



## Liquid phase acetoxylation of $\alpha$ -pinene over Amberlyst-70 ion-exchange resin

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### ABSTRACT

Heterogeneously-catalyzed and solvent-catalyzed liquid phase acetoxylation of  $\alpha$ -pinene with acetic acid acting as both a solvent and a reagent was studied. Both solvent-catalyzed and catalytic experiments were carried out and various reaction conditions were studied. The influence of temperature, pressure, solvent and gas milieu were taken into account. Bornyl, fenchyl, verbenyl as well as  $\alpha$ -terpinyl acetates, limonene, camphene and  $\gamma$ -terpinene were found among reaction products. The addition of the catalyst allowed for maximization of the yield of bornyl acetate. The predominant products obtained were  $\alpha$ -terpinyl, verbenyl and bornyl acetates. The reaction pathways were identified and evaluated.

The aim of this work was to study the feasibility of batch acetoxylation of  $\alpha$ -pinene. The analysis of the complex product distribution is not trivial and, consequently, resolving the reaction network was important. The optimized reaction conditions were searched for aiming at an efficient conversion of  $\alpha$ -pinene to a mixture of valuable products.

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### 1. Introduction

Nowadays, many research groups are involved in the production of value-added chemicals from renewable feed-stocks due to imminent future threat of lack of fossil resources. Various streams available from chemical pulping and biorefinery process streams contain substantial amounts of terpenes and of those  $\alpha$ -pinene is often predominant [1].  $\alpha$ -Pinene is a comparably cheap terpene that can be upgraded to numerous valuable products [2].

In recent years, the demand for alternative flavoring agents for food, other alimentary products and perfumes has increased. The industry evidently desires to reach maximally favorable flavor and aroma characteristics. The same time, it is important to improve the production and purification processes of terpene esters. Also, to counter-effect the products tendency to spoil is of high importance [3].  $\alpha$ -Terpinyl acetate is a valuable monoterpene ester and is widely used as a fragrance in soaps and perfumes because of its excellent alkali stability [4]. The mentioned acetylated product is conventionally produced via  $\alpha$ -pinene treatment with mineral acids, followed by an etherification step of the intermediate

$\alpha$ -terpineol. The equipment corrosion, environmental pollution, large consumption and non-recyclability of the mineral acid are some of the severe drawbacks of the conventional process [5,6]. The related product, bornyl acetate, is an important component for fragrance industry. It is used for soaps, bath products and air fresheners. Alternatively, this chemical is an intermediate for camphor production [7].

Earlier studies have been conducted in zeolite-catalyzed transformations of  $\alpha$ -pinene and limonene to acetylated products in alcoholic solvents [4,8–12]. In addition, liquid phase acetoxylation of  $\alpha$ -pinene and limonene in acetic acid was investigated over various zeolites and acidic ionic liquids by a few research groups [4,5,7,13], whereas Robles-Dutenhefner et al. [14] studied the same reaction over silica-supported heteropoly-acid (PW). Also, hydration and bio-conversion of limonene to  $\alpha$ -terpineol – which could be used for  $\alpha$ -terpinyl acetate production – has been studied [15–17]. Except via limonene hydration,  $\alpha$ -terpinyl acetate could also be produced from limonene and acetic acid with the help of e.g.  $\text{Fe}_2(\text{SO}_4)_3$  [18]. The reaction of  $\alpha$ -terpineol with acetic anhydride, in the presence of this catalyst, also gave rise to  $\alpha$ -terpinyl acetate. Furthermore, quite good results in  $\alpha$ -pinene oxidation were obtained over palladium acetate catalysts, with hydrogen peroxide in acetic acid solutions [19].

In this paper, we report  $\alpha$ -pinene acetoxylation to the valuable mixture of terpene acetates. Both the acetic-acid (solvent-catalyzed mode) and the heterogeneously catalyzed reaction networks (over an ion-exchange resin, mesoporous Amberlyst 70 catalyst) were resolved. Also, an analysis of the reaction kinetics was conducted.

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