

BIODIESEL PRODUCTION BY TRANSESTERIFICATION OF DUCK OIL WITH METHANOL IN THE PRESENCE OF ALKALI CATALYST

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Abstract

Duck oil was employed as a feedstock for the production of biodiesel by transesterification with methanol. The composition examination was conducted on the raw duck oil and the corresponding biodiesel products. The composition and content of fatty acid methyl ester (FAME) was evaluated during transesterification catalyzed by NaOH. The results demonstrated that the major constituent and content of FAME had not changed appreciably after transesterification. The biodiesel yield was over 98% in optimum condition.

Key words: duck oil; biodiesel; transesterification; alkali catalyst.

1. Introduction

Rapid growth in population coupled with industrial and technological developments is leading towards the depletion of limited fossil fuel resources of the world. Currently, research is progressively more directed towards exploration of alternative renewable fuels [1]. Biodiesel has drawn more and more attention in recent years because it is renewable and has less detrimental effects on environment as compared with conventional diesel derived from petroleum [2]. Biodiesel is an alternative diesel fuel, which is synthesized by the direct transesterification of vegetable oils or animal fats with a short-chain alcohol in the presence of a catalyst [3-5]. It is better than diesel fuel in terms of sulfur content, flash point, aromatic content and cetane number. In addition, it is non-toxic, bio-degradable, relatively less inflammable fuel compared to the normal diesel [6]. Biodiesel has been produced using various oils, such as soybean oil [7], palm oil [8], cottonseed oil, sunflower oil [9]. But the major obstacle in the commercialization of biodiesel production is its high material cost. Thus, it is necessary to develop non-edible oil as the raw material of biodiesel [10]. Waste oils and fats, which are much less expensive than edible vegetable oil, will meet the need to synthesize biodiesel because of its sleazy price and broad source [11]. Meanwhile, biodiesel from waste oils and fats is an effective strategy for reducing cost and solving the problem of waste oil by proper utilization of waste oil as fuel [12].

In this paper, roast duck oil was collected as a feedstock for biodiesel production by transesterification with methanol. Biodiesel production was conducted using alkali catalyst via the transesterification of roast duck oil with methanol. The fatty acid distribution of roast duck oil was analyzed before reaction by GC-MS. The yield of biodiesel was evaluated under

various reaction conditions in the presence of NaOH catalyst. The composition and the content of biodiesel sample derived from transesterification were also investigated in this study.

2. Materials and methods

2.1. Materials and reagents

Roast duck oil was collected from the roast duck restaurant (Jinan, China). Methanol, sodium hydroxide (NaOH) were obtained from Sinopharm (Shanghai, China). All solvents were AR grade and were used without purification and the water for the experiment was deionized water. Methyl stearate, methyl linoleate, methyl linolenate, methyl palmitate, methyl palmitoleate, methyl oleate and methyl heptadecanoate were purchased from J&K Chemicals (Beijing, China).

2.2. GC-MS analysis of roast duck oil

The sample mixture of roast duck oil after methyl esterification was dissolved in normal hexane. The composition of sample was analyzed by GC-MS, which was performed on a 6890 gas chromatograph (Agilent, American) equipped with a 5973N Plus mass spectrometer (Agilent, American). Oxygen-free nitrogen was used as carrier gas at a flow rate of 1.0 mL/min.

2.3. Experimental procedure

Weighed amounts of duck oil, methanol and catalyst were added to the 100ml neck flask. The neck flask was put in the stirred batch reactor with vigorous stirring. The desired reaction temperature was set as 50-80 . After the reaction, the reaction product became biphasic, the upper phase, which was mainly the desired biodiesel, could be separated simply by decantation after a long time standing and layering process; the lower phase, which was the glycerin, could be collected for purification. After revolving the superfluous methanol from the rustic biodiesel, the biodiesel yield was directly analyzed by gas chromatography.

2.4. GC analysis of biodiesel sample

To detect the yield of biodiesel, methyl heptadecanoate was used as internal standard substance, normal hexane as solvent. The yield of biodiesel samples after transesterification reaction was analyzed by a SP-6800 gas chromatograph equipped with a flame ionization detector and a capillary column AT.FFAP (30 m×Φ0.32 mm×0.33 μm). Biodiesel was analyzed by internal standard method under follow conditions: final oven temperature of 493 K, injector temperature of 523 K, detector temperature of 533 K, and a split ratio of 40/1. High purity nitrogen (99.999%) was used as carrier gas at a flow rate of 1.0mL/min. The weighed biodiesel sample was dissolved in normal hexane and 1mg internal standard solution of methyl heptadecanoate was added. The GC analysis was carried out by injecting 1μL sample solution into the gas chromatography. Methyl esters were quantified by comparing the peak areas between the samples and the standard compounds. The yield of biodiesel was calculated by the following equation:

$$\text{Yield}_{\text{FAME}} = \frac{\sum f_{\text{ester}} A_{\text{ester}}}{A_{\text{internal}}} \times \frac{m_{\text{internal}}}{m_{\text{esters}}} \times 100\%$$

In the above formula, A_{ester} is the peak area of fatty acid methyl esters, A_{internal} is the peak area of internal standard, m_{internal} is the mass of internal standard, m_{esters} is the mass of fatty acid methyl esters and f_{ester} is the correction factor of fatty acid methyl esters.

3. Results and discussion

3.1. The GC-MS examination of roast duck oil

Oils and fats are composed primarily of triglycerides. Triglycerides consist of a glycerin backbone with fatty acid radicals attached in place of the hydroxyls. The relative amounts of the different fatty acid radicals determine the properties of the specific triglyceride. The fatty acid distribution of roast duck oil was concluded from the content of fatty acid methyl

ester after methyl esterification. Fig.1 shows the fatty acid distribution of roast duck oil. The result of GC-MS analysis shows that major fatty acid distribution in roast duck oil were C16:0 (palmitic acid; 23.47%), C16:1(palmitoleic acid; 4.08%), C18:0 (stearic acid; 6.63%), C18:1(oleic acid; 47.45%), C18:2(linoleic acid; 13.27%), and C18:3(linolenic acid;1.02%).

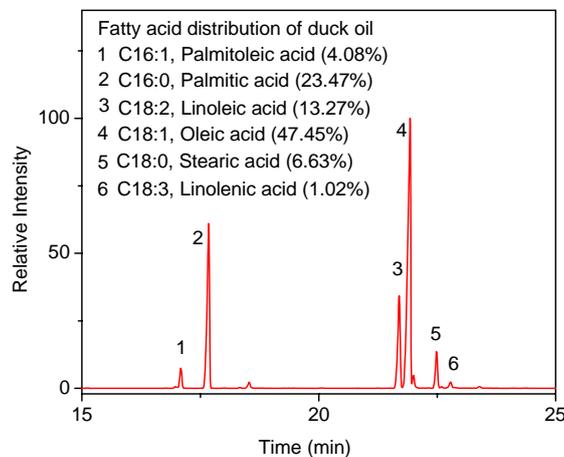


Fig 1. The GC-MS graph of roast duck oil after methyl esterification

3.2. Optimization of transesterification catalyzed by NaOH

3.2.1. Effect of reaction temperature on biodiesel yield

In the present work, the reaction temperature was varied within a range from 50°C to 80°C. Transesterification conditions: methanol/oil, 6:1; catalyst amount, 0.75 wt.% (of the feed mass of roast duck oil, similarly hereinafter); reaction time, 1h. The results (Fig 2a) indicate that the reaction rate was slow at low temperatures and the biodiesel yield was only 85% at 50°C after 1h. The biodiesel yield increased with the increase of reaction temperature to nearly 93% at 60°C, but at higher temperatures ($T > 60^\circ\text{C}$), the methanol was vaporized and formed a large number of bubbles in the interface, which inhibited the increase of biodiesel yield, then the yield of biodiesel decreased significantly. Thus, the optimum reaction temperature was 60°C.

3.2.2. Effect of methanol/oil molar ratio on biodiesel yield

The biodiesel yield increases as the molar ratio increases from 4:1 to 6:1 (Fig. 2b), this was obtained under transesterification conditions as follows: reaction temperature, 60°C; catalyst amount, 0.75 wt.%; reaction time, 1h. The maximum biodiesel yield of 93.1% is obtained when the molar ratio is very close to 6:1. However, beyond the molar ratio of 8:1, the excessively added methanol has no significant effect on the production yield. However, when the amount of methanol is over 8:1, glycerol separation becomes more difficult, thus decreasing the biodiesel yield. Based on this, the optimum molar ratio of methanol to oil is 6:1.

3.2.3. Effect of catalyst amount on biodiesel yield

Effect of catalyst dosage was investigated with the mass ratio of alkali catalyst to roast duck oil varying within the range of 0.5-1.25%, under otherwise identical conditions as: reaction temperature, 60°C; methanol/oil, 6:1; reaction time, 1h. The biodiesel yield was found to increase with increasing catalyst dosage and the maximum was obtained at the dosage of 1.0% with a value being 98.2% at 1h (Fig. 2c). However, with further increase of the catalyst amount, the biodiesel yield decreases, which is possibly due to the effect of saponification. Accordingly, only a yield of 87.2% is obtained when the mass ratio is 1.25%.

Therefore, the optimum catalyst amount can be confirmed to be 1.0% with the maximum biodiesel yield of 98.2%.

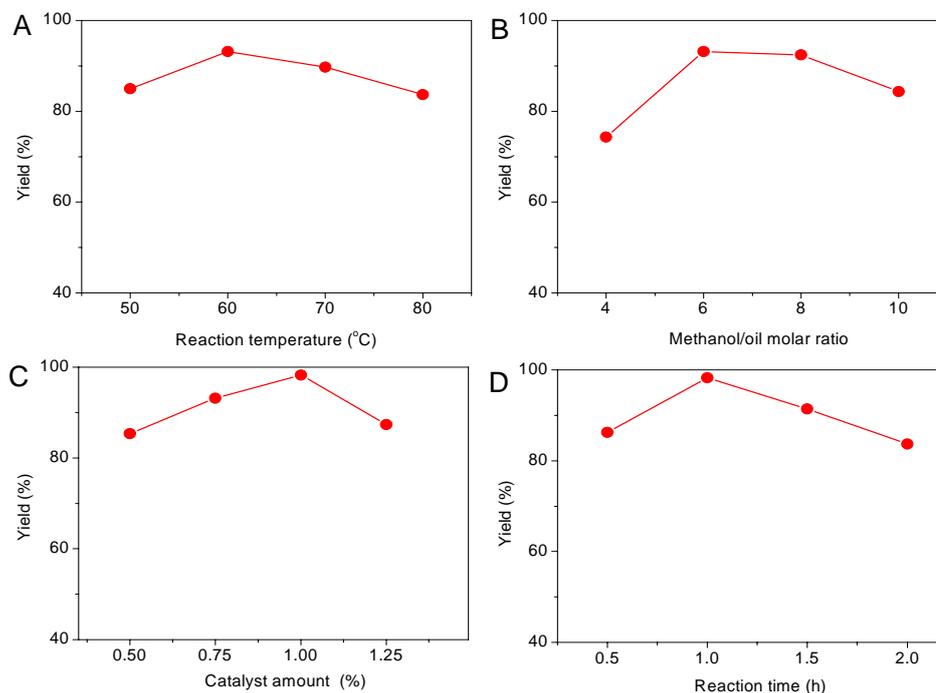


Fig 2. Effects of variables on biodiesel yield: (a) reaction temperature (b) methanol/oil molar ratio (c) catalyst amount (d) reaction time.

3.2.4. Effect of reaction time on biodiesel yield

Transesterification reactions herein were conducted under following conditions: reaction temperature, 60°C; methanol/oil, 8:1; catalyst amount, 1.0 wt.%. Fig.2d reveals that the reaction is strongly dependent on reaction time. In the beginning, the reaction is slow due to the mixing and the dispersion of methanol into oil, and the biodiesel yield increases very quickly in the reaction time range from 0.5 to 1h. Moreover, excessive reaction time leads to a bit reduction in the product yield due to the backward reaction, resulting in a loss of esters as well as causing more fatty acids to form soaps. Therefore, the optimum reaction time is 1h.

3.3. The GC graph of biodiesel sample

The fatty acid methyl ester in biodiesel sample were identified and quantified by comparing their retention times and peak areas to those of standard sample. Fig 3 shows that the outcome in chromatograph of the compounds is in the sequence as: methyl palmitate (4.123min), methyl palmitoleate (4.348min), methyl heptadecanoate (4.890min), methyl stearate (5.923min), methyl oleate (6.232min) and methyl linoleate (6.882min). Table 1 shows that the biodiesel sample consisted of five methyl esters: methyl palmitate (C16:0) 25.77%, methyl palmitoleate (C16:1) 3.99%, methyl stearate (C18:0) 5.27 %, methyl oleate (C18:1) 52.12%, and methyl linoleate (C18:3) 12.85%. These experiment results proved that the composition and content of methyl ester in biodiesel had no major changes compared to the roast duck oil.

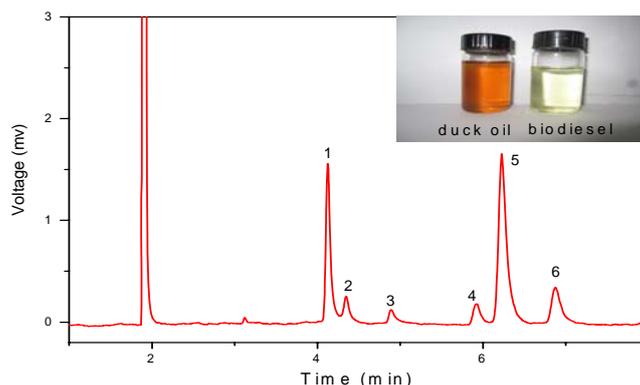


Fig 3. The GC graph of biodiesel sample.

Table 1. The chromatograph peak order and content of methyl ester.

Peak order	The name of methyl ester	Molecular formula	Retention time (min)	Content (%)
1	Methyl palmitate	C16:0	4.123	25.77
2	Methyl palmitoleate	C16:1	4.348	3.99
3	Methyl heptadecanoate	C17:0	4.890	-
4	Methyl stearate	C18:0	5.923	5.27
5	Methyl oleate	C18:1	6.232	52.12
6	Methyl linoleate	C18:3	6.882	12.85

4. Conclusion

The production of biodiesel from roast duck oil was evaluated by transesterification with methanol in the presence of NaOH. The results demonstrate that the major composition and content of fatty acid methyl ester (FAME) has not changed appreciably. The major composition of biodiesel is methyl oleate, with a content of 52.12%. The yield of biodiesel was obtained as 98% with NaOH catalyst at 60°C under the optimum condition. The roast duck oil, used in the preparation of biodiesel, illustrates a good prospect of application and appears to be a promising feedstock for biodiesel production.

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