# **Base Catalyzed Glycerolysis of Benzyl Acetate**

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Received February 15, 2011: Revised March 17, 2011: Accepted May 17, 2011

**Abstract:** Glycerol was successfully used as a green solvent and as an acyl acceptor in the transesterification of benzyl acetate using representatives' soluble and solid base catalysts. It was found that increasing the reaction temperature, the reaction time, the substrate concentration or the catalysts loading increased the yield of benzyl alcohol. Using glycerol as a solvent also enabled the separation of product by simple extraction with diethyl ether and catalyst recycling.

Keywords: Base catalyst, glycerol, green solvent, transesterification.

## **1. INTRODUCTION**

The hydrolysis of esters is a basic organic transformation [1, 2]. Traditionally, the reaction is performed in an acidic or basic aqueous solution under mild conditions yielding the corresponding carboxylic acid and alcohol. Alternatively, due to low miscibility of most esters in water and since acidic or basic conditions lead to equipment corrosion, catalytic transesterification of ester in the presence of an alcohol that removes the carboxylic group from the ester and releases the corresponding alcohol (alcoholysis) was also extensively studied. The alcoholysis of ester is an equilibrium reaction, which usually requires excess amounts of alcohol to yield high conversion, and the presence of catalyst that can be either homogenous or heterogeneous [3-5]. Solid acids and bases as well as immobilized lipase are often employed for this purpose as they have the advantage of being easily separated from the reaction mixture, recycled and reused.

Various alcohols can be employed for the alcoholysis of an ester. We recently showed that glycerol can be successfully used as both a solvent and an acyl acceptor in the kinetic resolution of ester racemates via transesterification using immobilize Candida antarctica lipase B (CAL-B) as a catalyst [6]. Glycerol triacetate (triacetin) was also used simultaneously as a solvent and an acyl donor in the kinetic resolution of racemic mixture of alcohols and in the production of isoamyl acetate, a characteristic banana flavor ester used in the food industry, via teansesterification, using CAL-B or acidic ion exchange as a catalyst [7, 8]. Besides its green character, the use of triacetin allowed easy product work-up and catalysts recycling. Both, glycerol and triacetin are renewable, recyclable and nontoxic green solvents that can be used as an alternative reaction medium for various organic reactions [9-11].

In this paper we report on our study about the glycerolysis of benzyl acetate, using sodium hydroxide and magnesia as representative soluble and solid base catalysts, using glycerol as a green solvent and as an acyl acceptor (Fig. 1). The effects of reaction conditions and catalyst type and loading on benzyl alcohol yield were studied. In addition, product separation procedure and catalyst recycling were also examined.

## 2. EXPERIMENTAL

In a typical procedure, 0.1 g of benzyl acetate was added together with 0.01 g of catalyst to a vial with 5 g of alcohol (all purchased from Aldrich). The mixture was placed in a preheated oil bath and heated to the required temperature (45-100 °C) after which it was magnetically stirred for 1-5 h. At the end of the reaction, the reaction mixture was cooled and extracted with  $3 \times 10$  mL diethyl ether. The organic phase was concentrated under reduced pressure, and the resulting crude product was analyzed by GC analysis using an HP-5 column (30 m × 0.25 mm, 0.25 µm thick).

Two catalyst recycling methods were tested. The first reaction cycle in both methods was run as follows: 1 g of benzyl acetate and 0.1 g of solid catalyst were added to a vial with 10 g of glycerol. The vial was then heated at 75 °C for 1 h. For the first catalyst recycling method, the catalyst was filtrated at the end of the reaction and the product was extracted by  $5\times10$  mL diethyl ether and analyzed by GC. The filtrated catalyst was then added to a fresh mixture of benzyl acetate in glycerol, and the reaction was repeated. For the second method, the product was extracted by  $5\times10$  mL diethyl ether from the glycerol-catalyst mixture without the filtration of the catalyst, to which was added fresh benzyl acetate.

Microwave assisted reactions were conducted at atmospheric pressure in a domestic microwave (Crystal WP900, 900W) in a vial, which was covered with a watch glass. The substrate was dissolved in 5 g glycerol followed by addition of the catalyst. After the vial was covered with the watch glass, the reaction mixture was heated in the microwave oven at low intensity from 26 °C to 56 °C for duration of 40 s and at full intensity from 26 °C to 61 °C for 5 s. At the end of the reaction the vial was cooled to room temperature in ice, and the reaction mixture was extracted with petroleum ether for GC analysis.

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Fig. (1). Transesterification of benzyl acetate in glycerol.

### **3. RESULTS AND DISCUSSION**

The synthesis of benzyl alcohol is usually produced *via* synthesis of benzyl chloride by chlorination of toluene that is then hydrolyzed under alkali conditions [12, 13]. This multistage process includes many steps of separation and purification after the respective reactions. Thus it is not advantageous economically and environmentally. Moreover, the hydrolysis step requires an excess amount of alkali base resulting in a large amount of a salt solution contaminated with organic compounds that has to be treated. However, benzyl alcohol can also be produced by oxyacetoxylation from toluene, acetic acid, and oxygen to benzyl acetate followed by hydrolysis of the ester. As ester alcoholysis can be accomplished using heterogeneous acids and bases and alcohol as an acyl acceptor it is more favored to avoid byproduct salts formation as in aqueous hydrolysis [14, 15].

As previously mentioned, esters can be alcoholized through transesterification using alcohol, which can simultaneously be used as a solvent and as an acyl acceptor, using various homogeneous and heterogeneous catalysts [3-5]. Hence, the investigation began by testing the progress of benzyl alcohol yield with time in glycerol in several temperatures (Fig. 2). In general, as expected, increasing the reaction time or temperature in the range of 1-5 h and 45-100 °C respectively, increased the product yield. Yet, it can be seen from the results in Fig. (2) that increasing the temperature behind 75 °C did not significantly change the product yield. At the end of the reaction, benzyl acetate was easily separated from the reaction mixture by simple extraction with diethyl ether. As glycerol was used as both a solvent

and an acyl acceptor it may yield glycerol monoacetate, glycerol diacetate, and/or triacetin as by-products. However, the high boiling points and high solubilities of these potential by-products in glycerol allow the product to be easily separated from the reaction mixture.

Magnesia is commonly used solid base catalyst. It is well known that the basic sites on magnesia surface adsorb oxygen and moister from air that affect catalytic performance. Hence, the effect of pretreatment temperature and time on magnesia performance in the transesterfication of benzyl acetate was first examined (Fig. 3). As illustrated in Fig. (3), both pretreatment time and temperature affect the product yield, and increase in oven temperature decreases the required time to release the adsorbed molecules and activate the basic sites on the surface, thereby increasing the product yield. Therefore, based on energy efficiency measurements, the catalyst was preheated at 300 °C for 2 h for all subsequent experiments of the study.

The progress of benzyl alcohol yield with time in glycerol in several temperatures was also studied over magnesia (Fig. 4). As previously detected with NaOH, increasing either the reaction temperature or the reaction time increased the yield of benzyl alcohol, and again, at temperature above 75 °C the effect of temperature was negligible after 2 h. As the active sites of the two representatives' homogeneous and heterogeneous catalysts are different by strength and amount the comparison of the performance of the two catalysts was done on equal mass basis. It was found that the soluble base is more active than the solid base and using NaOH yielded 37% yield after 1 h at 55 °C while employing MgO required



Fig. (2). Effect of reaction temperature on the reaction progress with time of benzyl acetate in glycerol using NaOH as catalyst. Reaction conditions: 0.1 g benzyl ester, 0.01 g NaOH, 5 g glycerol. ( $\blacklozenge$ ) 45°C; ( $\blacksquare$ ) 55°C; ( $\blacktriangle$ ) 100°C.



Fig. (3). Effect of MgO activation conditions on the yield of benzyl acetate in glycerol. Reaction conditions: 0.1 g benzyl ester, 0.01 g MgO, 5 g glycerol. ( $\diamond$ ) 80°C; ( $\blacksquare$ ) 300°C; ( $\bigstar$ ) 450°C.



Fig. (4). Effect of reaction temperature on the reaction progress with time of benzyl acetate in glycerol using MgO as catalyst. Reaction conditions: 0.1 g benzyl ester, 0.01 g MgO, 5 glycerol. ( $\blacklozenge$ ) 45°C; ( $\blacksquare$ ) 55°C; ( $\bigstar$ ) 75°C; (x) 100°C.

75 °C to reach 33 % yield after an hour. Yet, though the performance of the soluble base was higher than this of the solid one, solid catalyst is advantageous from industrial point of view, as it can be easily separated from the reaction mixture by filtration and recycled.

Increasing the substrate to catalyst ratio (S/C), by either increasing benzyl acetate amount or decreasing MgO loading, increased the initial reaction rate, which was calculated by the amount of reacted substrate per g of catalyst divided by reaction time (Fig. 5).

The recycling of magnesia was also tested using two different methods: running the first reaction cycle and filtration of the catalyst that was subsequently employed in second cycle with fresh benzyl acetate and glycerol, or running the second catalytic cycle by extraction of the product from the glycerol-catalyst mixture without the filtration of the catalyst, to which was added fresh benzyl acetate (Table 1). Thus, to test the viability of MgO reuse, the first reaction cycle was run for 1h at 75 °C after which the catalyst was filtrated and the product and the residual substrate were fully extracted by diethyl ether (Table 4, entry 1). After the first reaction cycle, the catalyst was filtrated and added to a fresh mixture of benzyl acetate in glycerol and the reaction was run again under similar conditions. Two cycles of catalyst reuse were done by this method resulting in a small decrease of yield in each cycle (Entries 2 and 3), probably due to the catalyst lost during recycling procedure. Since glycerol was used both as a solvent and an acyl acceptor, recycling of the glycerol together with the heterogeneous catalyst was also



Fig. (5). Effect of S/C on initial reaction rate in the transesterification of benzyl acetate in glycerol using MgO as catalyst. Reaction conditions: 0.1 g benzyl ester, 0.01 g MgO, 5 g glycerol,  $75^{\circ}$ C, 1h.

tested by extraction of the product and the residual substrate from the glycerol-MgO mixture with diethyl ether followed by the addition of fresh benzyl acetate. This recycling procedure yielded similar product yield as the first reaction cycle (Table 1, entries 4 and 5), supporting our previous assumption that the loss of catalyst during filtration was the reason for the decrease in the product yield in the former recycling procedure.

 Table 1.
 Recycling of MgO in the Glycerolysis of Benzyl Acetate<sup>a</sup>

Entry	Procedure	Conversion
1	First cycle	33
2	Second cycle of the catalyst, fresh glycerol	27
3	Third cycle of the catalyst, fresh glycerol	25
4	Second cycle of the catalyst and glycerol <sup>b</sup>	32
5	Third cycle of the catalyst and glycerol <sup>b</sup>	32

<sup>a</sup>Reaction conditions: 1 g benzyl acetae, 0.1 g MgO, 10 g glycerol, 75 °C, 1 h. Catalyst seperation by filtration and product extraction by diethyl ether. <sup>b</sup>Recycling of the glycerol-MgO mixture after extraction of the product without previ-

"Recycling of the glycerol-MgO mixture after extraction of the product without previous separation of the catalyst.

Finally, microwave-promoted heating was recently reported to enhance organic reactions, including the hydrolysis of esters, relative to conventional heating [16-18]. Thus, using an unmodified home microwave, the transesterification of benzyl acetate in glycerol under microwave irradiation was also tested in an open reaction vessel with MgO as the catalyst. Heating the reaction mixture for up to 40 s at low intensity (from 26 °C to 56 °C) or for 5 s at high intensity (from 26 °C to 61 °C) resulted in 23 % yield, while under conventional heating at 55° C for 1 h the yield was 27%. It seems that glycerol that has high dielectric constant and three hydroxyl groups adsorbs microwave irradiation efficiently [18]. Furthermore, the markedly low vapor pressure and high boiling temperature of glycerol make it an attractive solvent

for microwave-promoted organic synthesis under atmospheric pressure [10].

## 4. CONCLUSIONS

Glycerol can be successfully used as a green solvent and an acyl acceptor in the transesterification of benzyl ester to benzyl alcohol by using soluble and solid base. Using glycerol in the reaction facilitated efficient separation of the product from the catalyst and recycling of the catalyst, and it allowed the conventional heating method to be replaced with the more efficient microwave-promoted heating. The yield of benzyl alcohol was increased by increasing the reaction time and the temperature while maintaining the loading of the catalyst. Heating the reaction in an unmodified home microwave instead of using conventional heating resulted in higher reaction rate.

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