

高含游离脂肪酸的香果树籽油制备生物柴油的方法^{*}颜 健, 邱 颀, 陆 璐, 周 琳, 李忠荣, 邱明华^{**}

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摘要: 目前生物柴油因其环保和可再生利用资源的特性备受关注。多数生物柴油是通过甲醇和碱催化食用油得到的, 而大量非食用油也可以制备生物柴油。本文报道用高含游离脂肪酸油快速高效低成本制备成其单酯的二步法工艺。先用 1% H_2SO_4 以少于 1.5% 量对甲醇和云南特产香果树 (*Lindera communis*) 籽的粗原料油以 10:1 摩尔比组成的混合液酸催化酯化游离脂肪酸; 之后再对醇和得到的油脂产品按摩尔比 15:1 的混合液碱催化转化为单甲酯和甘油。本方法是一个直接甲酯化制备生物柴油的工艺简洁、降低成本的新技术。文中还讨论了该工艺影响转化效率的主要因素, 如摩尔比, 催化量, 温度, 反应时间和酸度。香果树生物柴油不重蒸, 而其生物柴油的主要特性, 如粘度、热值、比重、闪点、冷滤点等与生物柴油标准的匹配度, 也做了报道, 研究结果将为香果树生物柴油以非重蒸油料制备生物柴油产品, 作为潜在的柴油燃料替代产品提供技术支撑。

关键词: 香果树籽油; 生物柴油; 甲酯化

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Biodiesel Production from High FFA Oil of *Lindera communis* (Lauraceae)

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Abstract: Currently, biodiesel has become more attractive because of its environmental benefits and the fact that it is made from renewable resources. Most of the biodiesel are from the refined edible type of oil using methanol and alkaline catalyst. However, larger amount of non-edible oil are available. A two-step rapid and efficient low-cost transesterification process was developed to convert the high FFA crude oils to its mono-esters. Firstly, acid catalyzed esterification reduced the FFA content of the gross *Lindera communis* oils to less than 1.5% with 10:1 molar ratio methanol to oil in the presence of 1% H_2SO_4 (wt) as acid catalyst. Secondly, alkaline catalyzed transesterification converted the products of the first step to single ester (biodiesel) and glycerol with 15:1 molar ratio methanol and the product oil of first step. The major factors affected the conversion efficiency of the process were discussed, such as molar ratio, amount of catalyst, temperature, reaction time and acid number. The biodiesel from *Lindera communis* oil was not re-distillation, but its important properties such as viscosity, calorific value, specific gravity, flash point, cloud point and pour point were matched with the standard demand. This study supported the biodiesel product from unrefined *L. communis* oil as a potential replace to the diesel fuel.

Key words: *Lindera communis* oil; Biodiesel; Esterification

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One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). In the 1930s and 1940s, vegetable oils were used as diesel fuels from time to time, only in emergency situations. Recently, because of the increase in crude oil price, limited resource of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuel. Vegetable oils are becoming a promising alternative to diesel fuel because they have more advantages than diesel fuel, such as renewable resources, local production and friendly to environment. They have practically no sulfur content and no storage difficulty, furthermore, they have excellent lubrication properties. In view of the several advantages, vegetable oils have potential to replace petroleum-based fuels in the long run.

In the recent years, systematic efforts had been made by several researchers to use the various vegetable oils as fuel in compression ignition engines. The calorific value of vegetable oil is comparable to that of diesel. However, their use in direct injection diesel engines is restricted by some unfavorable physical properties, particularly its viscosity. The viscosity of vegetable oil is about ten times higher than that of diesel. Therefore, the vegetable oil causes poor fuel atomization, incomplete combustion and carbon deposition on the injection and valve seats resulting in serious engine fouling (Karmee and Chadha, 2005). This necessitates reduction in viscosity of the vegetable oils for use as fuel in engines. The commonly employed methods to reduce the viscosity of the oils are blending with diesel, emulsification, pyrolysis, cracking and transesterification (Ramadhas *et al.*, 2004). Among these, transesterification of vegetable oils appears to be more suitable. The transesterification reaction consists of transforming triglycerides into fatty acid esters by means of the action of an alcohol, with glycerin remaining as byproduct (Encinar *et al.*, 1999).

The difficulty with alkaline catalyzed esterification of these oils is that they often contain larger a-

mounts of FFA. The FFA quickly reacts with alkaline to product soaps that inhibit accomplishment of the reaction and separation of the ester and glycerin. However, Wide varieties of high free fatty acids (FFA) oils are available in larger quantities. *Lindera communis* oil is typical non-edible high FFA oil. *L. communi* Hemsl. (Lauraceae), a perennial plant, is widely distributed in Yunan, Gansu, Sichuan, Guizhou, Hunan, Hubei, Guangdong, Guangxi, Fujian, Shanxi, Taiwan and Zhongnan byland. *Lindera communis* seed kernel (55%–60% of seed) contains 50%–55% (wt) of fawn-coloured oil. *L. communi* tree yields 2-seeded ellipsoidal capsule, and varies in size 0.5–0.8 cm long, brown, weighing 37 mg more or less. Seed is half-ellipsoid, weighing about 24 mg. *L. communis* oil is considered as a potential feedstock for biodiesel product. The purpose of the present study is to develop a method for esterification of high FFA vegetable oils.

1 Results and discussion

The FFA content of *L. communis* oil is corresponding acid value of 27.5 mg KOH/g, which is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst (Ghadge *et al.*, 2005). Therefore, in order to reduce the acid value (ie. for reducing FFA), the FFA oil was firstly converted to esters in first-step treatment process using acid catalyst, then the sample was continued to react to get biodiesel with alkaline catalyst. So, the ratios between oil and methanol, catalyst amount, duration time were discussed in following part.

1.1 Acid esterification (first step)

1.1.1 Effect of methanol to oil molar ratio

First of all, the molar ratio of methanol to plant oil is considered as an important factor that affects the conversion efficiency as well as cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. Molar ratio is the ratio of number of between molar of methanol and molars of glycerides in the oil (oil average molecular weight about 820). Transesterifica-

tion reaction requires three molar of alcohol for each molar of oil. However, in practice, the molar ratio should be higher than that of theoretics in order to drive the reaction towards completion. Canakci and Van advocated the use of large excess quantities of methanol (15 : 1–35 : 1) while using the sulphuric acid as catalyst (Canakci and Van, 1999). The conversion efficiency of the first step in relation with molar ratio was obtained (Fig. 1). The maximum conversion efficiency was achieved very close to the molar ratio of 10 : 1. Further increase in molar ratio there was only a little improvement in the conversion efficiency. So we suggest that trial would be carried with molar ratio 10 : 1.

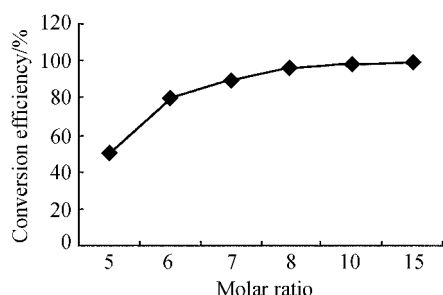


Fig. 1 Effect of molar ratio on conversion efficiency (step 1)

1.1.2 Effect of acid catalyst amount

The amount of acid catalyst used in the process of the first step also affects the conversion efficiency. The catalyst amount was varied in the range from 0.3%–2.5% for six different values (0.3, 0.5, 1, 1.5, 2, 2.5% of sulphuric acid). The effect of catalyst amount on the conversion efficiency was shown in Fig. 2. The acid-catalyst process attained the maximum conversion efficiency at 1% of sulphuric acid.

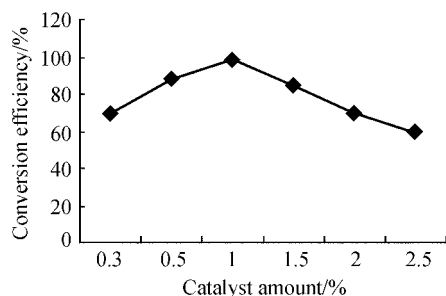


Fig. 2 Effect of acid catalyst amount on the conversion efficiency (step 1)

Besides, it was noted that excessive addition of sulphuric acid darkened the color of the product, while lower amount of sulphuric acid addition affected the yield of the next step.

1.1.3 Effect of reaction temperature and duration

At room temperature, the ester reaction was noted to be extraordinary low even after a day, even stirring. With increase in temperature, the reaction took place at a faster rate. The optimum temperature for the reaction was found in the range of $55\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$. At higher temperature, there was a chance of increase in darkness of the product and increase the product total cost of biodiesel.

Reaction time was also a factor that affected the yield of the first step, even next step. We sampled the mixture during reacting at 0.5 h, 1 h, 1.5 h, 2 h, 3 h, 4 h, 8 h, then measured the conversion efficiency. We found that the reaction was almost accomplished in 1 h.

1.2 Alkaline esterification (second step)

1.2.1 Effect of methanol to oil molar ratio

The amount of methanol required for esterification was analyzed in terms of the molar ratio. Theoretically, the methanol/triglyceride molar ratio required is 3 : 1. But, in practice this is not sufficient to complete the reaction. Higher molar ratio is required to drive the reaction to completion at a faster rate and good conversion efficiency. We observed that lower molar ratio required longer period, even the reaction did not arise. The effect of molar ratio on conversion efficiency was shown in Fig. 3. It showed that yield of the process became higher with increase methanol volume, arrived the maximum ester yield at the molar ratio of 10 : 1. The conversion efficiency had little change with further increase methanol volume, but the lucidity continued clearer optically. Based on the two sides above, molar ratio of 15 : 1 was optimal. The excess methanol was removed from the product. Then the mixture was poured into flask. After a while, the glycerin and little impurity were discharged at low layer. The upper layer was washed 3–4 times by hot water ($55\text{ }^{\circ}\text{C}$), then was

dried. At last, the yellowy liquid was biodiesel.

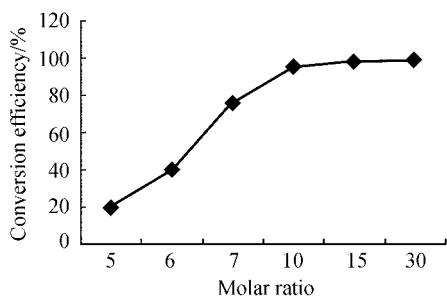


Fig. 3 Effect of molar ratio on conversion efficiency

1.2.2 Effect of alkaline catalyst amount

The alkaline catalyst potassium hydroxide concentration was used in the experiment from range of 0.3%–2.5% (weight of KOH/weight of oil). The maximum conversion efficiency was arrived at 1% of KOH. Addition excess catalyst gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels, while the reaction did not take place if the amount of KOH was not enough. The effect of catalyst amount of conversion effect was shown in Fig. 4.

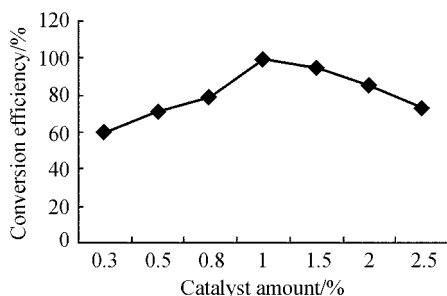


Fig. 4 Effect of alkaline catalyst amount on conversion efficiency

1.2.3 Effect of reaction temperature

Other research achieved best results at 45 °C and up to 70 °C while using rubber seed oil and brassica carinata oil (Ramadhas *et al.*, 2005; Pilar *et al.*, 2004), respectively. However, the maximum yield of biodiesel from *L. communis* oil was obtained at the temperature of (55 ± 5) °C. The decrease in yield was observed when the reaction temperature went above 60 °C.

1.2.4 Effect of reaction duration

It had been observed that the ester yield slightly

increase in reaction duration. Results obtained from the present experiments revealed that the reaction was completed for 30 minutes. We noticed that lucidity of the mixture suddenly changed when the reaction was finished. If we prolonged time, the yield was not increase.

1.3 Investigation of method of washing with hot distilled water

This method was applied by washing the mixture with distilled water at three different temperatures (25, 50, 80 °C) in two-step process. When the reaction was finished, the methyl ester and glycerin were separated in funnel. The crude ester phase was washed with hot distilled water 3 : 2 (oil : water, v) in the following order: former two times without stirring and the third time with gently stirring. We observed that separation was difficulty using room temperature water (25 °C) because oil and cold water did not dissolve. However, using hot water (80 °C), separation time was further longer and the yield was lower than 50 °C. So the best temperature was 50 °C. Hot water (± 50 °C) was sprayed over the surface of the ester two times and stirred gently in third time. Lower layer was discarded and at last yellow color layer (biodiesel) was separated.

1.4 Characterization of *L. communis* oil

The oil was used as feedstock for biodiesel product in this study, so the fatty acid composition of the oil and biodiesel from *L. communis* were tested by GC-MS. The results were shown in the Table 1. The oil mainly was made up of C₁₀, C₁₂, C₁₆ and C₁₈, which was match the biodiesel standard.

1.5 Properties of methyl esters of *L. communis* oil

The fuel properties of *L. communis* oil methyl ester in comparison with that of other esters (Ghadge *et al.*, 2005) was shown in Table 2, respectively. We concluded that the fuel properties were quite comparable to those of other esters and diesel. The present results showed that the transesterification process improved the fuel properties of the oil with respect to specific gravity, viscosity, flash point, and acid value. The viscosity of the biodiesel was closer

to that of diesel. Therefore, the existing engine was not modified. The calorific values of biodiesel were lower than diesel because of the oxygen content. Biodiesel containing higher oxygen helped to complete combustion of the oil in the engine. The flash point was much higher than that of diesel. The flash point was increased if the biodiesel and diesel were mixed at percentage. Hence, it was safe to store and transport the blends of biodiesel-diesel as compared to diesel alone. The tested result showed that methyl esters of the oil matched with DIN V 51606 biodiesel standards (see Table 2).

Table 1 Composition of the oil and biodiesel from *L. communis*

| Systemic name | Structure | Content / % | |
|--------------------------------------|-------------------|--------------|-----------|
| | | Material oil | Biodiesel |
| Octanoic acid methyl ester | C _{8:0} | | 0.43 |
| Decanoic acid methyl ester | C _{10:0} | 18.66 | 31.21 |
| Undecanoic acid methyl ester | C _{11:0} | | 0.19 |
| Dodecanoic acid methyl ester | C _{12:0} | 31.51 | 41.74 |
| Tetradecanoic acid methyl ester | C _{14:0} | 1.04 | 1.77 |
| Hexadecanoic acid methyl ester | C _{16:0} | 12.93 | 11.19 |
| Octadecanoic acid methyl ester | C _{18:0} | 0.65 | 0.63 |
| Cis-9-octadecenoic acid methyl ester | C _{18:1} | 18.19 | 12.70 |
| Linoleic acid methyl ester | C _{18:2} | 5.37 | |
| Eicosanoic acid methyl ester | C _{20:0} | | 0.14 |

2 Experimental

2.1 Esterification Procedure

Experiments were conducted in a laboratory scale setup of which 500 mL glass flask with condenser that retained any vaporized methanol to the reacting mixture. A hot plate with magnetic stirrer arrangement was used for heating the mixture in the flask. The mixture was stirred at the same speed for all tests. The temperature range of 50 °C–60 °C was maintained during experiment. One trial was carried out for each reactant and process condition. The results were presented in Fig. s. Once the reaction was finished no matter acid and alkaline catalyst, the mixture immediately changed limpidity.

2.2 Analysis for material oil and biodiesel product

Firstly, Kernels were separated by breaking the capsules with machine, dried to remove the moisture. The kernels were crushed in the crusher and the oil was filtered. The crude oil was reacted with boron trifluoride-methanol complex for GC-MS (HP GC6890/MS5972) analysis. The biodiesel was obtained by two step methods described in the paper for GC-MS and properties of biodiesel. The machine equipped with a HP-25 capillary column (30 m × 0.25 mm i. d., 0.25 μm film thickness) and a mass

Table 2 Properties of biodiesel from *L. communis* oil

| Property | | Biodiesel from <i>L. communis</i> oil | German (DIN V 51606) | Mahua biodiesel |
|--------------------------|--------------------|---------------------------------------|----------------------|-----------------|
| Specific gravity (15 °C) | g/cm ³ | 0.875 | 0.875–0.90 | 0.88 |
| Calorific values | MJ/Kg | 37.9 | | 37.0 |
| Flash point | °C | 123 | 110 | 208 |
| Pour point | °C | –15 | | 6 |
| CFPP | °C | –11 | 0–10/–20 | |
| Viscosity at 20 °C | mm ² /s | 3.22 | | |
| Viscosity at 40 °C | mm ² /s | 5.0 | 3.5–5.0 | 3.98 |
| Sulfated ash | Wt% | No detection | 0.03 max | |
| Ash content | Wt% | | | 0.01 |
| Carbon residue | Wt% | | | 0.02 |
| Acid Value | mgKOH/g | 0.034 | 0.05 | 0.20 |
| Chroma | | 3.5 | | |
| Water content | mg/kg | No detection | 300 max | 0.04 |
| Erode for CU | | 1 | 1 | |
| Distillation | °C | | | |
| 50% | | 293.0 | | |
| 60% | | 309.0 | | |
| 80% | | 332.0 | | |
| 95% | | 338.0 | | |

spectrometer 5792. The carrier gas was helium, at a flow rate of 1 mL/min. Column temperature was initially 50 °C for 1 min, then gradually increased to 180 °C at 5 °C/min, and finally increased to 260 °C at 15 °C/min. For GC-MS detection, an electron ionization system was used with an ionization energy of 70 eV. The extracts were diluted 1 : 100 (v/v) with diethyl ether, and 1.0 µL of the diluted samples was injected automatically in splitless mode. Injector and detector temperatures were set at 250 and 280 °C, respectively.

3 Conclusion

The product of biodiesel from low-cost, high FFA feedstock was investigated in the present study. We found that the material with high FFA could not be transesterified with the alkaline catalyst. The reason was the catalyst (KOH or NaOH) to react with the fatty acid to form soap that prevented the reaction and separation from glycerin and ester. A two-step was useful for the oil with high FFA. The first step (acid catalyst) reduced the content of FFA (less than 1.5%) and converted the fatty acid to methyl ester. The second step (alkaline catalyst) converted the first product to mono-ester and glycerin. The effects of methanol to oil molar ratio, catalyst amount, reaction temperature, reaction time and water washing method were analyzed in each step. No matter acid catalyst or alkaline catalyst, the ratio of methanol to oil was of importance in all conditions. The molar ratio of methanol to oil 10 : 1 completed the process of reaction with 0.5–1 hour. We noticed that the react mixture suddenly changed lucidity, suggesting the reaction was downright finished. The abundance sulphuric acid darkened the product and reduced the conversion efficiency. The excess alka-

line reduced the yield for adding wash times. The maximum ester was achieved at the reaction temperature in (55 ± 5) °C. The viscosity and acid value was nearer to that of diesel. Point flash (about 127 °C) was greater than that of diesel. Calorific value was slightly lower than that of diesel. In a word, the two-step method was useful for the non-edible oil with FFA. According to our estimate, one tree of 10-year-old *Lindera communis* can produce 3 kilograms of dried fruit for one year. The present study revealed that biodiesel from unrefined the *L. communis* oil was quite suitable as an alternative to diesel.

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