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Ultrasonic-assisted synthesis of fatty acid ethyl ester and its purification by washing with DES

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ABSTRACT

Ultrasonic-assisted synthesis and separationof of fatty acid ethyl esters by transesterification of soybean oil with ethanol were investigated. An increased reaction rate was observed by use of ultrasound irradiation during the transesterification of soybean oil. The resulting product mixtures were purified with deep eutectic solvent synthesized by choline chloride and urea. Washing temperature, DES amount and duration of washing process at three levels were assigned as the control variables. The effect of the temperature and duration of the washing on glycerin and KOH removing efficiency was also investigated. AT the volume ratio of DES solvent to product 1:1, temperature is 70 °C, and washing time 6 min, the residue of glycerin in the upper layer of products is as low as 0.01007% after treatment, and no alkaline was detected in the fatty acid ethyl esters product.

KEYWORDS

Soybean oil;
Fatty acid ethyl esters;
Transesterification;
Deep eutectic solvent (DES);
Ultrasonic-assisted synthesis.

INTRODUCTION

Application of fatty acid methyl esters fuel used in diesel engines has been reported for many years. It is characteristic of renewable, biodegradable, less harmful gas emissions such as sulfur oxideÿunburned hydrocarbons, and particulate material. It can be produced by transesterification of triglycerides with methanol, using an alkali or acid as catalyst. Methanol is mainly sythesized from natural gas or coal. From an enviromental point of view, ethanol will be an ideal alternative of methanol. It can be produced from renewable agricultural sources and has lower toxicity, higher heat content, higher cetane index and lower cloud and pour points[1-3].

Transesterification reaction of triglycerides (TG) with ethanol is a sequence of three consecutive and reversible reactions with KOH or sodium hydroxide as a catalyst. The overall reaction is:

$$TG + 3CH_3CH_2OH \overset{catalyst}{\rightleftharpoons} GL + 3FAEE$$

The stepwise reactions are:

$$TG + CH_3CH_2OH \rightleftharpoons DG + FAEE$$

$$DG + CH_3CH_2OH \rightleftharpoons MG + FAEE$$

$$MG + CH_3CH_2OH \rightleftharpoons GL + FAEE$$

The resulting fatty acid ethyl esters contain unreacted components, residual catalyst, water, unreacted alcohol, glycerol and soaps. Refinement

of the crude product is necessary, involved in neutralization of residual catalyst, evaporation of unreacted ethanol and water washing or dry washing for removing these impurities. These processes are complicated, time-consuming and diseconomic. A new purification procedure of crude fatty acid ethyl esters products need to be developed.

A pursue of green solvent has being not ceased. Deep eutectic solvent (DES) has been shown to have properties similar to ionic liquids. It is characteristic of biodegradable, environmently friendly, low cost, non-toxicity, non-reactivity with water and ease of preparation in high purity. DES has being applied in many research areas, such as media for organic and inorganic reactions as well as the separation of some mixtures[4-8]. It can be promising solvent of purifying fatty acid ethyl esters.

Ultrasound energy has been successfully used to increase the conversion and the yield of reactions, change reaction pathway and/or initiate reaction in biological, chemical, and electrochemical systems by improving mixing and mass transfer especially in biphasic systems[9-13]. The ultrasound in fatty acid ethyl esters production will be expected to enhance the emulsification of immiscible liquid reactants by microturbulence generated by radial motion of cavitation bubbles.

The objective of the present work was to study ultrasound-assisted catalytic transesterification of ethanol and triglycerides of soybean oil to produce fatty acid ethyl esters with potassium hydroxide as a catalyst. In addition, separation and purification process of the products were investigated using deep eutectic solvent (DES) synthesized by choline chloride and urea instead of water washing.

EXPERIMENTAL

Reagents and samples

Refined commercial edible-grade soybean oil, which free fatty acids (FFA) and moisture content were 0.318% and 0.04%, respectively, was used in the transesterification reactions. Pretreatment of the raw oil was not necessary. Its iodine value was 130/100 g of soybean oil. Absolute ethanol (99.5%), potassium hydroxide (85%), urea (99.0%), choline chloride and other reagents were purchased from reagent companies. And potassium hydroxide was dissolved in ethanol before use. All the chemicals used were of analytical grade.

The experiments were carried out using ultrasonic cleaner of 300W, which total capacity is 30 dm3, and frequency of 25 kHz. When the sound waves are applied to the KOH, ethanol, and oil in the reaction vessel, cavitation takes place by the implosive formation, growth, and collapse of bubbles. Cavitation increases intermolecular activity and mixes the ethanol and oil to create a potassium ethoxide in oil emulsion.

Synthesis of DES

A hydrogen bond donors and quaternary ammonium salts were dried under vacuum at 60 °C for 24 h before use. And the molar ratio of quaternary ammonium salt (choline chloride) to hydrogen bond donor (urea) is 1:2 in our study. The mixtures were prepared by weighing each compound directly into a flask and all precautions were taken for isolating the mixture from air moisture. Then, the eutectic mixtures were prepared through heating and stirring in a magnetic heating stirrer at 80 °C until a colorless

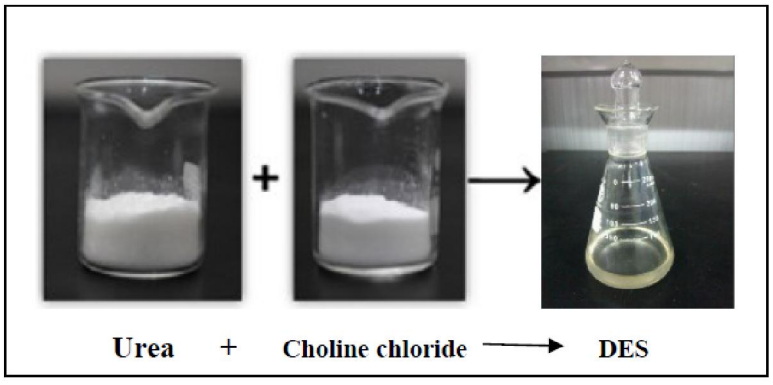

Figure 1 : Diagram of DES preparation process

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and homogeneous liquid was formed (typically 2 h).

Alkali catalyzed transesterification of soybean oil

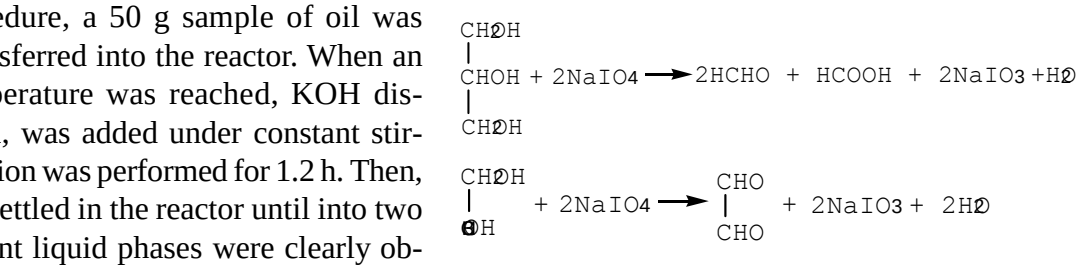
The conventional reaction was two-step batch transesterification reaction, which utilized a suitable ethanol: oil molar ratio and catalyst-to-oil ratio. During the procedure, a 50 g sample of oil was weighed and transferred into the reactor. When an appropriate temperature was reached, KOH dissolved in ethanol, was added under constant stirring, and the reaction was performed for 1.2 h. Then, the mixture was settled in the reactor until into two distinct transparent liquid phases were clearly observed. These two phases were the ester rich phase and glycerol rich phase, respectively. After the phase separation, the ethyl ester rich phase goes up to second step reaction, in which 50% of anhydrous ethanol and 50% of catalyst applied during the first step was added. The unreacted ethanol was distillated out by vacuum rotary evaporator in order to separate the mixture of the second reaction. The ester mixture after a second separation was treated with DES and analyzed.

All ultrasonic experiments were performed at ambient temperatures of 22 °C–27 °C, i.e., without using external heating. After starting the sonication process, the temperature of the reaction mixtures were in the range of 39 °C~52 °C because of the heating effect of the ultrasound waves. During the procedure, soybean oil and a previously prepared solution of ethanol and potassium hydroxide were fed into a vessel. After fully mixing, the reaction vessel was immersed directly into the ultrasonic cleaner. The product mixture was treated as above-mentioned procedure after reaction goes complete.

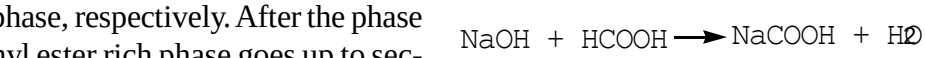
Glycerol determination and TG conversion calculation

Glycerin content in the product was determined according to saponification-periodate oxidation method. The conversion of soybean oil was calculated by the measured value of glycerin content. Glycerol can be stoichiometricly oxidized by sodium periodate to generate formic acid and formaldehyde, and sodium periodate was again deoxidated by excess ethylene glycol to form sodium iodate and glyoxal. Then, the formed formic acid was titrated with standard sodium hydroxide solution, using phenolphthalein as indicator. The equations are as follows:

a) Redox reaction



b) Titration reaction



Certain amount of samples was accurately weighed. A certain amount of water was added to dilute, and then 25 ml of sodium periodate solution of 0.1 mol/L was added to the sample solution. The resulting solution was shaken fully in the dark place for 15 minutes. Then, 5 ml of ethylene glycol solution of 50% (g/ml) was added. Another fully shake was done in the dark place for 20 minutes. 0.5 ml phenolphthalein indicator was dropped. It was titrated with sodium hydroxide standard solution of 0.1 mol/L until the solution goes to pink. It was calculated that per mL NaOH standard solution is equivalent to 9.21 mg of glycerin.

The calculation method of glycerin content and TG conversion of transesterification is as follows:

$$\text{Glycerin content} = \frac{(V_1 - V_0) \times C_{(NaOH)} \times 92.1}{m \times 1000} \times 100\%$$

Where V_0 is the volume of NaOH standard solution consumed in blank experiment; V_1 is the consumed volume of NaOH standard solution of titrating the sample; $C_{(NaOH)}$ is the concentration of NaOH standard solution; m the quality of the sample being analyzed.

$$\text{TG Conversion} = \frac{m_1}{m_2} \times 100\%$$

Where m_1 is the actual amount of the formed glycerin; m_2 is the theoretical value of glycerol amount.

RESULTS AND DISCUSSION

Optimization of soybean oil ethanolysis reaction conditions

Previous experimental studies indicate that the optimal conditions of the transesterification reaction were found to be as follows: reaction time 80 min, temperature 40 °C, potassium hydroxide catalyst loading 1.3wt%, molar ratio of ethanol to oil 9:1 and stirrer speed of 800 rpm. Under these conditions, the mixtures after the reaction were separated easily by settlement, and the obtained fatty acid ethyl ester yield reached 97.17%.

The use of ultrasound enhances the reaction rate of homogeneously catalyzed ethanolysis, which results in higher FAEE yields in a shorter reaction time. Ultrasound-assisted base catalyzed ethanolysis of triglycerides under optimal reaction conditions gives 96.10% FAEE yield in less than 30 min. The results obtained under ultrasonic irradiation can be explained by the formation of a stable microemulsion that results from the ultrasonic cavitation.

A comparison of the ultrasound-assisted and chemical method for the synthesis of ethyl esters by transesterification is shown in TABLE 1. The superiority of the ultrasound-assisted method was observed.

Comparison of deep eutectic solvent washing with water washing

The removal of the residual KOH catalyst and glycerin in the products is one of the most important steps in the process of biodiesel production. The conventional method is water washing. A certain amount of hot water was mixed with the product mixture and stirred for a period of time. The soluble impurities such as alkaline catalyst or glycerine were washed into the aqueous phase. Product-washing water is referred to the waste water resulted from washing the product mixture to remove impurities. The content of glycerol in the resulting wastewater may indirectly represent the amount of residual glycerin in the refinement product. From the results of glycerol content in product-washing water in TABLE 2, it can be seen that the DES of strong polarity can effectively extract glycerol and alkaline catalyst from fatty acid ethyl ester phase.

For water-washing process, saponification from strong alkaline will affect the washing effect and the quality of products, and the settlement becomes more difficult after washing. In contrast, DES-washing avoids the saponification. The main advantages are that low glycerin residues in products after washing, undetected alkaline, and easy settlement of product mixtures.

Optimization of product purification process with DES

In order to determine the optimal conditions of removing impurities in the soybean oil fatty acid ethyl ester, with the DES as solvent. An orthogonal experiment was carried out and the results are shown in TABLE 3. The optimized conditions of extraction were as follows: the volume ratio of the DES to the product mixture 1:1, temperature 70 °C, and washing time 6 min, the residue of glycerin in the upper layer of the FAEE products is as low as 0.010 07% after treatment, and no alkaline was detected. Thus, it was proved that DES solvent washing not only greatly reduces the glycerol content in the FAEE

TABLE 1 : Comparison of ultrasound-assisted and chemical synthesis of ethyl esters by transesterification

Method of synthesis	Oil: ethanol molar ratio	Catalyst Dosage, wt%	Reaction time, min	Reaction Temperature, °C	Yield, %
Chemical synthesis	1:9	2	80	40	97.17
Ultrasound-assisted synthesis	1:12	1.3	30	Without external heat	96.10

TABLE 2 : Comparison of products refined by washing with water and DES

	The product mixture	Washing with water	Washing with DES
Glycerol Content, %	0.261 3	0.105 8	0.010 07
Alkaline	Stronger	Weaker	No alkaline
(after washing)	(PH?9.2)	(PH?8.0)	(PH?7.0)

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TABLE 3 : Results of products purification with DES

No.	DES:Biodiesel (Volume ratio)	Temperature /°C	Washing time /min	Glycerin residues /%	Alkaline
1	1:1	30	2	0.02389	—
2	1:1	50	4	0.02109	—
3	1:1	70	6	0.01007	—
4	1:2	30	4	0.03907	—
5	1:2	50	6	0.01687	—
6	1:2	70	2	0.02028	—
7	1:3	30	6	0.04253	—
8	1:3	50	2	0.03887	—
9	1:3	70	4	0.02541	—
K1	0.018	0.035	0.028		
K2	0.025	0.026	0.029		
K3	0.036	0.019	0.023		
R	0.018	0.016	0.006		

"—" represents the products after purification with DES has no alkaline.

product of transesterification, but also residual alkaline catalyst in FAEE products was completely eliminated without waste water discharge during the whole process.

In addition, DES has strong hygroscopic property and can fully remove water in the product mixture. It was verified that the water content of the FAEE products accord with completely the specification of biodiesel after purified with DES.

Idea design of coupling transesterification

With potassium hydroxide being as catalyst, transesterification process of ethanol and triglyceride to produce biodiesel is designed as follows. For the soybean oil-ethanol-FAEE-DES system, miscibility between components will affect the separation scheme of product mixtures composed of reactants, product and catalyst. DES is soluble with soybean oil and ethanol at the beginning of the reaction. As the reaction progresses, the content of fatty acid ethyl ester is increased and DES becomes to be immiscibile with fatty acid ethyl esters. However, the occurrence of excess alcohol makes the system still in a homogeneous state. Therefore, ethanol should be maintained at a level as low as possible to ensure the effective separation of the catalyst and reaction mixture.

Product characterization

From the infrared characterization of fatty acid ethyl esters, it can be seen that the absorption peak of wave number is 3009.15 cm^{-1} for aliphatic unsat-

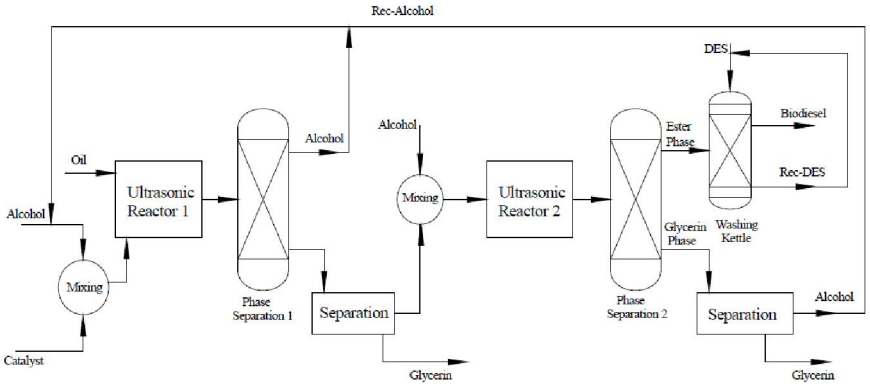

Figure 2 : Proposed process of fatty acid ethyl ester production

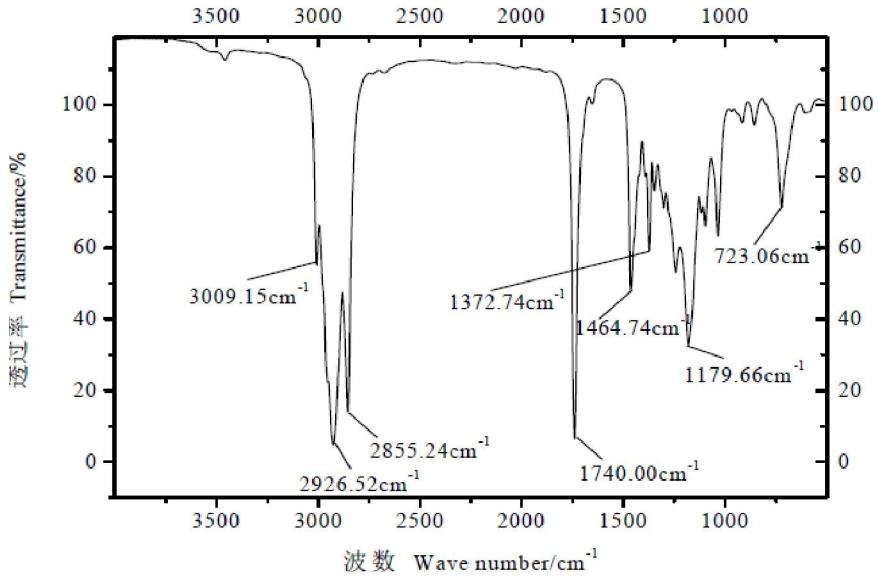

Figure 3 : Infrared spectrogram of fatty acid ethyl ester from soybean oil

urated hydrocarbon =C-H stretching vibration absorption peak, the two absorption peaks's waves number of 2855.24 cm^{-1} and 2926.52 cm^{-1} were saturation asymmetric stretching vibration absorption peak of methyl and methylene, respectively. The absorption peak at 1740.00 cm^{-1} is vibration absorption peak -C=O of saturated aliphatic ester, where the absorption function is very strong, it is proved that the transesterification is complete. There are two absorption peaks, respectively at 1372.74 cm^{-1} and 1464.74 cm^{-1} are the scissor vibration absorption peak of methyl of benzene and vibration absorption peak of methyl dC-H symmetric bending. At 1179.66 cm^{-1} is a strong stretching vibration absorption peak of saturated esters C-(C=O)–O. 723.06 cm^{-1} is plane vibration absorption peaks of methylene. From what has been discussed above, we can make sure that the products of transesterification are fatty acid ethyl ester.

CONCLUSIONS

The present study has shown that ultrasonic irradiation can improve significantly the transesterification of soybean oil. The process provides a feasible and effective method for the production of fatty acid ethyl esters with soybean oil and ethanol. Additional studies are necessary to evaluate the industrial viability of the process. It is worthy to mention that ethanol: soybean oil molar ratio, is a key factor to influence the separation procedure of transesterification process for meeting the needs of high quality fatty acid ethyl esters as a biodiesel. Products purification with DES solvent, can avoid the serious pollution problem caused by washing process with water, so the present process has significant advantages. In this respect, DES washing is promising method of purifying refined soybean oil transesterification products.

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