

Transesterification of vegetable oil with potassium carbonate/active carbon catalyst

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Abstract

It is a hot topic of producing biodiesel with heterogeneous catalyst nowadays. Transesterification of oil with methanol using potassium carbonate/active carbon as catalyst, and the effects of catalyst dosage, methanol proportion, reaction time, etc., on the reaction were studied. The results showed that potassium carbonate/active carbon had strong catalysis for the transesterification of oil with methanol; potassium carbonate/active carbon could be reused by recovery. The transesterification rate could be above 98% by two-step transesterification.

Key words: grease; transesterification; solid catalyst; potassium carbonate/active carbon

1. Introduction

Transesterification with renewable animal and vegetable oils can attain mixture of fatty acid methyl esters and ethanol esters. The mixture is called biodiesel. Conventional synthesis techniques of biodiesel rely on homogeneous acid/base catalysts (Edgar et al., 2005). However, in the conventional homogeneous manner, removal of these catalysts is technically difficult and a large amount of wastewater is produced to separate and clean the catalyst and the product. To avoid the problem of products separation, it has been proposed to replace the homogeneous catalysts by a heterogeneous catalyst, suggesting that the production of alkyl esters will be simplified when heterogeneous catalysts are utilized.

Many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oil to prepare fatty acid methyl esters. For example, CsX zeolites, anionic clays, calcium carbonate rock, EST-10, Li/CaO and Na/NaOH/ γ -Al₂O₃ have been found to be efficient heterogeneous catalysts for the transesterification of vegetable oil (Kim et al., 2004). However, they are quite expensive or complicated to prepare, which limits their industrial application.

In this work, the potassium carbonate/active carbon catalyst was adopted for the production of biodiesel from rapeseed oil.

2. Experimental

2.1 Catalyst preparation

Active carbon, obtained from NanKai Gongyun Co. (Tianjin, China), was dried in 221 K for 1.5 h to remove the absorbed water on the surface. To prepare modified Potassium carbonate/active carbon catalysts with different K₂CO₃ loadings, the active carbon was impregnated with an aqueous solution of K₂CO₃. Samples with various K₂CO₃ loadings, given in weight percentage, were impregnated thoroughly on the surface of active carbon. The pretreated impregnated samples were dried in 221K and then heated in an oven at 932K for 5 h before use for the reaction. The loading amounts of K₂CO₃ were calculated on the basis of the amounts of the starting materials.

2.2 Transesterification procedure

Commercial edible grade oil was obtained from market and was refined again to reduce free fatty acid and water contents further. The transesterification reaction was carried out using different methanol/oil molar ratios and various amounts of catalyst. The mixture was stirred and refluxed for the required reaction time. After the reaction time finished, the mixture was filtered and the residual methanol was separated from the liquid phase via rotary evaporation prior to analysis.

For GC analysis, the reaction mixture, after methanol was removed completely, was washed three times with a saturated aqueous NaCl solution for removal of the formed glycerin. The separated organic phase was dried with anhydrous MgSO₄, and then submitted to GC analysis (Agilent, GC 6890). The conversion efficiency of the edible oil to methyl esters was determined by the content of the methyl esters.

3 Results and discussion

3.1 Influence of loading amount of K_2CO_3 on the conversion

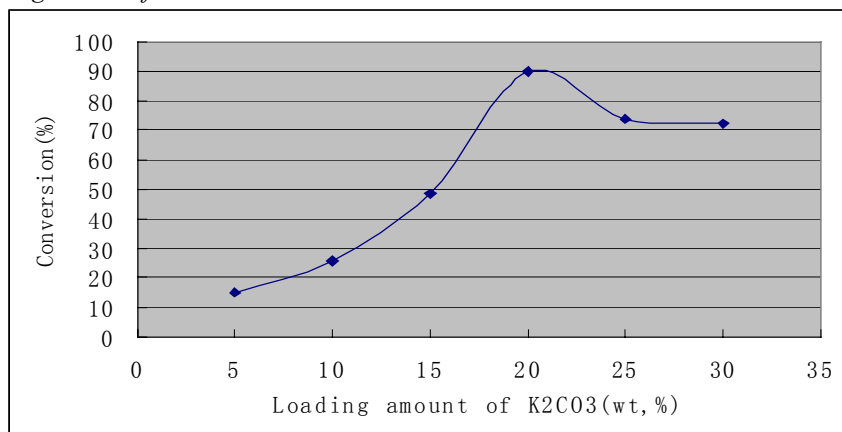


Fig. 1. Influence of loading amount of K_2CO_3 on the conversion.

Reaction conditions: methanol/oil molar ratio 8:1, catalyst amount 5 wt.%, reaction time 5 h and reaction temperature 158 K.

The dependence of the activity of K_2CO_3/C catalysts on the loading amount of K_2CO_3 was investigated. The results are shown in Fig. 1. As expected, the active carbon did not present any particular catalytic activity, most likely due to the lack of strong basic sites on which the transesterification reaction could occur. However, loading of K_2CO_3 onto the active carbon produced a dramatic increment of basic strengths on the K_2CO_3/C catalyst as mentioned previously, and due to this, resulting in an increase in the conversion to methyl ester (Fig. 1). Thus, the production of biodiesel in the reaction of vegetable oil with methanol needed strong basic sites. As shown in Fig. 1, when the loading amount of K_2CO_3 increased, the conversion increased and the highest conversion of 85.6% was registered at loading of 20%. However, when the loaded K_2CO_3 was over 20%, the conversion decreased. It was very likely that the amount of loaded K_2CO_3 higher than 20% resulted in the agglomeration of the active K_2CO_3 phase or the cover of basic sites by the exceeded K_2CO_3 , hence lower the surface areas of active components and lower the catalytic activity.

3.2 Influence of methanol/oil molar ratios on the conversion

Fig. 2 shows the effect of methanol/oil molar ratios on the conversion. By increasing the amount of loading methanol, the conversion of vegetable oil increased considerably. When the methanol/oil molar ratio was very close to 6:1, the conversion reached the maximum value of 91.56%. However, beyond the molar ratio of 8:1, the excessively added methanol had no significant effect on the conversion. Therefore, the optimum molar ratio of methanol/oil to produce methyl esters was approximately 8:1. However, it has been found that the methanol/oil molar ratio of 6:1 could give the best conversion when the transesterification reaction was carried out using conversional homogeneous catalysts such as NaOH and KOH. Generally, homogeneous catalysts have higher activities than heterogeneous catalysts. However, recent studies on the transesterification of vegetable oil with methanol in the presence of ETS-10 zeolite, and metal catalysts (Suppes et al., 2004) showed that heterogeneous catalysts containing occluded reactor gave >90% conversion at 393 K in 24 h with 6:1 molar ratio of the oil to methanol, and that ZnO gave the highest conversion of 80% at 393 K in 24 h among the metal catalysts.

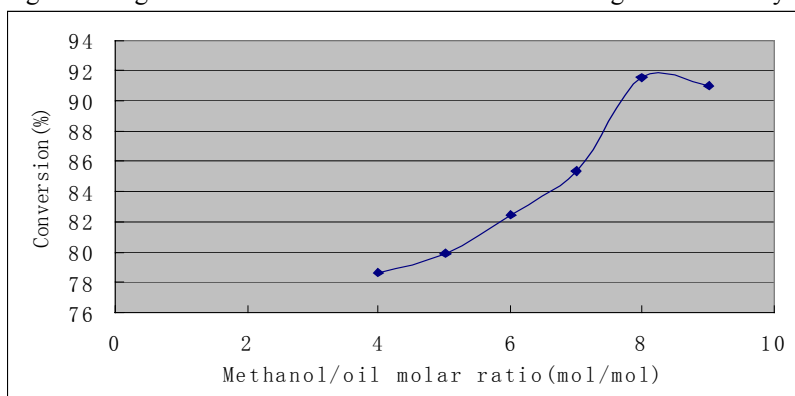


Fig. 2. Influence of methanol/oil molar ratios on the conversion.

Reaction conditions: catalyst amount 5 wt.%, reaction time 5 h and reaction temperature 158 K.

3.3 Influence of catalyst amount on the conversion

The effect of the catalyst amount was studied. The catalyst amount was varied in the range of between 1.0% and 6.0%,

the percent was weight ratio of catalyst/starting oil. Fig 3 showed that the transesterification reaction was strongly dependent upon the amount of catalyst applied. The transesterification procedure did not occur without addition of a catalyst, and the presence of the K_2CO_3/C catalyst really increased the reaction rate. Increased catalyst amount from 1% to 5% resulted increased conversion of methyl esters (from 37.65% to 89.46%). However, with the increasing in the catalyst amount, the conversion was decreased, which was possibly due to the rise of a mixing problem of reactants, products and solid catalyst.

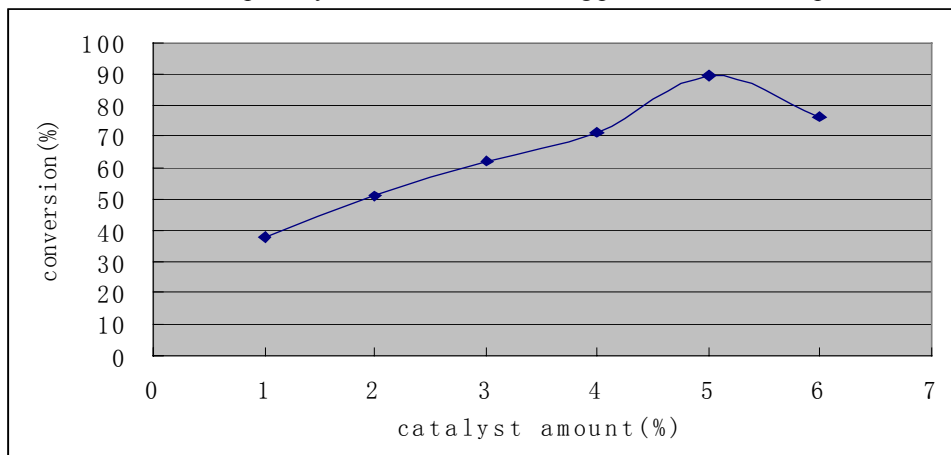


Fig. 3. Influence of catalyst amount on the conversion

Reaction conditions: methanol/oil molar ratio 8:1, reaction time 5 h and reaction temperature 158 K.

In order to study the stability of K_2CO_3/C catalyst, the separated catalyst was reused without activation treatment, the conversion was 62.01%

3.4 Influence of reaction time on the conversion

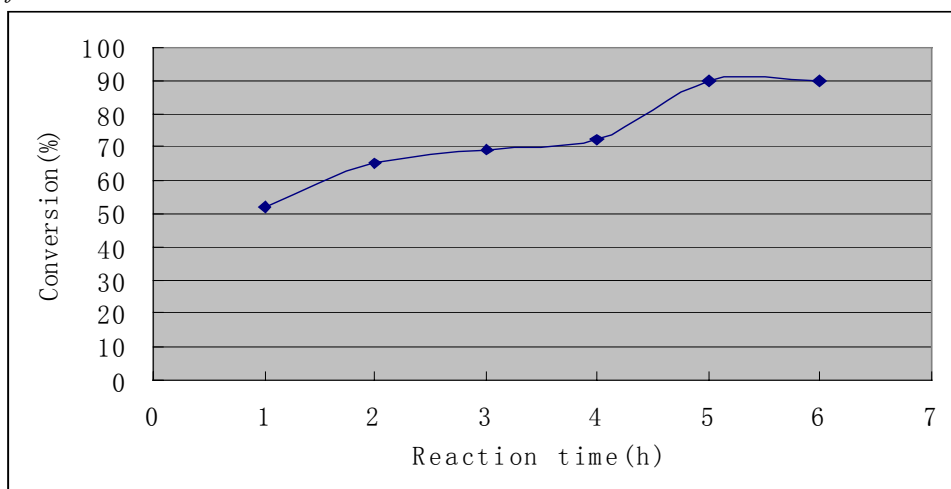


Fig.4. Influence of reaction time on the conversion.

Reaction conditions: methanol/oil molar ratio 8:1, catalyst amount 5 wt.% and reaction temperature 158 K.

Fig 2 illustrates the change of the conversion as a function of reaction time. The optimum reaction time for the production of biodiesel was determined by performing reactions at varying reaction time. For the same reaction conditions, the conversion increased in the reaction time range from 1 h to 6 h, when the reaction time reached 5 h, the conversion rate was the best (90.13%). Therefore, 5 h reflux of methanol was considered as optimum reaction time.

The effect of mixing played an important part in the transesterification reaction. The reaction was carried out at two randomly chosen stirring speeds (300rpm and 600rpm). At lower stirring speed, the oil conversion reached 58.6% after 5 h of reaction, whereas at 600 rpm the oil conversions. The result showed that an efficient mixing of the reagents was essential to reach a high conversion of the oil.

3.5 Influence of stability of catalyst on the conversion

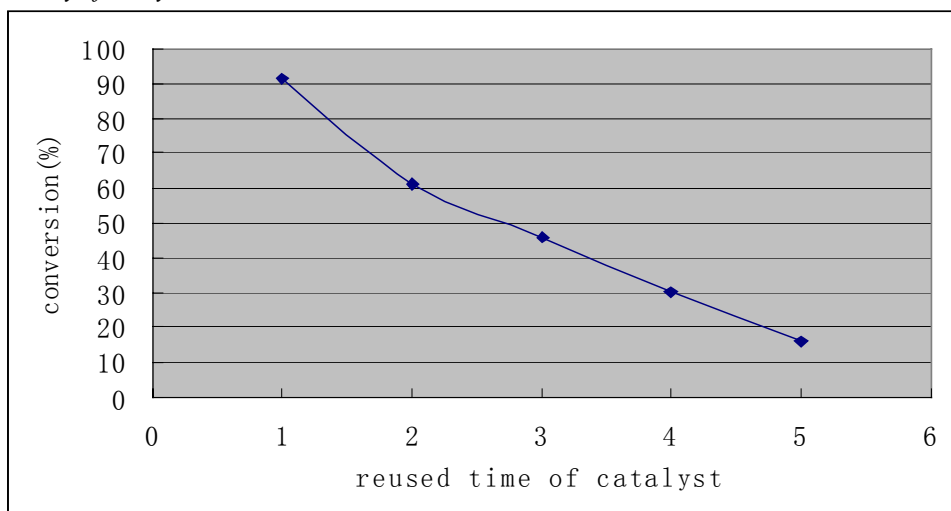


Fig.5. Influence of stability of catalyst on the conversion.

Reaction conditions: catalyst amount 5%, reaction time 5 h, reaction temperature 158 k and methanol/oil molar ratio 6:1.

In order to study the stability of K_2CO_3/C catalyst, it was reused by separating the catalyst without activation treatment. The result showed that the conversion decreased greatly after the first transesterification reaction. Hence, the solid catalyst must be activated after it was used. The treatment process is generally that washing it thoroughly with organic impregnant and heating in an oven for 2 h at 398 k.

4. Conclusion

The loading of K_2CO_3 on the active carbon resulted in an increase in the basic strength over the active carbon, and the supported catalyst can easily be separated and reused after time. After being loaded with K_2CO_3 , the pore structure of active carbon, necessary for catalysis could be retained. This approach was successfully used in an attempt to increase the catalytic activity of solid catalyst towards the transesterification reaction.

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