

Liquid phase acetoxylation of α -pinene over Amberlyst-70 ion-exchange resin

M. Golets^{a,*}, S. Ajaikumar^a, D. Blomberg^b, H. Grundberg^c, J. Wärnå^d, T. Salmi^d, J.-P. Mikkola^{a,d,**}

^a Technical Chemistry, Department of Chemistry, Chemical-Biological Center, Umeå University, SE-90187, Umeå, Sweden

^b Processum Biorefinery Initiative AB, SE-89186, Örnsköldsvik, Sweden

^c Aditya Birla Domsjö Fabriker AB, SE-89186, Örnsköldsvik, Sweden

^d Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500, Åbo-Turku, Finland

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ABSTRACT

Heterogeneously-catalyzed and solvent-catalyzed liquid phase acetoxylation of α -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 α -terpinyl acetates, limonene, camphene and γ -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 α -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 α -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 α -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 α -pinene is often predominant [1]. α -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]. α -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 α -pinene treatment with mineral acids, followed by an etherification step of the intermediate

α -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 α -pinene and limonene to acetylated products in alcoholic solvents [4,8–12]. In addition, liquid phase acetoxylation of α -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 α -terpineol – which could be used for α -terpinyl acetate production – has been studied [15–17]. Except via limonene hydration, α -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 α -terpineol with acetic anhydride, in the presence of this catalyst, also gave rise to α -terpinyl acetate. Furthermore, quite good results in α -pinene oxidation were obtained over palladium acetate catalysts, with hydrogen peroxide in acetic acid solutions [19].

In this paper, we report α -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.

* Corresponding author. Tel.: +46 0 76 104 3381.

** Corresponding author at: Technical Chemistry, Department of Chemistry, Chemical-Biological Center, Umeå University, SE-90187, Umeå, Sweden. Tel.: +46 0 70 620 0371.

E-mail addresses: Mikhail.Golets@chem.umu.se (M. Golets), Jyri-Pekka.Mikkola@chem.umu.se (J.-P. Mikkola).

2. Experimental

2.1. Materials

The reagents, glacial acetic acid and acetone were used as received from Sigma–Aldrich AB. The gases, oxygen, nitrogen and hydrogen were purchased from commercial sources (AGA AB) and had a purity of 99.999%. The terpenes and their derivatives, α -pinene, β -pinene, α -terpineol, limonene, γ -terpinene, borneol, bornyl and α -terpinyl acetates were purchased from Sigma–Aldrich AB at a purity level of 95%. Amberlyst 70 catalyst was obtained as a gift from Rohm and Haas AB and used as received.

2.2. Apparatus and general reaction procedure

A laboratory scale high-pressure reactor (PARR), equipped with a stirrer and a heating jacket, was used to carry out α -pinene acetoxylation tests. First, the catalyst in a quantity of 0.1 g was loaded in the reactor vessel. Then 5.5 g of α -pinene (measured to 0.1 g accuracy) and 120 ml of acetic acid were introduced as a mixture in the reaction zone. The reactor temperature was maintained by heating jacket and cooler system controlled by a PC. The influence of different gas pressures on the reaction was studied. The stirring speed of 1000 min⁻¹ was applied in order to eliminate any external mass-transfer limitations.

2.3. Product analysis

The progress of the reaction was monitored by withdrawing samples at different time intervals during the course of the reaction. The reaction products were analyzed by means of a gas chromatograph (GC) (Agilent Technologies, Model no. 7820A), equipped with a HP-5 capillary column (30 m long, 0.32 mm internal diameter and 0.25 μ m film thickness) and a FID detector. Nitrogen was used as the carrier gas in the GC (flow 1.0 mL/min) with the following temperature programming: the detector and injection port temperature of 250 °C, column temperature ranging from 70 to 220 °C with the holding time of 0.5 min at the initial temperature and the heating ramp of 20 °C/min. The reaction products and substrate have had the following retention times (min): α -pinene (1.920); camphene (2.120); verbenyl acetate (2.400); limonene (2.510); γ -terpinene (2.770); fenchyl acetate (3.620); bornyl acetate (4.070); α -terpinyl acetate (4.490); by-products (from 6.500 to 8.000). α -Pinene conversion was defined as the concentration ratio of converted species (products) to the initial concentration of α -pinene. GC–MS analysis (gas chromatography coupled to mass spectrometry) was utilized in the detailed product analysis and identification. For the GC–MS analysis, a device by Thermo Trace DSQ was used. The column parameters were: VF-5MS, 30 m, 0.25 mm I.D., phase 0.25 μ m and a constant nitrogen flow rate of 1.5 ml/min was applied. The injection temperature was 230 °C and the initial temperature of the oven was 50 °C, maintained for 1 min, where after a temperature ramp (20 °C/min) was commenced up to 300 °C. For the precise product analysis by means of GC, several terpene standard solutions were applied. The standards of anticipated reaction products were diluted in acetone (0.3 ml) before injection to the GC. The concentration of the products was expressed in terms of wt% to the whole amount of the reacted α -pinene in the product mixture. The α -pinene conversion, product selectivities and yields were calculated as follows:

$$X(\%) = \frac{\text{initial } \alpha\text{-pinene GC peak area} - \text{final } \alpha\text{-pinene GC peak area}}{\text{initial } \alpha\text{-pinene GC peak area}} \times 100 \quad (1)$$

$$S_Y(\%) = \frac{\text{GC peak area of the product Y}}{(\text{GC peak area of } \alpha\text{-pinene})_{\text{initial}} - (\text{GC peak area of } \alpha\text{-pinene})_{\text{final}}} \times 100 \quad (2)$$

$$\text{Yield}(\%) = X(\%) \times \frac{S_Y}{100} \quad (3)$$

A tailor-made mixture cocktail of high purity standards (95 wt%) of containing the main predominant reaction products, including both acetates, was analyzed by means of GC. The mixture also included α -pinene. The concentration of each species in the amount of each mixture was similar (0.2 g) compound was equal to the amount of other compounds and was 0.2 g. Also, the calibration of each compound was performed on individual bases analyzed with GC separately for comparison. It was shown by the analysis that the peak area was not influenced by the rather small variations in molecular mass or density and was equal for all terpene and terpene acetate species.

2.4. Preliminary catalyst characterization

The acid site concentration of the catalyst was measured by means of a titration method described elsewhere [20]. Further, fresh and spent catalyst samples were analyzed by means of nitrogen physisorption measurements. Samples of the Amberlyst 70 catalyst exposed to the reaction conditions at 100 °C were analyzed. The analysis of surface area, pore diameter and volume were carried out by a Micromeritics Tristar 3000 analyzer in accordance to the Brunauer–Emmett–Teller (B.E.T.) method. A sample of 0.1 g was degassed at 120 °C for 1 h in vacuum (10⁻⁵ torr) in order to remove the moisture from the pores of the material. By applying the B.E.T. method, the pore diameter and volume were calculated from the adsorption isotherms. The adsorption data was used to calculate the surface area up to a relative pressure of 0.2 bar. The SEM (scanning electron microscopy) images of fresh and spent catalyst particles were visualized with a Cambridge Stereoscan 360iXP electron microscope.

3. Results

3.1. Acetoxylation of α -pinene

For the studied reaction, α -terpinyl, fenchyl, verbenyl and bornyl acetates as well as limonene, camphene and γ -terpinene were all found in the product mixture. The other products were found in amounts less than 1 wt% and were considered negligible. The formation of by-products was not uniform in case of all prolonged reactions. A temperature range of 25–125 °C and a pressure range from atmospheric to 20 bar were considered. The influence of the gas atmosphere, i.e. nitrogen, oxygen or hydrogen atmosphere was also investigated. A pressurizing gas was needed to suppress the evaporation of the reactants involved. Glacial as well as aqueous acetic acid (2.5 wt% and 5 wt%, respectively) and also a blend of acetic acid and toluene or ethyl acetate (5 wt%) were tried as co-solvents. The influence of each factor was studied in catalytic (Amberlyst 70) and the solvent-catalyzed mode. Fig. 1 (Symbols: (•) 100 °C, 10 bars, N₂, cat; (–) 100 °C, 10 bars, N₂, no cat; (+) 75 °C, 10 bars, N₂, cat; (♦) 125 °C, 10 bars, N₂, cat; (□) 100 °C, 20 bars, H₂, cat; (▲) 100 °C, 20 bars, O₂, cat; (■) 100 °C, 20 bars, O₂, no cat; (▣) 100 °C, 20 bars, O₂, no cat, 5 wt % ethyl acetate/95 wt % acetic acid; (○) 100 °C, 20 bars, O₂, cat, 5 wt % toluene/95 wt % acetic acid; (×) 100 °C, 20 bars, O₂, cat, 95% aqueous acetic acid.) describes the conversion of α -pinene. Figs. 2 and 3 refer to the evolution of corresponding products under various reaction conditions.

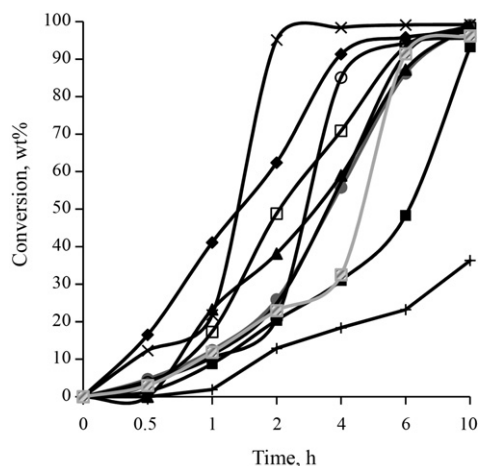


Fig. 1. α -Pinene conversion.

It was evident that camphene and fenchyl acetates were formed as parallel reaction products. The maximum yields of these products were reached at 100 °C and 20 bar, in the solvent-catalyzed reaction system when the solvent was a blend of acetic acid and ethyl acetate and oxygen was used to pressurize the reaction vessel. The yield of γ -terpinene was in the range of 15 wt% in several cases. Under the solvent-catalyzed reaction conditions, in glacial acetic

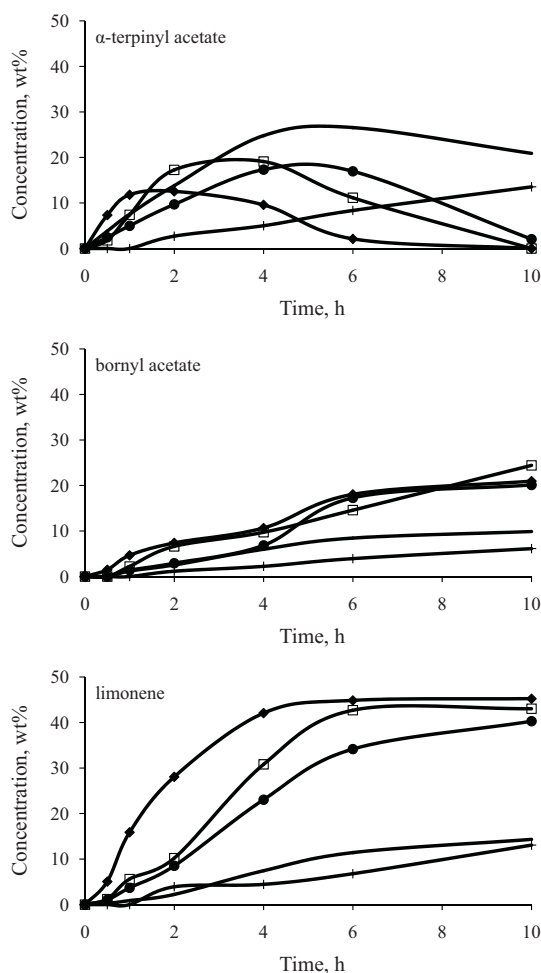


Fig. 2. The evolution of reaction products under nitrogen and hydrogen atmospheres.

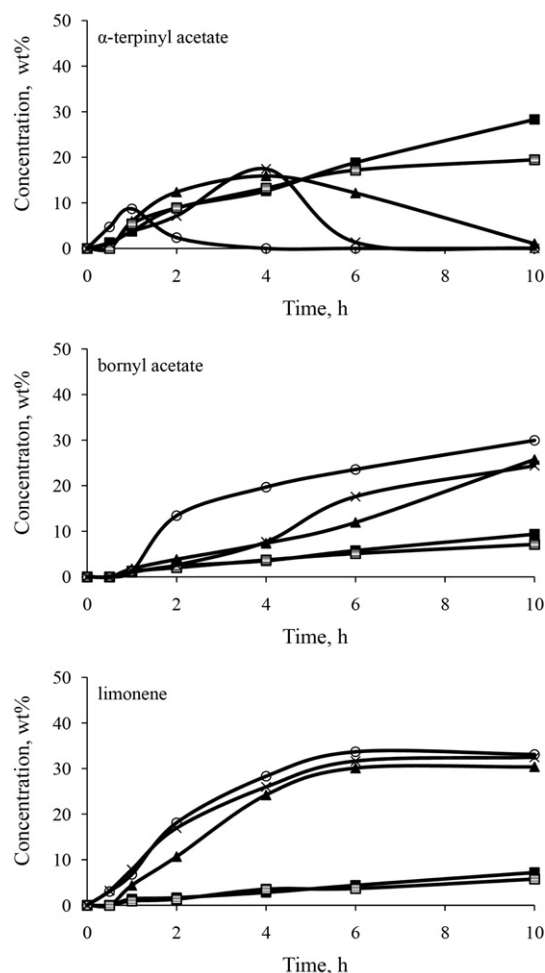


Fig. 3. The evolution of reaction products under oxygen atmosphere.

acid, verbenyl acetate formation could be maximized (16 wt%). After prolonged reaction times (10–18 h), by-products started to emerge. As a result of very long batch times, more than 30 wt% of by-products could be found. By-products were observed eluted in the GC chromatogram after the main reaction products. Under the optimized reaction conditions there were fewer by-products formed while the conversion was always high throughout the experimental matrix. The formation of the undesired by-products was favored by nitrogen atmosphere, in combination with harsh reaction conditions (up to 20 wt% of the final product mix, in 10 h), while oxygen atmosphere counter-effected the formation of by-products even during prolonged experimental runs (up to 18 h of batch time) in case of the solvent-catalyzed reaction. The reason of this observation will be discussed later.

Optimal reaction conditions were determined for the catalytic and solvent-catalyzed modes, respectively. The optimal reaction time and solvent type were chosen accordingly for each case. On the basis of earlier results, it was determined that around 10 h batch time is appropriate (Tables 1 and 2).

3.2. Catalyst characterization

Conventional titration (glass buret) method revealed that the number of acid sites in the Amberlyst 70 resin was reduced from 2.48 to 1.61 eq/kg upon exposure to the reaction solution. The initial value determined was in line with the manufacturer's data. The results of nitrogen physisorption for Amberlyst 70 are given in Table 3.

Table 1
Sample concentration data showing the evolution of products in catalytic reaction^a

Reaction time (h)	α -Pinene conversion (%)	Products concentration (wt%) ^b					
		Limonene	γ -Terpinene	Camphene	Fenchyl acetate	Bornyl acetate	α -Terpinyl acetate
0.5	12.3	3.0	1.8	0.6	0	0	4.7
1	21.8	6.8	4.8	1.4	0	1.2	8.7
2	95.1	32.1	10.8	6.4	2.4	13.4	2.4
4	98.4	34.3	1.7	2.9	5.8	19.7	0
6	99.1	31.7	2.4	2.6	5.8	23.6	0
10	99.2	31.1	2.4	2.6	7.4	29.9	0

^a 100 °C, 20 bar, O₂, 95% aqueous acetic acid, 10 h.

^b Proportionally to the whole amount of α -pinene.

Table 2
Sample concentration data showing the evolution of products in solvent-catalyzed reaction^a

Reaction time (h)	α -Pinene conversion (%)	Products concentration (wt%) ^b						
		Limonene	γ -Terpinene	Camphene	Fenchyl acetate	Bornyl acetate	α -Terpinyl acetate	Verbenyl acetate
0.5	1.4	0	0	0	0	0	1.3	0
1	8.8	1.4	0	0.7	0	1.0	3.8	4.7
2	19.8	1.7	1.3	0.8	0	2.4	8.8	5.6
4	31.0	2.8	1.9	1.3	0	3.5	12.6	6.3
6	47.7	4.4	3.1	2.0	3.0	5.8	18.8	9.8
10	90.1	7.2	5.0	3.4	5.0	9.4	28.3	16.0

^a 100 °C, 20 bars, O₂, glacial acetic acid, 10 h.

^b Proportionally to the whole amount of α -pinene.

Table 3
BET surface area, pore size and pore volume data for Amberlyst 70.

Catalyst	S_{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Concentration of acid sites (eq/kg)
Fresh	40.2	25.3	0.3	2.48
Spent	3.6	23.0	0.02	1.61

According to the results, the specific surface area and pore volume were significantly reduced, thus indicating catalyst deactivation. The average pore size of the catalyst was slightly reduced under the reaction conditions.

The SEM images scaled at 2.00 μm for Amberlyst 70, before and after the reaction, are presented in Fig. 4. It is evident that the surface has undergone morphology changes. The fresh resin had a sphere diameter of around 350–600 μm , while the spent catalyst contained spheres of around 400–800 μm , thus demonstrating swelling of the resin particles.

3.3. Recovery and reusability of the catalyst

The catalyst reusability was studied in a temperature range of 75–100 °C (Fig. 1). The catalyst was recovered by means of filtration and washed with acetone. Thereafter the catalyst was washed with 0.1 N HCl solution and dried. The same procedure was repeated

three times after each and every reaction cycle. The conversion of α -pinene obtained during the first batch was 96%, whereas the second and third batch resulted in 68% and 60% conversion, respectively. No abrasion of catalyst particles was observed at this temperature. Rather severe catalyst decomposition (about 30%) was observed at higher temperatures.

4. Discussion

It was evident that the role of the temperature was the decisive one: the overall trend was rapid α -pinene conversion at elevated temperatures. Within the temperature interval of 25–75 °C, the selectivity toward main products remained almost unchanged. Temperatures below 75 °C were found to be too low and resulted in a significant drop in conversion over time and, consequently, a reaction time exceeding 24 h was required. The α -terpinyl acetate formed during the course of the reaction was consumed to form

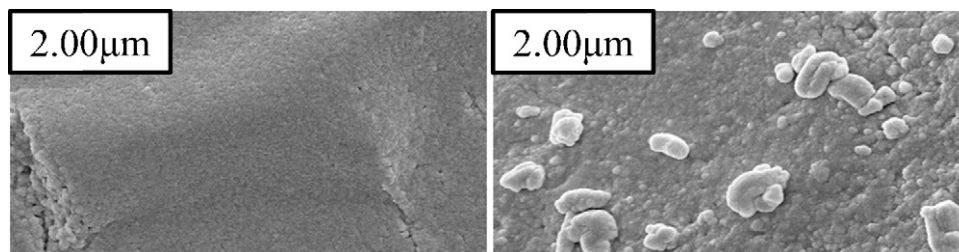


Fig. 4. Amberlyst 70 SEM images – fresh and spent catalyst samples.

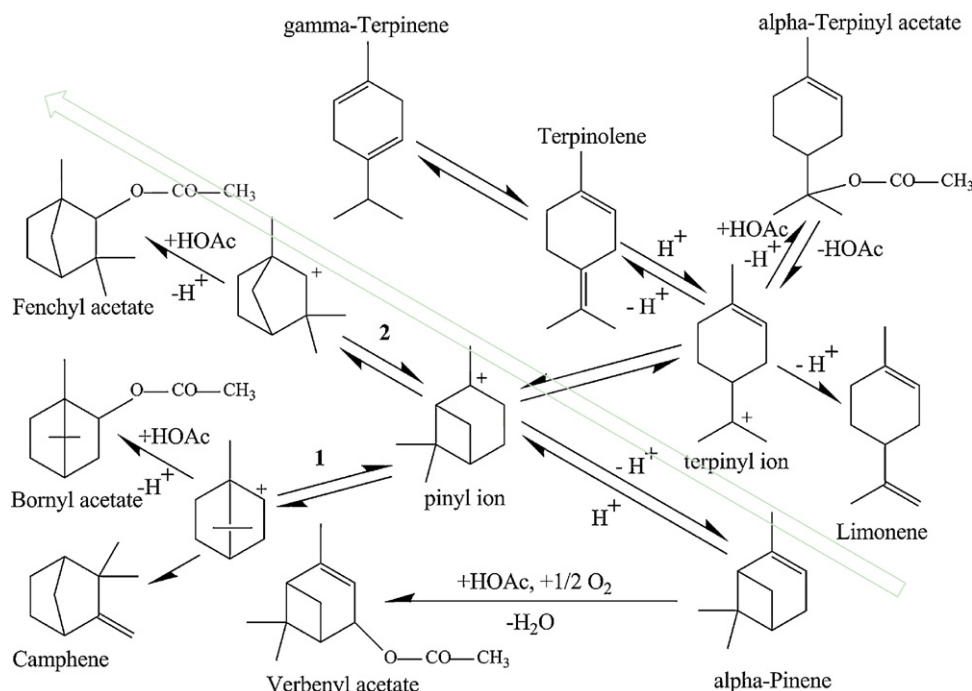


Fig. 5. The overall reaction network.

limonene in case of prolonged reaction time and high temperatures. Furthermore, bornyl and fenchyl acetates, as well as camphene and limonene were rapidly formed at 100–125 °C, although also some by-products started to form, thus resulting in decreased selectivity. In fact, toward the end of a batch, the reaction mixture turned at first yellow and then brown. Elevated temperatures were more beneficial in terms of γ -terpinene formation. Still, under optimized reaction conditions, α -terpinyl acetate yield was nearly 30 wt%. Our observations about the influence of temperature were in line with the literature results [9,14].

Interestingly, Hensen et al. [9] reported that pressure does not significantly influence the conversion and selectivity profiles. However, our results were quite the opposite. As can be seen (Figs. 2 and 3), the selectivity toward α -terpinyl acetate, limonene and γ -terpinene was significantly influenced when 10 respective 20 bar of gas pressure was applied. The optimal yield was always coupled to the optimal combination of several reaction parameters.

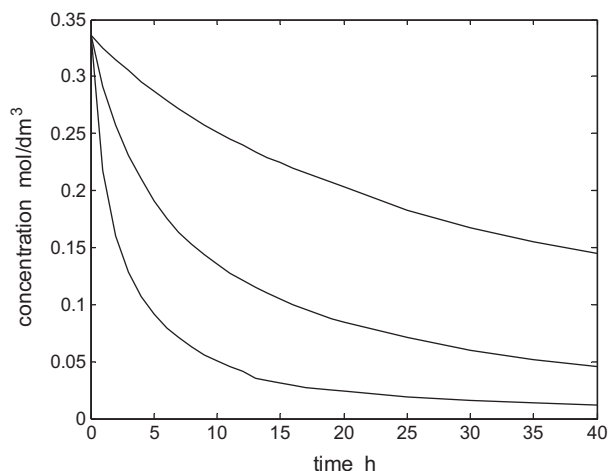


Fig. 6. Simulation of a CSTR reactor with the concentration of reactant as function of residence time (for temperatures 75, 100, 125 °C, respectively).

A pressure lower than 10 bar led to poor conversion, whereas higher pressure accelerated the conversion and influenced the selectivity profiles. This phenomenon could be explained by the partial evaporation of the reaction mixture. Elevated pressure levels should reduce the products that evolve to the gas (vapor) phase and thus increase their interaction with the solvent and the catalyst.

The aggressive reaction environment used caused serious catalyst deterioration and deactivation. As mentioned in Section 3.2, the pore volume and the concentration of acid sites of the catalyst were reduced under the high temperature and pressure conditions.

As already mentioned (Section 3.1), aqueous and glacial acetic acid milieus gave the best results both during the catalytic and solvent-catalyzed reaction experiments, respectively. Beneficial α -pinene conversion obtained in the presence of water could be explained by the stronger nucleophilic properties of water than that of acetic acid due to faster hydration. Williams and Whittaker [21] showed that water addition increases the α -terpinyl acetate yield and, at the same time, has an insignificant effect on bornyl acetate formation. At increased water concentrations, a significant drop in the conversion albeit rise in selectivity due to prevention of by-products formation has been observed [14]. In our case, in aqueous acetic acid, about 50 wt% less by-products were formed, even during prolonged batch times. Similar effect was observed even when more than 10 wt% of water was added. The conversion decreased significantly since water addition inhibits the acetoxyla-tion reaction [14]. In our case, the use of 2.5 wt% aqueous acetic acid solution resulted in less α -terpinyl acetate and more bornyl acetate, compared to the case when glacial acetic acid was applied as the solvent. The aggressive reaction conditions and the influence of the gas atmosphere used contributed to this behavior. Toluene and ethyl acetate blends with acetic acid resulted in average behavior in terms of conversion and selectivity.

The influence of nitrogen, oxygen and hydrogen gas atmospheres was studied. Nitrogen was assumed as a 'neutral' gas, which provided the pressure only, although by-products formation was observed in several cases. The plausible reason for this is the high temperature applied. The use of hydrogen led to average conversion and selectivity in all cases. Accelerated limonene degradation

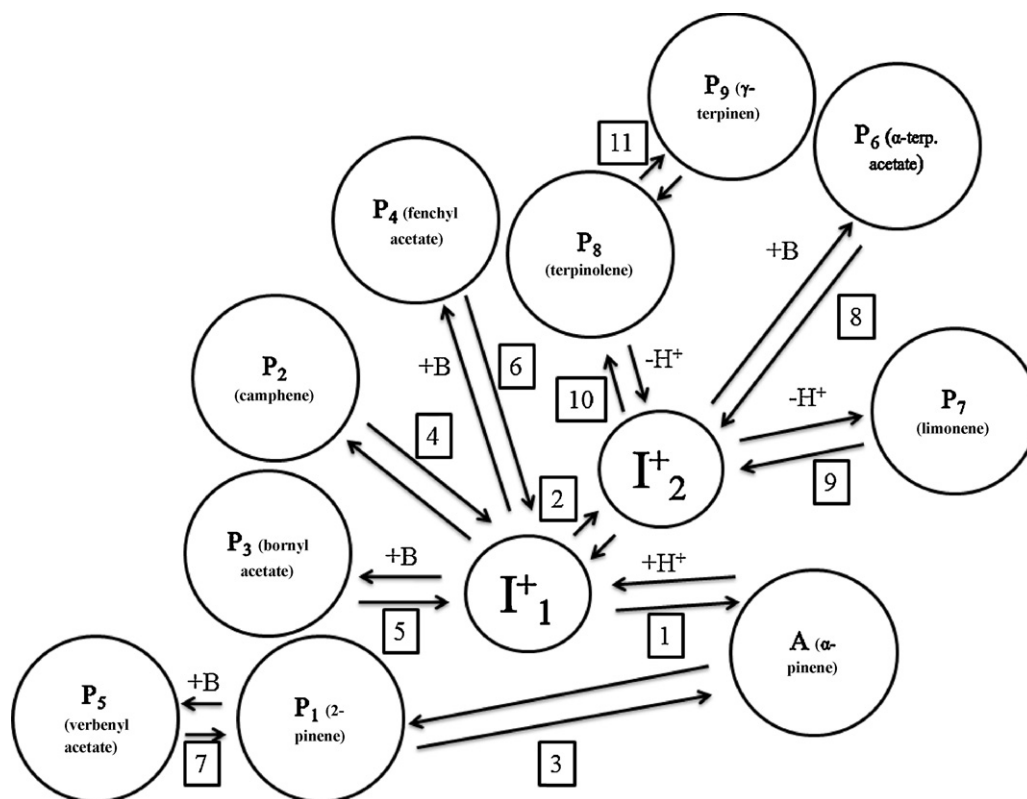


Fig. A.1. Description of the reaction network used in the kinetic modeling (B–acetoxylation agent, I_1^+ –pinyl ion, I_2^+ –terpinyl ion).

due to fast hydration was a serious drawback, promoted by the presence of hydrogen molecules. The best yields under otherwise optimized combination of reaction parameters were obtained in oxygen atmosphere.

Fig. 5 represents the reaction network. The pinyl ion is rapidly formed from α -pinene, followed by a rearrangement taking place without a capture by nucleophiles [21]. As shown already earlier that, in addition to the ring-opening reaction, two ring-enlarging reactions are also possible [4,5]. The observed high selectivity toward bornyl acetate versus fenchyl acetate could be explained by the fact that the ring-enlargement reaction with an isopropyl group proceeds easier than with a methyl group. Further, the ring-enlarging reaction (1) is preferred in comparison to the reaction (2). With increasing α -pinene conversion, the terpinyl ion attacks on the olefinic compounds present in the system and can result in the formation of by-products [14].

In general, both heterogeneously- and solvent-catalyzed reactions were successful when the optimized reaction conditions were applied. Both reaction modes allowed obtaining valuable products. As mentioned (Figs. 2 and 3), the additional acidity, provided by the Amberlyst 70, stimulated the bornyl acetate formation without cleavage of the internal pinyl ring, whereas, the formation of α -terpinyl acetate was solvent-catalyzed. Verbenyl acetate was only formed in under the solvent-catalyzed mode. Plausibly, this product is formed directly from α -pinene due to its allylic oxidation by O_2 followed by the acetoxylation without any ring rearrangements.

Under oxygen atmosphere, a portion of α -pinene was oxidized to α -pinene oxide. As the next step, this compound further reacted with acetic acid and dehydrated leading to additional formation of the verbenyl acetate. The amount of terpinyl ions found in the reaction mixture can thus be considered directly proportional to the lower yield of by-products. Our observation was supported by the literature [22].

The effect of the temperature on the initial rate of α -pinene acetoxylation according to the optimized experimental data was described by the Arrhenius plot. The data set was modeled with the help of the following set of equations:

$$r = \frac{d[n]}{dt} = k[n] \quad (4)$$

$$[n]_t = [n]_0 e^{-kt} \quad (5)$$

$$\ln[n]_t = \ln[n]_0 - kt \quad (6)$$

A strong Arrhenius-type temperature dependence was demonstrated with glacial acetic acid for bornyl acetate, also supported by the experimental observations. However, less obvious correlation can be seen in terms of limonene and α -terpinyl acetate. When observing the Arrhenius plots, the activation energies for the three main reaction products were as follows: 106, 29.1 and 16.6 kJ/mol for bornyl acetate, limonene and α -terpinyl acetate, respectively.

The experimental data was fitted with a kinetic model implemented in the ModEst (Profmath Oy) software. The simulation of the Continuous Stirred-Tank Reactor (CSTR) reactor with the concentration of reactant as function of residence time was included (Fig. 6) [23]. The details of kinetic modeling are described in Appendix A.

5. Conclusions

In this paper we investigated a one-stage process for α -pinene liquid-phase acetoxylation transformation to value-added products, both under catalytic and solvent-catalyzed modes. The catalyst used was Amberlyst 70 ion-exchange resin. A wide range of process parameters was studied. The importance of various process parameters can be summarized as follows: temperature, catalytic/solvent-catalyzed process, gas type, solvent composition and pressure. Serious catalyst deactivation was observed when

Table A.1The numerical values of parameters and their errors^a.

Estimated	Estimated	Est. relative error of parameters	Std. error (%)	Std error (%)
k10	0.295E-01	0.427E-02	14.5	6.9
k3	0.881E-01	0.910E-02	10.3	9.7
k5	0.281E-01	0.439E-02	15.6	6.4
k9	0.458E-01	0.432E-02	9.4	10.6
Ea10	0.534E+05	0.850E+04	15.9	6.3
Ea3	0.533E+05	0.603E+04	11.3	8.8
Ea5	0.538E+05	0.916E+04	17.0	5.9
Ea9	0.537E+05	0.558E+04	10.4	9.6

^a Units: k3, k9 and k10 – 1/h; k5 – dm³/(mol h); E_a – J/mol.**Table A.2**

Parameter correlation matrix.

1									
–0.390	1								
0.016	–0.395	1							
0.027	–0.345	0.025	1						
–0.651	0.316	0.010	0.017	1					
0.312	–0.589	0.311	0.308	–0.370	1				
0.010	0.315	–0.651	0.015	0.026	–0.379	1			
0.017	0.313	0.016	–0.618	0.044	–0.314	0.040	1		

harsh experimental conditions were applied; still, the optimal product yield was rapidly reached. As a summary: a typical product mixture in the solvent-catalyzed reaction contained 28 wt% of α -terpinyl acetate, 9 wt% of bornyl acetate, 5 wt% of γ -terpinene, 5 wt% of fenchyl acetate, 7 wt% of limonene and 16 wt% of verbenyl acetate, whereas 30 wt% of bornyl acetate and 31 wt% of limonene, respectively, were obtained in the catalytic process. Thus, the catalytic reaction mode resulted in a significantly higher yield of the valuable bornyl acetate. Increased temperatures or hydrogen atmosphere resulted in extensive formation of by-products whereas verbenyl acetate was formed only upon solvent-catalyzed reaction. Moreover, oxygen atmosphere is beneficial since the use of it prevents the by-products formation to a large extent upon the solvent-catalyzed reaction. According to the kinetic model, the reaction pathways in line with the routes toward limonene and bornyl acetate formation are the predominant ones. The modeling results are in strong correlation with the experimental observations. Industrially feasible operations and scale-up of the studied process requires the evaluation of several aspects and more studies taking into account the separation aspects are needed.

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Appendix A.

Reaction network was organized in line with Fig. A.1 and the actual reaction network (Fig. 5).

The temperature dependency was expressed with the Arrhenius equation as:

$$A_j = k_j \times e^{\frac{E_{a_j}}{R} \left(\frac{1}{T_{\text{temp}}} - \frac{1}{T_{\text{mean}}} \right)} \quad (\text{A.1})$$

The reaction rates were expressed by meant the following set of equations:

$$r_3 = A_3 \times \left(C_A - \frac{C_{P_1}}{K_{eq3}} \right) \times C_H \quad (\text{A.2})$$

$$r_4 = A_4 \times \left(C_A - \frac{C_{P_2}}{K_{eq4}} \right) \times C_H \quad (\text{A.3})$$

$$r_5 = A_5 \times \left(C_A \times C_B - \frac{C_{P_3}}{K_{eq4}} \right) \times C_H \quad (\text{A.4})$$

$$r_6 = A_6 \times \left(C_A \times C_B - \frac{C_{P_4}}{K_{eq6}} \times C_H \right) \quad (\text{A.5})$$

$$r_7 = A_7 \times (C_{P_1} \times C_B - C_{P_5}) \quad (\text{A.6})$$

$$r_8 = A_8 \times \left(C_A \times C_B - \frac{C_{P_6}}{K_{eq8}} \right) \times C_H \quad (\text{A.7})$$

$$r_9 = A_9 \times \left(C_A - \frac{C_{P_7}}{K_{eq9}} \right) \times C_H \quad (\text{A.8})$$

$$r_{10} = A_{10} \times \left(C_A - \frac{C_{P_{8,9}}}{K_{eq10}} \right) \times C_H \quad (\text{A.9})$$

$$r_{11} = A_{11} \times (C_{P_8} - C_{P_9}) \quad (\text{A.10})$$

The batch reactor model is expressed as following:

$$\frac{dC_A}{dt} = -r_3 - r_4 - r_5 - r_6 - r_8 - r_9 - r_{10} \quad (\text{A.11})$$

$$\frac{dC_B}{dt} = -r_5 - r_6 - r_7 - r_8 \quad (\text{A.12})$$

$$\frac{dC_{P_1}}{dt} = r_3 - r_7 \quad (\text{A.13})$$

$$\frac{dC_{P_2}}{dt} = r_4 \quad (\text{A.14})$$

$$\frac{dC_{P_3}}{dt} = r_5 \quad (\text{A.15})$$

$$\frac{dC_{P_4}}{dt} = r_6 \quad (\text{A.16})$$

$$\frac{dC_{P_5}}{dt} = r_7 \quad (\text{A.17})$$

$$\frac{dC_{P_6}}{dt} = r_8 \quad (\text{A.18})$$

$$\frac{dC_{P_7}}{dt} = r_9 \quad (\text{A.19})$$

$$\frac{dC_{P_{8,9}}}{dt} = r_{10} - r_{11} \quad (\text{A.20})$$

The following objective function was minimized for the parameters estimation.

$$Q = \sum_t \sum_i (C_{i,t,\text{exp}} - C_{i,t,\text{model}})^2 w_{i,t} \quad (\text{A.21})$$

The experimentally recorded concentrations predicted by the model are denoted $C_{i,t,\text{exp}}$ and $C_{i,t,\text{model}}$, respectively. For all experimental points, the weight factors w_i were set to 1. The reaction rate constants and the reactor mass balances were solved simultaneously (ModEst). The objective function was minimized with the Levenberg–Marquardt or Simflex methods and the ODEs describing the reactor model were solved by the backward difference method implemented in the software.

The reactions 5, 9 and 10 were considered for the parameter estimation. In terms of these reactions, the primary products were covered. Although modeling trials with all products included were performed, the parameter estimation result was unsatisfactory due to low concentrations of the minor products P2, P4 and P6. In order to take into account the formation of these by-products and in order to keep the mass balance consistence, a dummy reaction r3 was used. Reactions 5, 9 and 10 were best described as irreversible reactions when using our data. The parameter estimation also reflected this fact. Table A.1 introduces the estimated parameters, whereas the correlation matrix for the estimated parameters is listed in Table A.2.

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