1 wt% H_2SO_4, at a temperature of 65 °C, and using 30 % (wt/wt) acetonitrile as co-solvent. This step reduced the concentration of FFAs in the reaction mixture from 15.93 wt% to 2.00 wt% in 60 minutes. In the second stage, the base-catalyzed transesterification process generated FAMEs with 99 % efficiency was performed in 30 minutes under the optimal conditions as follows; a methanol-to-oil molar ratio of 6:1, 1 wt% KOH, at a temperature of 40 °C, and 20 % (wt/wt) acetone as co-solvent. It also revealed that the produced BDF quality passed the standards JIS K2390 and EN 14214 regarding FAME yield, FFAs and water contents. It is noted that the reaction occurred more easily due to use of acetonitrile and acetone as co-solvents which dissolve reagents and catalyst to form a homogeneous solution. Co-solvent reaction system gave higher FAME yield in shorter separating time for FAME from glycerin in the products.

In chapter 3, production of BDF starting from another abundant available feedstock - Vietnamese catfish oil has been investigated. In this study, the co-solvent method was used for the base-catalyzed transesterification reaction of Vietnamese catfish oil to generate BDF. The effects of separation factors (reaction temperature, catalyst amount, acetone amount, reaction time, and methanol: catfish oil molar ratio) on the BDF yield from the transesterification of catfish oil were determined, with and without co-solvent. It was employed a central composite orthogonal design to optimize the transesterification of catfish oil using methanol and KOH as a reactant and catalyst, with both non-solvent and co-solvent processes. The data showed that the co-solvent process offered several advantages compared with the non-solvent method. The research results also demonstrated that isopropanol had similar effects to acetone on transesterification yields except for the need for a somewhat higher reaction temperature.

In chapter 4, the kinetic of forward and back reaction of transesterification were investigated. The transesterification of tri-glyceride (TG) with methanol are shown in formula (1) to (3), where GL is glycerin. The back reaction of FAME with GL are shown in formula (5) to (7):

$$TG + CH_3OH \xrightarrow{k_{TG \to DG}} DG + FAME \qquad (1)$$

$$DG + CH_3OH \xrightarrow{k_{DG \to MG}} MG + FAME \qquad (2)$$

$$MG + CH_3OH \xrightarrow{k_{MG \to FAME}} FAME + GL \qquad (3)$$

$$r_{forwardreaction} = k_{forwardreaction}\left[TG\right]\left[CH_3OH\right] \approx k_f\left[TG\right] \qquad (4)$$

$$GL + FAME \xrightarrow{k_{FAME \to MG}} MG + CH_3OH \qquad (5)$$

$$MG + FAME \xrightarrow{k_{kMG \to DG}} DG + CH_3OH \qquad (6)$$

$$DG + FAME \xrightarrow{k_{DG \to TG}} TG + CH_3OH \qquad (7)$$

$$r_{backreaction} = k_{backreaction}\left[FAME\right]\left[GL\right] \approx k_b\left[FAME\right] \qquad (8)$$

We calculate the reaction rate constants and activation energy of the forward and back reactions. In the experiments, we used excess amounts of methanol than TO and glycerin than FAME. Therefore, we can consider that these reactions are pseudo-first-order reactions. The kinetic data for the transesterification of TO with methanol are as follows: Rate constants of

k_f were measured as 0.36, 0.47 and 0.58 min^{-1} at 20, 40 and 60 °C, respectively. Rate constants of the back reaction, k_b, were measured as 5.3×10^{-3}, 2.2×10^{-2} and 5.8×10^{-2} h^{-1} at 30, 50 and 70 °C, respectively. The activation energies of the forward and back reactions were found to be 10.38 and 51.82 kJ mol^{-1}, respectively. The rate constants of the back reaction at 70 °C for methyl octanoate, methyl butyrate and methyl acetate were 0.33 h^{-1}, 0.57 h^{-1} and 0.4 min^{-1}, and the activation energies were 37.87, 25.37 and 18.0.2 kJ mol^{-1}, respectively. The results show that the co-solvent method is one of the best choices for the solution to accelerate the forward reaction because transesterification occurs at low temperature, while giving a high FAME yield. In this temperature range, the back reaction takes place very slowly. The back reaction rates for shorter alkyl-chain esters with glycerin were very high because the shorter chain has low steric hindrance.

In chapter 5, the content of this thesis was summarized.

審査結果の要旨

本論文は、気候変動緩和策および地球温暖化対策として利用拡大が期待されているバイオディーゼル燃料(BDF)を、高品質で安価に製造する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）非食用油であり､利用が期待されている *Jatropha curcas* oil を用いた BDF 製造において、共溶媒法を用いた最適製造条件の確立および遊離脂肪酸を前段階としてエステル化することで､BDF の収率向上と従来法で問題となっている副生物である石鹸の生成を押さえた製造法を確立した。この方法により他の用途への利用が可能となる高純度のグリセリンが副生物として得られることを示した。また、共溶媒法が従来法に比べ最終生成物の BDF の分離時間を著しく短縮できる原因について調べ､二層の密度差が重要であることを示した。

２）従来法では粘度が高くて利用できなかったなまず油や、廃食用油を用いた共溶媒法による BDF 製造の最適条件を求めた。また、種々の溶媒や、従来法である無溶媒での製造条件を調べ、共溶媒法に適した溶媒の条件などを明らかにした。

３）従来法では過剰量のメタノールを加える必要があり、純度と製造コストの削減には限界があった。BDF 生成反応の正反応と逆反応を速度論的に研究し、速度定数や活性化エネルギーを求めた。これらのデータから、上記の問題は、逆反応のためであることを見出し、共溶媒法では、この逆反応が著しく抑えられ、そのため少ないメタノール量で高収率の BDF を製造できることを明らかにした。

以上の諸成果は、BDF 製造における共溶媒法のもつ化学的、物理的特徴を明らかにするとともに、共溶媒法による種々の原料からの BDF 製造技術を確立し、さらに共溶媒法の優位性を科学的な見地から明らかにしたものであり、低コストで高純度の BDF およびグリセリン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示したものである。学位論文審査委員会は、本論文の審査ならびに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。