Rapid Transesterification of Vegetable Oils with Phase Transfer Catalysts

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Introduction

Base-catalyzed transesterification of vegetable oils with methanol is not a homogeneous reaction, but is characterized by slow reaction rates at both the initial and final reaction stages [1]. The initial slow reaction rate is due to the immiscible nature of the reactants. The slow reaction rate at the final stage is due to catalyst extract by the immiscible and dense glycerol phase and the subsequent depletion of the catalyst from the reactants [1]. It was shown that either the use of cosolvent or methanol under supercritical conditions could reduce or eliminate the mass transfer limitation, resulting in fast transesterification [2, 3].

The use of phase transfer catalysts (PTCs) is another reasonable and promising approach to overcome mass transfer limitation during transesterification. A suitable phase transfer agent can facilitate the interphase transfer of species, making the reaction between reagents in two immiscible phases possible [4]. Most common PTCs are quaternary ammonium or phosphonium salts, crown ethers and cryptates [4]. Our goal was to find out whether transesterification could be accelerated by PTCs. PTCs with different anions and cations were compared. Individual operating variables such as the molar ratios of methanol/oil, total OH^-/oil, PTC/base catalyst and agitation including ultrasound were further investigated for transesterification with PTCs. Effects of these operating variables on transesterification with PTCs were highlighted. The total and free glycerol contents in the final products obtained from transesterification with effective PTCs were also analyzed in order to determine if glycerol specifications in the biodiesel standards could be met.

Materials and Methods

Base-catalyzed transesterification at moderate temperatures was carried out in a 500 mL three-neck flask equipped with a magnetic stirrer, a reflux condenser (to prevent methanol losses), a thermometer and a sampling port. The flask was immersed in an oil bath to keep reaction temperature constant throughout the reaction. Potassium hydroxide (KOH, reagent grade, ≥90%, flakes) and PTCs such as cetyltrimethylammonium bromide (CTMAB), 1.0 M tetrabutylammonium hydroxide solution in methanol (TBAOH), tetrabutylammonium acetate (TBAAc), tetrabutylammonium nitrate ($TBANO_3$), 40 wt% benzyltrimethylammonium hydroxide solution in methanol (BTMAOH) were purchased from Sigma-Aldrich Canada Ltd..

Results and Discussion

The effect of different PTCs, including CTMAB, TBAOH, TBAAc, BTMAOH, $TBANO_3$, was investigated for base (KOH) catalyzed transesterification of soybean oil. Methyl ester contents versus reaction time are plotted in Fig. 1. Figure 1 shows that PTCs such as CTMAB, TBAOH, TBAAc, BTMAOH and $TBANO_3$ increased transesterification rates especially at the initial stage of the reaction, i.e. the first 3 min. For example, 88.6 wt% ME was produced in 3 min transesterification without PTC. However, for base catalyzed transesterification assisted with $TBANO_3$, CTMAB, TBAOH, TBAAc and BTMAOH, ME formation in 3 min was 91.1, 94.6, 95.1, 96.1 and 96.3 wt%, respectively. For the cases of CTMAB, TBAOH, TBAAc and BTMAOH, ME contents were significantly increased.

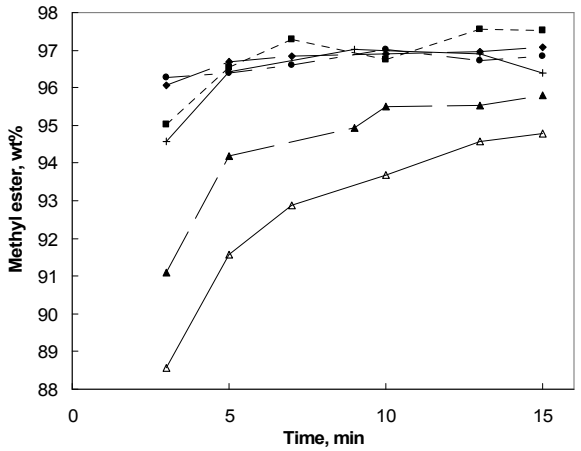

Figure 1. ME content as a function of reaction time with different PTCs (total molar OH^-/oil = 0.22, molar MeOH/oil = 6, 60°C, magnetic stirring 700 rpm. Δ KOH catalyzed transesterification without PTC, filled symbol KOH catalyzed transesterification with PTCs, molar PTC/KOH=1: ▲ $TBANO_3$, + CTMAB, ■ TBAOH, ♦ TBAAc and ● BTMAOH).

Investigation of different operating variables has shown that, similarly to transesterification without PTC, ME content increased with MeOH/oil and total OH^-/oil molar ratios. A higher final ME content was obtained with ultrasound compared to that with magnetic stirrer. An optimal molar ratio of PTC to base catalyst was determined as 1. The effect of PTC on transesterification rate depended not only on the structures of PTC cations but also those of PTC anions. Product analyses showed that ME content higher than 96.5 wt% was achieved after only 15 min of rapid transesterification (tetrabutylammonium hydroxide or tetrabutylammonium acetate as PTC, MeOH/oil molar ratio of 6, total OH^-/oil molar ratio of 0.22, PTC/KOH molar ratio of 1 and 60°C). Free and total glycerol contents in the final products from 15 min transesterification with PTC were lower than maximum allowed limits in the standard specifications for biodiesel.

References

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