

Investigation of Biodiesel Production from Canola Oil Using Amberlyst-26 as a Catalyst

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The transesterification of canola oil to fatty acid methyl esters was studied using Amberlyst-26 as a solid catalyst. The influence of reaction conditions, such as the reaction time, methanol to oil molar ratio, amount of catalyst, effect of co-solvent, and alcohol and oil types, were determined. When the reaction was carried out at 45 °C with a canola oil to methanol molar ratio of 6:1, a reaction time of 1.5 h, and 3 wt.% of catalyst, oil conversion was about 67%. Methanol was much more reactive than ethanol and isopropyl alcohol (IPA) in the transesterification reaction. The conversion of canola oil did not change much with the addition of tetrahydrofuran (THF) as a co-solvent; however, in the presence of n-hexane as a co-solvent in the reaction mixture, the conversion of canola oil decreased. Canola oil had the highest conversion among the other oils used, including sunflower and corn oils. All the results suggest that Amberlyst-26 cannot serve as an economical solid catalyst for the high-yield production of biodiesel from canola oil.

Key Words: Biodiesel, heterogeneous catalyst, Amberlyst-26.

Introduction

Biodiesel synthesized via transesterification of oils and fats from plant and animal sources is a realistic alternative to diesel fuel because it is made from renewable resources and has lower emissions than petroleum diesel. It is biodegradable and contributes a minimal amount of net greenhouse gases or sulfur to the atmosphere. The transesterification process combines the oil with an alcohol, usually methanol.¹ Transesterification can be catalyzed by both acids and bases. Homogeneous base catalysts, including sodium or potassium hydroxides or alkoxides, are used for industrial applications. Base catalysts are preferred to acid catalysis such as sulfuric

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or sulfonic acids given the corrosiveness and lower activity of the latter;^{2,3} however, with this conventional method removal of these catalysts is technically difficult and a large quantity of waste water is produced while separating and cleaning the catalyst and the product. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts, primarily because of environmental constraints and the simplification of existing processes.⁴

Many types of heterogeneous catalysts, such as alkaline earth metal oxides and various alkaline metal compounds supported on alumina or zeolite, can catalyze transesterification reactions. For example, Kim et al.⁵ prepared a solid superbase of Na/NaOH/ γ -Al₂O₃ that had almost the same catalytic activity under optimized reaction conditions as a conventional homogeneous NaOH catalyst. Xie et al.⁶ achieved conversion of 87% when the reaction of methanol was carried out at reflux for the transesterification of soybean oil using KNO₃/Al₂O₃ as a solid-base catalyst. Wang et al.⁷ reported that the yield of biodiesel produced with SrO as a catalyst was in excess of 95% within 30 min at temperatures below 70 °C. Reddy et al.⁸ produced biodiesel using nanocrystalline CaO under room temperature; however, the reaction rate was slow and it took 6-24 h to obtain high conversion with their most active catalyst. They also observed deactivation after 8 cycles with soybean oil and after 3 cycles with poultry fat. Lopez et al.⁹ achieved 80% conversion of triacetin (a model compound for larger triglycerides found in vegetable oils and fats) after 8 h with Amberlyst-15 at a loading of 2 wt.%, with the reaction carried out under otherwise identical reaction conditions. Vicente et al.¹⁰ utilized ion-exchange resins (anionic Amberlyst-A26 and A27 and cationic Amberlyst-15) for the transesterification of sunflower oil and methanol, but conversion was less than 1% with each resin.

Amberlyst-26 is used to catalyze reactions such as aldol condensation in which a strong basic catalyst is required. It is also used to remove anionic transition metal complexes and mercaptans from hydrocarbons, in addition to removing acids from hydrocarbons and other non-polar solvents, as well as oleic acid from chlorinated hydrocarbons, and to de-acidify phenol-acetone solutions. Its porous structure makes it a good polymeric catalyst in non-aqueous and aqueous media, and it has no pH limitations.¹¹ Amberlyst-A26 OH is a strong base type 1 anionic macroreticular polymeric resin based on a crosslinked styrene divinylbenzene copolymer that contains quaternary ammonium groups.¹² The functional group was given as $-N(CH_3)_3^+$. The declared exchange capacity (meq/g) was reported as 4.4.¹³

In the present study the transesterification of canola oil with methanol was studied in a heterogeneous system, using Amberlyst-26 as a super base catalyst. The effect of the reaction time, methanol to oil molar ratio, amount of catalyst, co-solvent, and alcohol and oil types was investigated.

Experimental

Commercial edible grade canola oil was obtained from a market. A 250-cm³ 3-necked glass flask with a water-cooled condenser was charged with 50 g of canola oil, different volumes of anhydrous alcohol, and various amounts of Amberlyst-26 catalyst.

The reaction procedure was as follows: after dispersion of the catalyst in alcohol the oil was added with stirring and the mixture was heated to 45 °C. As shown in the Table, Amberlyst-26 has an upper temperature limit of 60 °C. In order to prevent decomposition of the catalyst a reaction temperature of 45 °C was chosen. All of the experiments were performed under atmospheric pressure. After the reaction the solid catalyst was

separated by filtration. The liquid was put into a separating funnel and was kept at ambient temperature for 24 h, after which 2 liquid phases appeared. The upper layer was biodiesel and the lower layer was glycerol. The conversion of canola oil was calculated from the quantity of total glycerol in the product. The procedure was carried out according to the AOCS Official Method Ca 14-56. Conversion was not affected by the rate of rotation of the stirrer (range: 400-1000 rpm) and the mixing rate was kept constant at 1000 rpm. All data points reported were reproduced in triplicate and 95% confidence intervals, determined according to Student's t-distribution are reported.

Table. Physical properties of Amberlyst-26 resins.¹¹

Shape	Surface area	Pore size	Temperature limit	Particle size
Beads	~ 30 m ² /g	0.30 mL/g pore volume 400 Å mean pore size	60 °C	16-45 mesh (350-1200 μm)

Results and Discussion

The conversion of canola oil was investigated at room temperature and at 45 °C. No reaction occurred when the reaction was performed at room temperature. Although as previously mentioned Amberlyst-26 has an upper temperature limit of 60 °C; in order to prevent decomposition of the catalyst 45 °C was chosen as the reaction temperature.

The dependence of canola oil's conversion on reaction time was studied over an Amberlyst-26 catalyst at 45 °C. The reaction time varied between 0.5 and 8 h, and included 7 different reaction times used with different batches. As can be seen from Figure 1, conversion increased with reaction times between 0.5 and 1.5 h; however, as the reaction time increased (from 1.5-8 h) conversion decreased to 63% and remained unchanged after 4 h. The transesterification process consisted of a sequence of 3 consecutive and reversible reactions. This may have been due to the reversibility of the transesterification reaction. The highest conversion of canola oil (66.67%) was obtained after 1.5 h of reaction. The standard error was calculated in order to represent uncertainty in our measurements. Based on 3 measurements, y-error bars are also represented on the graph. The standard error was ± 0.07-0.12. Almost 60% conversion of canola oil was obtained within the first 30 min.

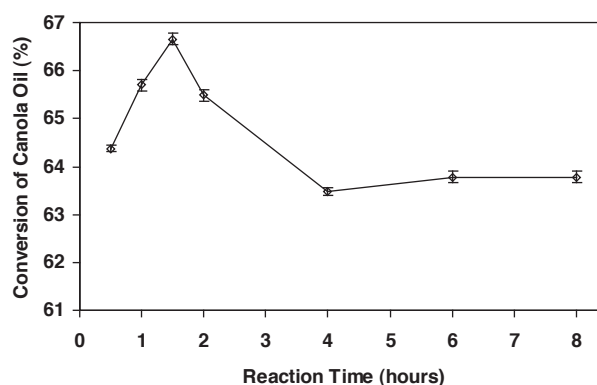


Figure 1. Conversion of canola oil as a function of reaction time. Reaction conditions: methanol/oil molar ratio, 6:1; amount of catalyst, 3 wt.%; temperature, 45 °C.

The methanol to canola oil molar ratio is an important factor that affects the conversion of canola oil. Stoichiometrically, 3 moles of methanol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to drive the reaction towards completion and produce more methyl esters as products. Figure 2 shows the effect of the methanol/oil molar ratio on the conversion; by increasing the amount of loading methanol the conversion decreased. The highest conversion rate (66.67%) was achieved with a molar ratio of 6:1; however, beyond the molar ratio of 6:1, as methanol loading increased, conversion decreased. It should be indicated that the weight concentration of the catalyst, based on the oil, was kept constant at 3 wt.% in all the experiments, because the catalyst content decreased as the methanol content increased. The transesterification reaction is an equilibrium-limited reaction, and a backward or forward reaction can be favorable, depending on the composition of the reaction mixture during the reaction period. This phenomenon has also been reported by other researchers.¹⁴

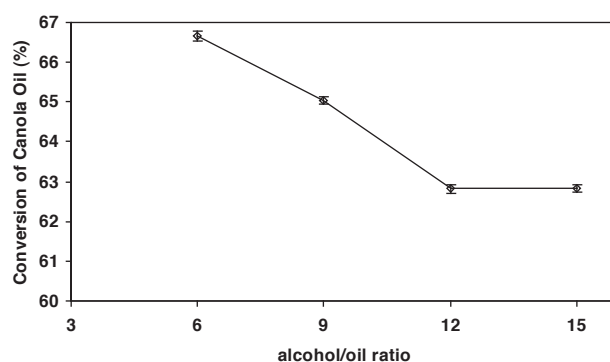


Figure 2. Conversion of canola oil as a function of the methanol/oil molar ratio. Reaction conditions: amount of catalyst, 3 wt.%; temperature, 45 °C; reaction time, 1.5 h.

The effect of the quantity of catalyst on the conversion of canola oil was investigated. The weight concentration of the catalyst, based on the oil, ranged between 1.5 wt.% and 6 wt.%. The reaction profiles shown in Figure 3 indicate that the conversion of canola oil first increased with an increase in the quantity of catalyst from 1.5 wt.% to 3 wt.%; however, with additional increases in the quantity of catalyst conversion decreased, which was possibly due to problems associated with mixing the reactants, products, and solid catalyst in such a heterogeneous system. At 3 wt.% of catalyst, conversion of up to 66.67% was obtained.

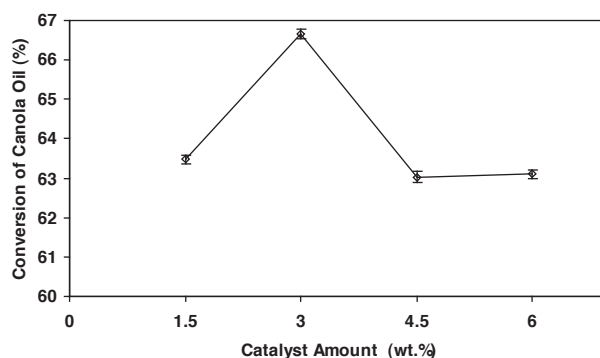


Figure 3. Conversion of canola oil as a function of the amount of catalyst. Reaction conditions: reaction time, 1.5 h; methanol/canola oil molar ratio, 6:1; temperature, 45 °C.

Methanol, ethanol, and IPA were compared to determine the effects of different types of alcohol on the transesterification of canola oil. As shown in Figure 4, the highest conversion of canola oil was obtained when methanol was used in the transesterification reaction; ethanol and IPA resulted in lower rates of canola oil conversion. These results suggest that steric effects control these catalytic activities.

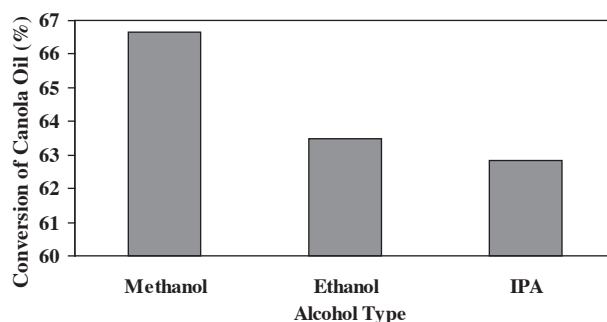


Figure 4. Conversion of canola oil as a function of alcohol type. Reaction conditions: amount of catalyst, 3 wt.%; reaction time, 1.5 h; alcohol/canola oil molar ratio, 6:1; temperature, 45 °C.

Generally, a co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact between the reactants. In order to conduct the reaction in a single phase, co-solvents like THF and n-hexane were tested. As shown in Figure 5, under the same conditions the conversion of canola oil did not change with the addition of THF as a co-solvent. In the presence of n-hexane as a co-solvent in the reaction mixture, conversion of canola oil decreased. The transesterification process consists of a sequence of 3 consecutive and reversible reactions, transforming the triglyceride into a diglyceride, then into a monoglyceride, and finally into glycerin and fatty acid methyl esters. Because the co-solvents did not effectively homogenize the methanol and oil phase, they did not increase the rate of formation of mono and diglyceride intermediates.

Canola, sunflower, and corn oils were compared in terms of their effects on transesterification. As shown in Figure 6, the highest conversion was obtained when canola oil was used in the transesterification reaction.

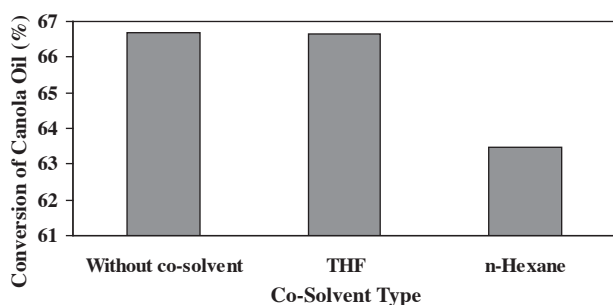


Figure 5. Conversion of canola oil as a function of co-solvent type. Reaction conditions: amount of catalyst, 3 wt.%; reaction time, 1.5 h; alcohol/canola oil molar ratio, 6:1; temperature, 45 °C; co-solvent content, 10 wt.%.

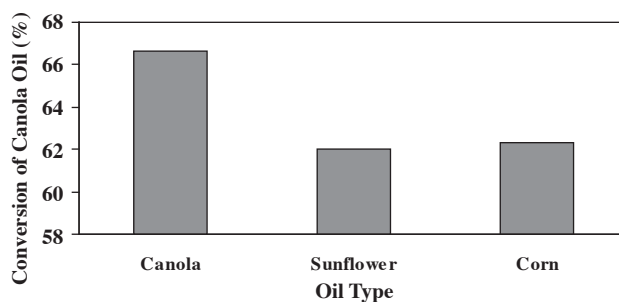


Figure 6. Conversion of canola oil as a function of oil type. Reaction conditions: amount of catalyst, 3 wt.%; reaction time, 1.5 h; alcohol/oil molar ratio, 6:1; temperature, 45 °C.

Conclusions

The transesterification of canola oil with methanol in a heterogeneous system using Amberlyst-26 as a catalyst was studied. The effect of the reaction time, methanol to oil molar ratio, and amount of catalyst, as well as co-solvent, alcohol, and oil types was investigated. Our results show that methanol was the best alcohol for this reaction condition and the use of THF and n-hexane as co-solvents decreased product yield. Using sunflower and corn oils resulted in lower conversion than was obtained with canola oil. The highest triglyceride conversion (66.67%) was achieved after 1.5 h of reaction at 45 °C, with a 6:1 molar ratio of methanol to canola oil and 3 wt.% of catalyst. It was concluded that Amberlyst-26 cannot serve as an economical solid catalyst for the high-yield production of biodiesel from canola oil with methanol.

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