Design of a comprehensive experiment of the synthesis of biodiesel catalyzed by CaO

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Abstract. An applied chemistry comprehensive experiment has been designed using CaO for synthesis of biodiesel. Effects of calcination temperature, methanol concentration, reaction temperature, reaction time and amount of catalyst on transesterification reaction are investigated. Based on experiment, the relationship between the catalyst structure and its properties was analyzed. Furthermore, this experiment can cultivate student's abilities of analyzing and solving problem. And it can build up the innovation consciousness, competition and team spirit of students. At the same time, the biodiesel and its preparation are line with the development requirements of green chemistry, so that students can establish environmental protection concept.

Keywords: CaO, Rapeseed oil, Biodiesel, transesterification, Comprehensive experiment.

1. Introduction
The limited supply of fossil fuel and current environmental concerns stimulates the production of alternative fuel from renewable resources worldwide. Biodiesel is a non-toxic biodegradable fuel produced from vegetable oils by the transesterification of triglycerides with methanol. Therefore biodiesel can be considered an environmental friendly and a renewable fuel arising from biomass[1]. Homogeneous-catalyzed transesterification of vegetable oils and animal fats cause major drawbacks such as instrument corrosiveness, difficulty in catalyst separation, and health hazard to operators due to the generation of massive waste stream from washing steps[2]. In contrast, the utilization of a successful heterogeneous catalyst will easier to separate and to purify, making the production process more cost-effective and environmental-friendly[3]. Some solid catalysts, basic or acid, have been tested in the transesterification reaction of triglycerides with methanol. Basic catalysts showed higher reaction rate than acid solid and they have been preferably studied[3]. CaO, as one of the conventional solid strong bases, has been used to catalyst or catalyst support in the biodiesel industry[4]. Among the catalysts that have been studied so far, calcium oxide shows required capability for transesterification reaction[5].
this study, design of a comprehensive experiment of the synthesis of biodiesel catalyzed by CaO, aiming to investigating the relationship between the catalyst structure and its properties. Furthermore, this experiment combines the basic chemicals theory and experimental skills together, which can put great role to the professional experimental skills of student, and then improve their abilities of analysis and problem-solving.

2. Design of the experiment

2.1. Objective
(1) Understand the transesterification mechanism of the rapeseed oil transformed into the substitute fuel-biodiesel.
(2) Master a method of synthesis of biodiesel catalyzed by CaO.
(3) Learn the basic working principles of gas chromatograph and analyze the date by internal standard method.

2.2. Principle
Biodiesel synthesized from rapeseed oil and methanol by transesterification in a traditional way, as shown in Figure 1. The process is here medium, every produce 10 biology derv to be able to produce 1 glycerine. Glycerol is the main by-product of biodiesel production. With the rapid development of biodiesel in demand and production, the effective utilization of glycerol was looked as an urgent task.

\[
\begin{align*}
\text{R}_1\text{COOCH}_3 \quad \text{R}_2\text{COOCH}_3 \quad \text{R}_3\text{COOCH}_3 \\
\end{align*}
\]

Fig.1 The reaction of rapeseed oil with methanol

This paper rebuilds traditional method by adding methyl acetate into processes and it makes maximum profit become true. The transesterification of methyl acetate and vegetable oil to prepare biodiesel has been developed to avoid the production of glycerol by producing glyceryl triacetate as a secondary product, instead, that can be used as an oxygenated derivative without separation from the fatty acid esters.[6-7] The by-product triacetin is a valuable molecule, which has got widespread applications in food, feed, printing, tanning, cigarette, cosmetic, pesticide and pharmaceutical industries and also have many medical applications. Further, triacetin is used as a solvent in the preparation of celluloid, photographic Wlms, as a component in binders for solid rocket fuels and as a gelatinizing agent in explosives[8]. And above all, the by-product triacetin can be also converted to methyl acetate to achieve the efficient use and recycling of the resources.
2.3. Materials
Refined rapeseed or canola oil was purchased locally (Xi’an, China) and used with further purification. Analytical reagent grade \( \text{CH}_3\text{COOCH}_3 \), \( \text{CH}_3\text{OH} \), \( \text{CaO} \) were purchased from Sinopharm Chemical Regents Co., Ltd. Loated at Beijing, China. \( \text{C}_{18}\text{H}_{36}\text{O} \) (Methyl heptadecanoate) was purchased from Sigma.

2.4. Methods
The first step was to refine the rapeseed oil. The rapeseed oil was mixed with sodium hydroxide in a ratio to remove free fatty acids in the rapeseed oil. then, The sodium salt and water content were allowed to a minimum[9-11].

The laboratory scale transesterification was carried out in a 100 ml three-necked flask equipped with a water-cooled reflux condenser in an water bath with a magnetic stirrer. The catalyst was added as methanol was refluxed and sampling was started at 10-minute intervals. After 1 h, the samples were centrifuged at 3000 r for 0.5 h to recover the supernatant and the excess methanol was distilled off under a vacuum.[12-14] The prepared biodiesel was tested by GC7860 gas chromatograph using an internal standard analysis method. The GC (gas chromatograph) was equipped with a fused-silica capillary column (KB-Wax, 30m x 0.32mm x 0.25μm) using methyl heptadecanoate as the standard. The yield of biodiesel can be obtained from the following formula.[15-16]

\[
yield(\%) = \left[ \frac{\sum A_i - A_{MH}}{A_{MH}} \right] \frac{C_{MH}V_{MH} \times 100}{W}
\]

\( \sum A_i \) indicated the total peak area of methyl ester; \( A_{MH} \) represented the area of methyl heptadecanoate; \( C_{MH} \) expressed the concentration in mg/mL of the methyl heptadecanoate (1 mg/mL); \( V_{MH} \) expressed the volume in mL of the methyl heptadecanoate solution (1μ L); \( W \) expressed the weigh in mg of the sample.
2.5. **Attention**

The sodium hydroxide involved in the experiment is strong corrosiveness, and the laboratory should be equipped with emergency treatment agents and flushing nozzles. Before the experiment, the safety problems should be emphasized for the students. When suing sodium hydroxide, we should adopt protective measures timely. We should monitor any accidents at any time during the process. After experiment, the waste liquid should be poured into the assigned waste liquid barrel, and a special one should be treated harmlessly, and no water should be poured into the sink and the sewer.

3. **Questions and exercises**

(1) What are the advantages to tri-component coupling transesterification when compared to traditional biodiesel production?

(2) Why should the methyl heptadecanoate be added as the internal standard in the test?

(3) What’s the role of adding the cyclohexane in the process of refine rapeseed?

4. **Conclusion**

The design of this experiment which involves wide knowledge and has the practical and applied nature is essential for college students. Two different methods in synthetic biodiesel—traditional transesterification system and tri-component coupling transesterification system—are compared in this experiment. Let students grasp the principle of quantitative analysis of internal standard method and the operation methods of gas chromatograph. At the same time, this experiment can improve the ability of the students' experiment operation ability, and strengthen the students' awareness of environmental protection. This experiment is carried out in groups, which is conductive to improving the students' cooperation ability and team spirit.

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