Acid catalysed transesterification of benzyl acetate in glycerol

ADI WOLFSON*, SHAI NAIM, CHRISTINA DLUGY, DORITH TAVOR

*Corresponding author
Green Processes Centre, Chemical Engineering Department, Sami Shamoon College of Engineering, Bialik/Basel Sts., Beer-Sheva, 84100 Israel

KEYWORDS
Glycerol; transesterification; acid catalyst; green solvent.

ABSTRACT
The acid catalysed alcoholysis of benzyl acetate was successfully performed in glycerol that was simultaneously used as a green solvent and as the acyl acceptor. Both soluble and solid acid were employed, and it was found that increasing either the reaction temperature and time or substrate concentration and catalyst loading increased the conversion of benzyl alcohol. Using glycerol as the solvent also enabled the separation of product by simple extraction with diethyl ether, catalyst recycling, and microwave-promoted reactions.

INTRODUCTION
Benzylic alcohol, a valuable organic solvent and bacteriostatic preservative agent, is traditionally produced by the hydrolysis of benzyl chloride under alkali conditions (1, 2). As hydrolysis usually requires an excess amount of alkali base that produces a correspondingly large amount of waste, alternative benzyl alcohol production routes have been investigated. One such alternative is the oxyacetoxylation of toluene with acetic acid and oxygen that produces benzyl acetate (3, 4), which can then be hydrolyzed to benzyl alcohol in a more environmentally benign fashion by transesterification (alcoholysis) using homogeneous and heterogeneous catalysts (5-7). Traditionally, the reaction has been performed in an acidic or basic aqueous solution under mild conditions to yield the corresponding carboxylic acid and alcohol. But because of the low miscibility of most esters in water and equipment corrosion due to the acidic or basic conditions, catalytic transesterification of the ester in the presence of an alcohol, which removes the ester’s carboxylic group and releases the corresponding alcohol, i.e., alcoholysis, was also reported (5-7). Because alcoholysis of an ester is an equilibrium reaction, it requires excess alcohol to achieve a high conversion. We recently reported that glycerol can be used as both the solvent and the acyl acceptor in a green protocol for ester transesterification (8). Likewise, glycerol triacetate (triacetin) was also used simultaneously as solvent and acyl donor in the kinetic resolution of racemic mixtures of alcohols (8) and in the production of isomyl acetate, a characteristic banana flavour ester used in the food industry, using CAL-B or acidic ion exchange (Amberlist-36) as catalysts (9, 10). Both glycerol and triacetin are renewable, recyclable, nontoxic green solvents that have been used successfully as alternative reaction media in organic reactions (11-13). Besides their green characters, the use of glycerol and triacetin facilitated product work-up and catalyst recycling. In this paper we report on our study of the transesterification of benzyl acetate to benzyl alcohol in glycerol using sulfuric acid and Amberlist-36 as the representatives soluble and solid acid catalysts, respectively (Figure 1). We investigated the effects of reaction conditions, catalyst type and loading, product separation procedure, and catalyst recycling on benzyl alcohol conversion.

RESULTS AND DISCUSSIONS
As previously mentioned, although the hydrolysis of ester to the corresponding acid and alcohol is a fundamental transformation in organic synthesis, the low miscibility of most esters in water limits its application. Transesterification of the ester with an alcohol is an alternative pathway that can be accomplished with organic solvents. Using glycerol as both the solvent and the alcohol offers a more environmentally friendly synthetic procedure (8). Moreover, as glycerol acts as acyl acceptor and yields glycerol monoacetate, glycerol diacetate, and/or triacetin as by-products, their high boiling points and high solubilities in glycerol allow the product to be easily separated from the reaction mixture by simple extraction with diethyl ether, which can be than recycled, and allow the catalyst to be recycled.

Both soluble and solid acids are known to be efficient catalysts for alcoholysis reactions (14, 15). We therefore began our investigation by evaluating benzyl alcohol conversion with time in glycerol at several temperatures using a homogeneous acid catalyst (Figure 2). As expected, increasing the reaction time or temperature in the ranges of 1-6 h and 45-100°C, respectively, increased product conversion.

At 70°C, a maximum product conversion of 60 percent was achieved at equilibrium; however increasing the reaction temperature to 95°C allowed an equilibrium conversion of 80 percent to be achieved (Figure 2).

Though homogeneous acids are active catalysts, the separation and recycling processes are troublesome.

Figure 1. Transesterification of benzyl acetate in glycerol.
Thus, employing solid acid catalysts that can be easily filtered at the end of the reaction for reuse is advantageous. Because pretreatment of the representative solid catalyst, Amberlyst 36, is known to possibly affect its catalytic performance, we tested the effect of catalyst preheating temperature and time on benzyl alcohol conversion. As the acidic resin is unstable at temperatures above 100°C, catalyst pretreatment was tested from 40-80°C and it was found that preheating at 80°C for 1 h resulted in an optimal benzyl alcohol conversion that did not change when the heating time was extended. Thus the catalyst was preheated at 80°C for 1 h for all subsequent experiments of the study. As was previously shown for sulfuric acid, benzyl alcohol conversion in glycerol over Amberlyst 36 also increased with reaction time and temperature (Figure 3). A performance comparison of the homogeneous and heterogeneous catalysts under equal loading showed that under similar conditions, the soluble acid was more active than the solid acid. For example, using H2SO4 as catalyst produced a 78 percent conversion after 4 h at 95°C while employing Amberlyst 36 under similar conditions resulted in only a 34 percent conversion.

Increasing the substrate to catalyst ratio in the range of S/C=1-100 (g/g) with both homogeneous and heterogeneous catalysts, either by increasing the amount of benzyl acetate in a fixed catalyst loading regime or by decreasing the catalyst loading while retaining the amount of substrate, did not significantly change product conversion. This result implies that the reaction rate may follow a pseudo zero order.

Though performance of the soluble base was higher than that of the solid, from an industrial point of view, solid catalysts are preferable as they can be easily separated from the reaction mixture by filtration and then recycled. We therefore evaluated the recycling performance of Amberlyst 36 using two methods. The first procedure began with a reaction cycle that entailed heating a fresh mixture of benzyl acetate, glycerol, and catalyst for 1 h at 70°C followed by catalyst filtration and then full extraction of product and residual substrate by diethyl ether (Table 4, entry 1). The filtered catalyst was then added to a fresh mixture of benzyl acetate in glycerol, and the reaction was run again under similar conditions. Catalyst reuse resulted in a small decrease in the product conversion of the second cycle that can be attributed to the loss of catalyst during the recycling procedure and/or to the partial adsorption of substrate, product, or glycerol di- or mono-acetate, which were produced by the transesterification step in the first reaction cycle on the active sites (entries 2 and 3). Since glycerol was both solvent and acyl acceptor, in the second recycling procedure the product and the residual substrate were extracted from the mixture of glycerol together with the heterogeneous catalyst using diethyl ether followed by the addition of fresh benzyl acetate to the mixture of glycerol and Amberlyst 36. This method also resulted in a partial decrease in product conversion between the first and second cycles followed by a much smaller decrease in product conversion with the third reaction cycle.

Finally, relative to conventional heating, microwave-promoted heating was recently reported to enhance organic reactions, including the hydrolysis of esters (16-17). 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 Amberlyst 36 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 a product conversion of 23 percent, similar to that under conventional heating at 70°C for 1.5 h. It seems that glycerol, which has a high dielectric constant and three hydroxyl groups, adsorbs microwave irradiation efficiently (17). Furthermore, the markedly low vapour pressure and high boiling temperature of glycerol make it an attractive solvent for microwave-promoted organic synthesis under atmospheric pressure.

**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 glycerol (all purchased from Aldrich). The mixture was placed in a preheated oil bath and heated to the required temperature (40-95°C), after which it was magnetically stirred for 1-6 h.
At the end of the reaction, the reaction mixture was cooled and extracted with 3×10 mL diethyl ether. The organic phase was concentrated under reduced pressure, and the resulting crude product was analysed by gas chromatography (GC) analysis using an HP-5 column (30 m × 0.25 mm, 0.25 μm thick).

Two catalyst recycling methods were tested, and in both the first reaction cycle was performed 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 95°C for 1 h. For the first catalyst recycling method, the catalyst was filtered at the end of the reaction and the product was extracted by 5×10 mL diethyl ether and analysed by GC. The filtered catalyst was then added to a fresh mixture of benzyl acetate in glycerol, and the reaction was repeated. Under the second method, the product was extracted by 5×10 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 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 a 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.

**CONCLUSIONS**

Glycerol can be successfully used simultaneously as both a green solvent and an acyl acceptor in the transesterification of benzyl ester to benzyl alcohol using either a soluble or solid acid catalyst. 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 conversion 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 a higher reaction rate.

**REFERENCES AND NOTES**