

Oil phases and CH_3OH are insoluble at room temperature in the transesterification process, therefore, the efforts have been focused on improving the solubility without increasing the reaction temperature recently. Several organic solvents like acetone, diethylether or tetrahydrofuran have been proved to promote the transesterification reaction effectively as co-solvent at even room temperature.^{21–24} Inspired by the co-solvent method for transesterification to produce biodiesel, we started to investigate the preparation of epoxidized methyl esters by transesterification of epoxidized vegetable oils at room temperature (25 °C) (Scheme 2), in which the epoxy group could be well tolerated. This novel and sustainable protocol could make a large supply of epoxidized methyl esters become available and stimulate the development of new biobased products.

Materials and methods

Materials

Epoxidized soybean oil was purchased from Aladdin Chemical Reagent (Shanghai, China). CH_3ONa (>99%) was purchased from Aladdin Chemical Reagent (Shanghai, China). NaOH , KOH , Na_2CO_3 , methanol, acetone, ethyl acetate, tetrahydrofuran (THF), diethylether and *n*-hexane were analytical reagent grade and purchased from Kermel Chemical Reagent (Tianjin, China). Monoglyceride, diglyceride standards were purchased from Sigma-Aldrich Co. (St. Louis, MO). Methyl heptadecanoate standard was purchased from Sigma-Aldrich Co. (St. Louis, MO). Triglyceride (soybean oil) were purchased from a local supermarket (Zhengzhou, China). Epoxidized fatty acid methyl esters standards were prepared in our lab through epoxidation of corresponding fatty acid methyl esters.

Transesterification

Transesterification reactions were performed in 50 mL round-bottom flask. Epoxidized soybean oil (10.0 g) and a certain

amount of co-solvent were added to the flask. A solution of the established base concentration in methanol was prepared and added to the flask. Then the mixture was magnetically stirred at room temperature (25 °C) for 1 h. After the reaction completion, the product was washed with deionizer water to remove the remaining base catalyst. And the remaining water was dried by anhydrous sodium sulfate (Na_2SO_4). Finally, the product was dried under reduced pressure for 1 h.

Oxirane oxygen titrations

Epoxy oxygen group content (EOC) of the products was determined by the titration method with hydrobromic acid solution in acetic acid using AOCS standard test method Cd 9-57 (AOCS, 1998).

Gas chromatography analysis

The products were analyzed using an Agilent 7890 GC equipped with a DB-1HT column (30 m × 0.25 mm × 0.1 μm, J&W Scientific, Folsom, CA). Nitrogen was used as the carrier gas with flowing rate of 5 mL min⁻¹. The oven was programmed from an initial temperature of 50–180 °C at 15 °C min⁻¹, increased to 230 °C at 7 °C min⁻¹, and then to 380 °C at 30 °C min⁻¹ with a 15 min hold for a total run time of 35 min. Detection of eluents was made by FID and identified by retention times compared to known standards. Fatty acid esters, monoglyceride, diglyceride, and triglyceride standards were used. Internal standard method was used with methyl heptadecanoate as standard.

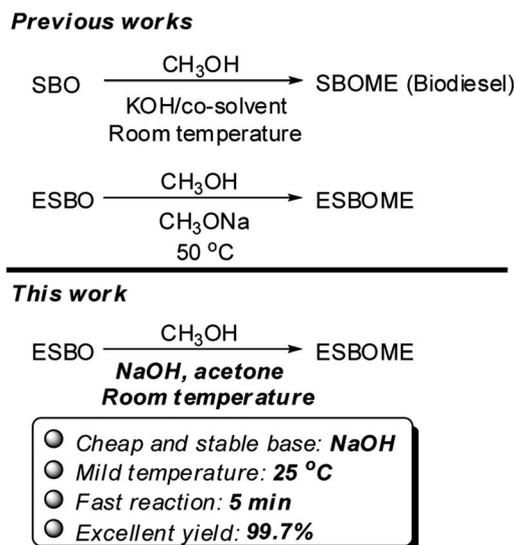
Statistical analysis

All experiments were performed in triplicate. The statistical significance of the ESBOME yield was analyzed by a significance testing of one-factor. Statistical significance was considered at $p < 0.05$.

Results and discussions

Effect of catalyst

As known, base plays a key role in the transesterification reactions. Thus, the effect of catalyst on epoxidized soybean oil methyl esters (ESBOME) production was evaluated by different commonly used alkaline bases (NaOH , KOH , CH_3ONa and Na_2CO_3) with 0.5% (wt% of oil) catalyst loading at room temperature (25 °C). Meanwhile, 20% (wt% of oil) acetone was added as co-solvent to increase the solubility of oil phases and CH_3OH and reduce the proportion of CH_3OH ,^{23,24} which was used as both reactant and solvent in transesterification reaction between oil and CH_3OH . Considering the sequence of reactant addition might influence the reaction rate, the solid base (e.g. NaOH) dissolved in methanol and the obtained mixtures (base-methanol) were added together into the reaction, which make the actual concentrations of different bases were the same in the reaction system. As shown in Fig. 1, KOH and NaOH showed higher catalytic efficiency than the same amount of CH_3ONa at room temperature, which might take place the side reaction with acetone. The methyl ester yield of ESBOME using KOH or



Scheme 2 The comparison of previous works for transesterification.



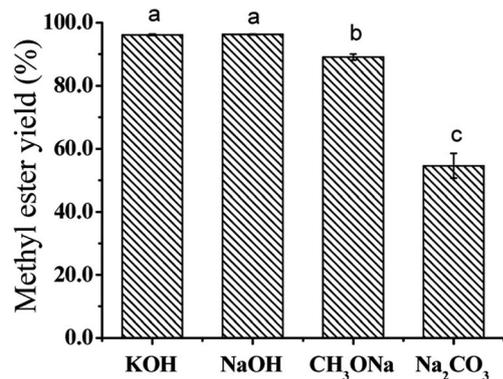


Fig. 1 Effect of different catalysts on the ESBOME production (reaction conditions: 25 °C, 20% (wt% of oil) acetone as solvent, 6 : 1 of methanol/oil molar ratio, 500 rpm, 1 h). Bars with the same letter are not significantly different.

NaOH as catalyst were 96.2% and 96.3%, respectively, which indicated that KOH and NaOH exhibited the similar catalytic activity towards the transesterification process. Less strong base such as Na₂CO₃ was also examined in this mild transesterification process giving much lower methyl ester yield of ESBOME (54.6%). Considering the reaction activity and the lower cost in the scalable production for biobased products, NaOH was chosen as the optimal catalyst at room temperature and applied in the following experiments.

Effect of catalyst loading

In order to investigate the effect of catalyst loading on ESBOME production, a series of experiments were conducted in the presence of NaOH catalyst at room temperature in the range of 0.10–1.30% (wt% of oil) (Fig. 2). In general, more NaOH base used in the transesterification process led to higher conversion of ESBO, which indicated that the transesterification rate was enhanced obviously with the increase of catalyst loading. And the transesterification process using only 0.1% NaOH catalyst led to 86.0% methyl ester yield of ESBOME. When the amount

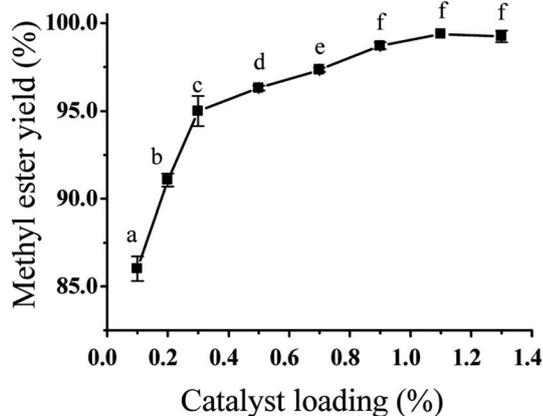


Fig. 2 Effect of catalyst loading on the ESBOME production (reaction conditions: 25 °C, 20% (wt% of oil) acetone as solvent, 6 : 1 of methanol/oil molar ratio, 500 rpm, 1 h). Bars with the same letter are not significantly different.

of catalyst NaOH was increased from 0.2% to 1.1%, the yield of ESBOME was significantly improved from 91.1% to 99.4%. However, further increasing the amount of NaOH (1.3%) could not increase the yield of ESBOME. Therefore, the optimum ESBOME production was achieved in methyl ester yield of 99.4% when 1.1% of NaOH was employed as the transesterification catalyst.

Effect of solvent type

Transesterification reaction between oil and methanol is initially heterogeneous due to the poor solubility of the oil in methanol.^{21,22} Therefore, mass transfer between the two phases strongly affects the transesterification reaction rate. The using of co-solvent in the transesterification reaction was an efficient approach to solve this problem and decrease the amount of methanol.²⁵ The effect of a variety of solvents such as acetone, ethyl acetate, THF and diethylether as co-solvent were tested. As shown in Fig. 3, acetone and diethylether showed the highest yields of ESBOME, which were all higher than 99%. Ethyl acetate and THF showed lower efficiency than acetone and diethylether. Considering diethylether as solvent is unsafe (the boiling point of diethylether is 34.6 °C) for scalable process and more expensive in cost, while acetone is less toxic and can be used in food and feed industries in scalability. Therefore, the following experiments were carried out using acetone as co-solvent.

Effect of molar ratio of methanol/oil

The molar ratio of methanol/epoxidized soybean oil strongly affected the transesterification reaction rate and conversion. Because the stoichiometric molar ratio of methanol/epoxidized soybean oil (ESBO) was 3 : 1 according to the transesterification reaction, excess amount of methanol was commonly used to ensure complete conversion of epoxidized soybean oil. Without extra co-solvent (*e.g.* acetone), large excess of methanol and enhanced temperature (60–70 °C) were required in

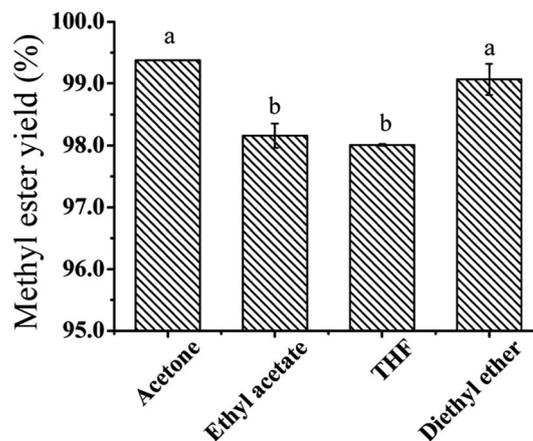


Fig. 3 Effect of different co-solvent on the ESBOME production (reaction conditions: 25 °C, 20% solvent (wt% of oil), 6 : 1 of methanol/oil molar ratio, 1.1% (wt% of oil) NaOH, 500 rpm, 1 h). Bars with the same letter are not significantly different.



transesterification of vegetable oils to produce biodiesel.²⁵ In this study, the molar ratio of methanol/ESBO ranging from 4 : 1 to 18 : 1 was optimized. As shown in Fig. 4, when the molar ratio of methanol/ESBO was increased from 4 : 1 to 14 : 1, the yield of ESBOME was increased slightly from 98.8% to 99.7%. Continuing increasing the amount of methanol (18 : 1) could not further promote the yield of ESBOME. Therefore, the optimal molar ratio of methanol/ESBO was 14 : 1 and the methyl ester yield of ESBOME could reach to 99.7% under such mild reaction conditions.

Effect of co-solvent amount

In the transesterification process, using acetone as co-solvent, methanol and epoxidized soybean oil could better integrate and the reaction rate was increased. However, the amount of co-solvent could also affect the substrates concentration in the reaction system. Therefore, the amount of co-solvent (wt% of oil) was investigated in the range of 0–25%. Fig. 5 showed the effect of co-solvent amount on the ESBOME production. Compared with none co-solvents, the yield of ESBOME was increased slightly (99.5% vs. 99.7%) after reaction for 1 h when 5% (wt% of oil) acetone was added as co-solvent. Continuing increasing the amount of acetone (10–25%), the yield of ESBOME exhibited no change (>99.5%).

Effect of reaction time

Moreover, the whole reaction process of the transesterification between epoxidized soybean oil and methanol was monitored in the presence and absence of co-solvent (acetone, 5%) (Fig. 6). Importantly, we found that the transesterification reaction between ESBO and methanol took place rapidly and complete conversion was detected only after stirring for 5 min at room temperature (25 °C). Without extra co-solvent, the transesterification reaction between ESBO and methanol took place much slower than that with acetone as co-solvent and 30 min was required to finish the transesterification process. The starting material ESBO had high viscosity at room temperature.

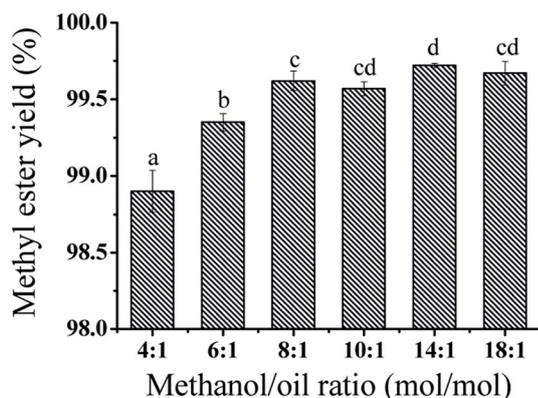


Fig. 4 Effect of methanol/oil molar ratio on the ESBOME production (reaction conditions: 25 °C, 20% acetone (wt% of oil), 1.1% NaOH (wt% of oil), 500 rpm, 1 h). Bars with the same letter are not significantly different.

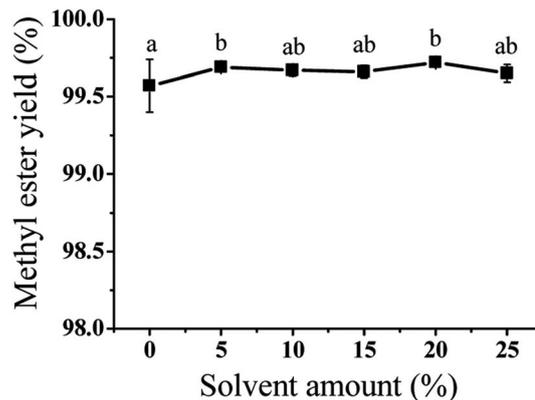


Fig. 5 Effect of co-solvent (acetone) amount on the ESBOME production (reaction conditions: 25 °C, 1.1% (wt% of oil) NaOH, molar ratio of methanol/oil 14 : 1, 500 rpm, 1 h). Bars with the same letter are not significantly different.

Acetone as co-solvent could reduce the viscosity of ESBO, and increase the interaction between methanol and ESBO, so that the rate of transesterification was improved. Based on these observations, it was concluded that 5% acetone as co-solvent could efficiently promote the transesterification reaction in a very short time (5 min) even at such mild temperature (25 °C). Considering the rapid reaction rate observed in this transesterification, the activation energy of this reaction was also calculated. The result indicated that the activation energy was 31.29 kJ mol⁻¹, which was relatively small and similar with the previous examples using NaOH as catalyst in transesterification vegetable oils with methanol.^{22,26} Thus, 5% acetone was chosen as co-solvent in the production of ESBOME through transesterification of ESBO with methanol.

This transesterification reaction occurs through three consecutive reactions.²² The first step is the reaction between one molecule of triglyceride (epoxidized soybean oil) and methanol to produce a diglyceride and one molecule of methyl ester (ESBOME). The obtained diglyceride reacts with methanol to form a monoglyceride and another molecule of ESBOME. In the final step, monoglyceride reacts with methanol to yield the

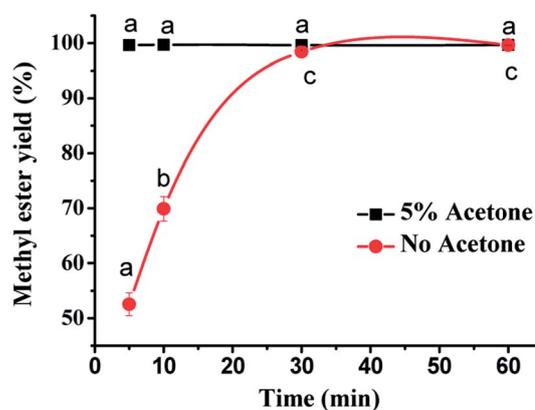


Fig. 6 Effect of co-solvent (acetone) on the reaction rate (reaction conditions: 25 °C, 1.1% NaOH (wt% of oil), molar ratio of methanol/oil 14 : 1, 500 rpm). Bars with the same letter are not significantly different.



third molecule of ESBOME and one molecule of glycerol. Thus three molecules of ESBOME and one molecule of glycerol are formed by the completion of the transesterification reaction. Triglycerides are first converted to diglycerides, and because they are formed in the methanol phase, they have a greater chance of reacting there rather than moving back to the oil phase. Therefore, diglycerides and monoglycerides could not be observed after the completion of the transesterification reaction.

In addition, the transesterification reaction of soybean oil was tested under the same reaction conditions (using 5% acetone as co-solvent). And the results showed that the transesterification reaction of soybean oil is slightly slower than that of epoxidized soybean oil. 95.1% yield of methyl esters was obtained after 5 min. The above results suggested that the solubility of soybean oil in methanol affected the transesterification reaction indeed.

The changes of the oxirane oxygen values during transesterification of ESBO were also evaluated (Fig. 7). The oxirane oxygen values of the starting material ESBO was 6.2. During the transesterification reaction catalyzed by NaOH at room temperature, the oxirane oxygen values of the samples had nearly no change when oxirane oxygen value was determined at 5 min, 10 min, 30 min and 60 min respectively. Based on these observations, it was concluded that the transesterification was completed in 5 min at room temperature without loss of the epoxide function, which made this method fully tolerate unstable epoxide group. Recently, real-time FTIR has become one of the efficient and *in situ* tools to monitor organic transformations compared with conventional analysis tools such as GC, GC-MS and HPLC,²⁷ which need pre-treatment before instruments analysis. Hence, real-time FTIR was used to monitor this transesterification progress at room temperature (25 °C) (Fig. 8), which also indicated that the epoxide group (845 cm⁻¹) had nearly no change during the whole transesterification reaction process.

Gas chromatography was used as an efficient tool to detect methyl esters, triglycerides (TG), intermediate transesterification products, monoglycerides (MG) and diglycerides

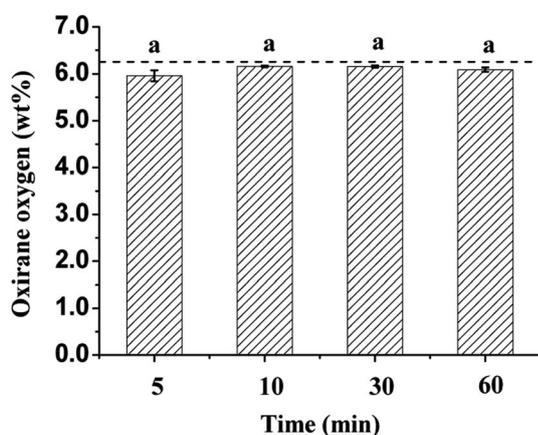


Fig. 7 Oxirane oxygen values changes during transesterification of ESBO. Bars with the same letter are not significantly different.

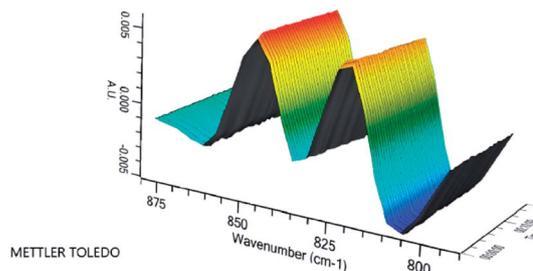


Fig. 8 The change of epoxide group (845 cm⁻¹) during the transesterification progress monitored by real-time FT-IR.

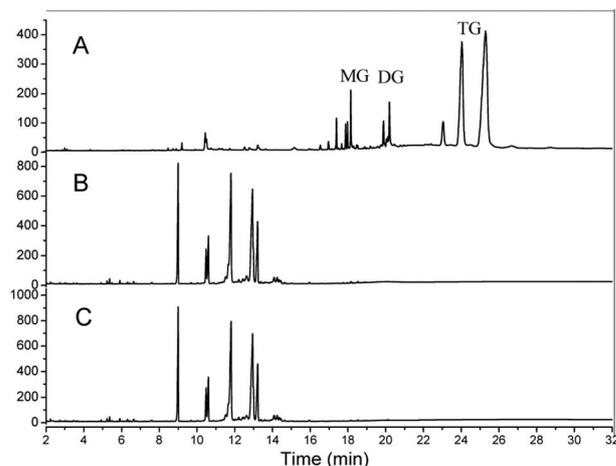


Fig. 9 Gas chromatogram of transesterification products: (A) monoglyceride (MG), diglyceride (DG), triglyceride (TG) standard compounds; (B) transesterification of ESBO after 5 min; (C) transesterification of ESBO after 60 min.

(DG) in one batch analysis of the transesterification products.¹⁷ The transesterification products were showed in the Fig. 9A. The transesterified epoxidized soybean oil were analyzed at 5 min (B) and 60 min (C) during the transesterification reaction, which suggested that the transesterification reaction proceeded rapidly. And the yield of ESBOME could reach to 99.7%, nearly completed at the first 5 min.

Conclusions

We have successfully developed a fast and simple method for transesterification of epoxidized soybean oil to prepare epoxy methyl esters at room temperature (25 °C). Epoxidized methyl esters were obtained in an excellent yield of 99.7% by the transesterification of epoxidized soybean oil (ESBO) with methanol catalyzed by 1.1% of cheap and stable sodium hydroxide (NaOH). Importantly, this transesterification was completed within 5 min at room temperature without loss of the epoxide function. In addition, 5% acetone served as an efficient co-solvent to promote the transesterification reaction rate. This novel protocol provides an efficient and sustainable method towards the synthesis of epoxidized methyl esters.



Conflicts of interest

There are no conflicts to declare.

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