Determination of phase diagram of reaction system of biodiesel

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Abstract

Phase behavior of biodiesel reaction system in which rapeseed oil (RO) was converted into biodiesel by heterogeneous catalyst was investigated experimentally for improving the reaction rate and the efficiency of products recovery. Ternary phase diagrams of methanol, glycerol and methyl ester at various temperatures were determined. The results showed that the distribution coefficients (K_m) of methanol between biodiesel and glycerol phases were impacted by volume of glycerol and temperature significantly. It is suggested that the mass transfer limitation in the heterogeneous reaction of RO methanolysis can be broken on a certain extent by increase the ratio of methanol to oil and the temperature simultaneously, while the energy consumption for products recovery can be controlled in a multistage reversed flow process.

Key words: Phase diagram, biodiesel, heterogeneous reaction system

Introduction

Drainage area of Yangtze River is the biggest rapeseed-planting region in china. In recent years, double-low rapeseed planting area is enlarging quickly under the promotion of local governments. The boost of yield and the significant reduction of sulfur content make rapeseed become a potential source for bio-fuel production in china.

Generally, rapeseed oil (RO) is converted into biodiesel by transesterification with methanol; methanolysis is another term to imply this process. To improve the reaction rate and the product separation of methanolysis, data of phase behavior of the reaction system is essential (Zhou et al., 2006; Negi et al., 2006). In this system, the miscibility between methanol and triglycerides (oil) often plays as a bottleneck in the reaction, because their molecular polarities are quite different. In process of methanolysis, an induced period at the initiation of reaction was often observed, which indicate mass transfer limitation exist in this system (Barnwal et al., 2005; Meher et al., 2006). Different research groups took efforts for break the mass transfer limitation. Methanolysis performed at presence of cosolvents or enhanced by ultrasonic energy were reported (Cerce et al., 2005; Stavarache et al., 2005).

Heterogeneous catalysts for oil methanolysis show remarkable advantages in product separation and purification, but the reaction rate is lower compared to those of reactions promoted by conventional homogeneous catalysts (Bournay et al., 2005; Komers et al., 2001). In this work, the phase behavior of major components in the reaction system was investigated to improve the efficiency of heterogeneous reaction system.

Material and Methods

Refined RO was purchased from a local RO mill; chemical reagents for methanolysis of RO, preparation of solid base catalyst were analytical grade. Hexadecane (>99%) used in gas chromatograph analysis as internal standard was purchased from Tianjin research center of chemical reagent, China. Methods for determination of phase diagram, interfacial tension and product concentrations of biodiesel reaction system were as following:

Ternary phase diagram of methanol-FAME-glycerol: To preparation of rapeseed FAME, methanolysis of RO was carried out at 64°C for 60min using sodium methoxide as catalyst. The reaction product was settled in a separating funnel to remove glycerol, then the ester phase was washed twice by 80°C distilled water and dried at 95°C under vacuum. The final product was analysis by gas chromatography to ensure that the content of FAME was above 99% in mass fraction.

Methanol, rapeseed FAME and glycerol in different weight ratio were injected into screw-sealed glass tubes. These tubes were shaken intensively, and then kept in an isothermal water bath at specific temperatures for 24h to achieve phase equilibrium. Samples from upper phase and lower phase were withdrawn respectively to determine the content of glycerol and FAME.

The content of glycerol was determined by gas chromatography after glycerol in each sample was esterified completely with acetic acid using BF_3 as catalyst. The analysis was done using a gas chromatogram (GC9800, Kechuang, China) equipped with a flame-ionization detector. The GC column was a 30m × 0.32mm × 0.25μm PEG-20M capillary column (Chromatographic Technology Development Research Center, Lanzhou, China). Nitrogen gas was used as the carrier. The injector and the detector temperature were 230°C and 260°C, respectively. The column was kept at 150°C for 2min, then heated linearly from 150°C to 240°C at a rate of 10°C per min. Finally, the column temperature was kept at 240°C for 8min. Hexadecane was used as an internal standard. For FAME analysis, the same program was used.

According to the data of glycerol and FAME content in each sample, the composition of each phase could be calculated. By piloting data and the corresponding tie line, the ternary phase diagram was obtained.

Preparation of solid base catalyst: Porous magnesia obtained by calcination of sodium bicarbonate at 500°C was impregnated in isochoric solution of acetic cadmium at the concentration of 12% for 6h, then the particles were collected to calcine at 700°C for 5h. Finally, calcine product was grind and sieved to obtain CaO/MgO solid catalyst with granularity at 80mashes.

Biodiesel production in heterogeneous reaction system: Heterogeneous reactions were applied to convert RO into biodiesel, two different processes were designed for comparison. The first was a one-stage process, the reaction was carried out with an initial catalyst concentration of 3%, an operation temperature of 60°C and with an alcohol/oil molar ratio of 6: 1. the reaction was stopped until the conversion rate of was achieved 98%. The second was a multi-stage process including several reversed flow. A scheme of the main reaction procedures is shown in Fig.1.

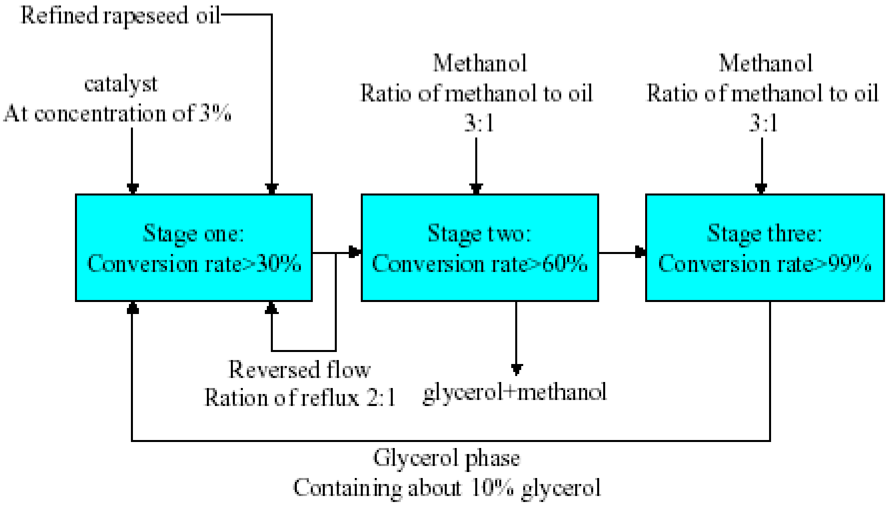

Figure1. Scheme of multistage reversed flow process

To evaluate the reaction rate of heterogeneous system, samples were withdrawn from the reaction system at intervals, mixed intensively with 0.1mol/L hydrochloric acid and settled in ice-water bath to terminate the reaction. Then hexane was used as solvent to extract FAME from the sample. The upper layer containing solvent and FAME was collected by centrifugation for gas chromatograph analysis. The conversion rate was calculated following the method described by She (She et al., 2005).

Results and discussions

Phase diagram of Methanol-FAME-glycerol. Reaction system for RO Methanolysis comprises reactants (triglycerides and methanol), intermediates (mono- and diglycerides) and final products (fatty acid methyl esters and glycerol), concentration of all components described above kept changing until the reaction reaches the end, therefore the process shows a very complex phase behavior. So we considered the oil of FAME as a single component, because of the molecular polarities of them is close compared to methanol and glycerol. Moreover, the influence of monoglycerides (MG), diglycerides (DG) and the solid catalyst was ignored in this study. Then phase diagram of Methanol-FAME-glycerol can be used to establish a simple but applicable description of the major relationships between each component in the reaction system.

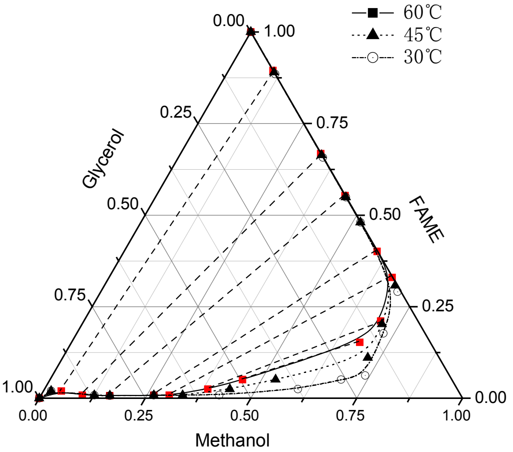

Figure 2. Ternary phase diagram of methanol-FAME-glycerol at different temperature

As shown in Fig.2, the phase diagram was divided into two parts by the joint curve of dots indicting the phase equilibrium data. The lower part denotes one liquid phase region; the upper part shows that two liquid phases will coexist. Temperature is a phase behavior effecting parameter can be manipulated easily for benefiting reaction or separation. According to the data in fig.2, higher temperature promotes solubilization of each component, enhances mass transfer and contact efficient of the reactants consequently. At lower temperature, the region of two liquid phases was larger. This phenomenon indicates that the separation of glycerol will be more complete at low temperature.

Distribution coefficient (K_m) of methanol. In reaction of methanolysis of RO, methanol not only serves as a reactant, but also acts as a solvent to facilitate mass transfer. Extreme sample reported was single-phase process developed for the transesterification of oil in a unique phase with the ratio of alcohol to triglyceride being 15:1 to 35:1. In commonly process in which alkali catalyst was used, excess methanol (generally at a molar ratio of 6:1) exists to switch the reaction to yield methyl esters. Therefore, there is more or less unconverted methanol should be recovered and reused in any process. Generally, methanol in glycerol phase is recovered by simple distillation; while methanol in FAME phase is removed from FAME by washing, rectification is used for methanol recovery, in which the energy consumption is much higher (Bouaid et al., 2005). From the energy-saving point of view, the distribution coefficient of methanol is an important factor.

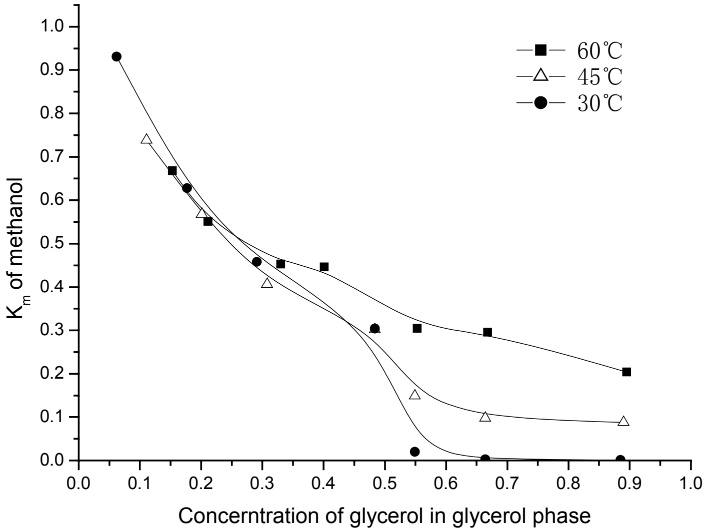

Figure 3. Distribution coefficient of methanol between FAME phase and glycerol phase

From Fig.3 it can be taken that the distribution coefficient (K_m) of methanol is temperature dependent. At a temperature of 30°C, unconverted methanol mostly existed in glycerol phase. It indicates that the hydrogen bonding between molecules of glycerol and methanol plays an important role in phase distribution. This phenomenon provides benefit for energy saving in methanol recovery, because simple distillation is enough for methanol-glycerol separation.

Comparison of one-stage process and multi-stage process. Preliminary studies for optimize the variables that effect the conversion rate of oil in heterogeneous reaction system was performed. Based on the result (data not shown) obtained in preliminary studies, we designed one-stage process. As shown in Fig.4, the reaction kinetics curve exhibited an S shape, in which the induced period lasted about 50min. It is indicated that the mass transfer limitation in heterogeneous system becomes a worse obstruct compared to those in homogeneous system. Increase the molar ratio of methanol to oil is an applicable measure to facilitate the reaction, but the energy consumption will increase at the same time. Concerning factors effecting the reaction rate, energy consumption and methyl ester yield, a multi-stage process was designed and evaluated as shown in Fig.5.

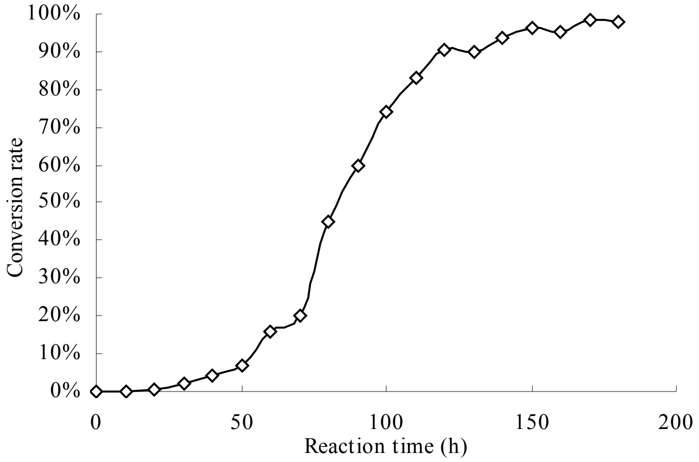

Figure 4. Reaction kinetics curve of one-stage process

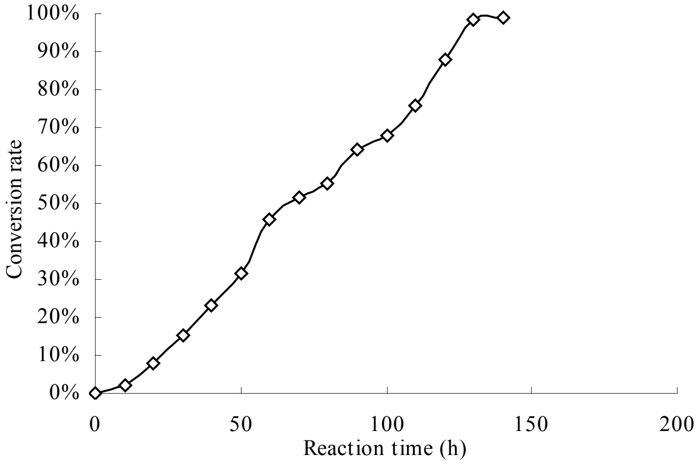

Figure 5. Reaction kinetics curve of multi-stage process

From the comparison of the reaction kinetics curve of each process, the multi-stage process shows several advantages as the following:

The reaction rate was increased. According to the kinetics curve, the induced period was reduced to 10min and the equilibrium time for reaction was reduced 40min.

The molar ratio of methanol to oil was reduced to 6:1; the unconverted methanol is mostly in glycerol phase. Therefore, the energy consumption for methanol recovery will be reduced.

The overall conversion rate of FAME will increased, it is due to the molar ratio of methanol to oil was reached about 30: 1 at the last stage of the process.

Conclusions

Temperature can affect solubility of oil in methanol and distribution of methanol between glycerol and FAME phase, it is a very useful parameter to enhance reaction or facilitate products separation. But at atmospheric pressure, the adjustable range is quite narrow. Multi-stage process provide another way to manipulate the reaction, different kinds of reversed flow can be chosen to change reaction balance or reaction rate, and to improve energy-saving. The multi-stage process in this study shows potential for industrial application.

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