



# Methoxylation of $\alpha$ -pinene over poly(vinyl alcohol) containing sulfonic acid groups

D.S. Pito<sup>a</sup>, I.M. Fonseca<sup>b</sup>, A.M. Ramos<sup>b</sup>, J. Vital<sup>b</sup>, J.E. Castanheiro<sup>a,\*</sup>

<sup>a</sup> Centro de Química de Évora, Departamento de Química, Universidade de Évora, 7000-671 Évora, Portugal

<sup>b</sup> REQUIMTE/CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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## ABSTRACT

The methoxylation of  $\alpha$ -pinene was studied using poly(vinyl alcohol) (PVA) containing sulfonic acid groups as catalysts. These groups were introduced by the direct reaction between  $-OH$  groups of PVA and sulfosuccinic acid (SSA). Poly(vinyl alcohol) catalysts were prepared using sulfosuccinic acid by varying the amount of SSA (5–40 mol%). It was observed that the amount of acid sites increases with amount of SSA. It was also observed that the diffusivity of  $\alpha$ -pinene through the polymeric catalysts decreases with the increase of crosslinking degree.

The conversion of  $\alpha$ -pinene increases when the amount of sulfosuccinic acid used in the polymer crosslinking is increased from 5% to 40%. However, when the crosslinking degree increases from 20% to 40%, the conversion of  $\alpha$ -pinene increases only slightly.

Good values of selectivity to  $\alpha$ -terpinyl methyl ether (about 60% near complete conversion) were obtained over poly(vinyl alcohol) with sulfonic acid groups.

Catalytic stability of the PVA\_SSA20 was evaluated by performing consecutive batch runs with the same catalyst sample. After the third batch it was observed a stabilisation of the initial activity.

A kinetic model was developed assuming that the  $\alpha$ -pinene is consumed according to the parallel reaction network. Since the concentration profiles of the reagent and the products do not exhibit any pronounced initial inductive period, the external and internal diffusion of the reagents and products on the catalyst were not considered. It was observed that the kinetic model fits experimental concentration data quite well.

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## 1. Introduction

Monoterpenes represent a sustainable and versatile feedstock, which have been used for synthesis of aroma chemicals [1–3].  $\alpha$ -Pinene is a renewable raw material usually obtained from pine gum or as a waste from the Kraft process [4]. Its acid catalysed methoxylation yields a complex mixture of monoterpene ethers, being  $\alpha$ -terpinyl methyl ether the main product. The  $\alpha$ -terpinyl methyl ether smells grapefruit-like and might be used as flavour and fragrance for perfume and cosmetic products, as additive for pharmaceuticals as well as in food industry [5]. Strong homogeneous acid catalysts, e.g. sulphuric acid, have been used [6–9], but the effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by the use of solid acid catalysts. Beta zeolite [10] and acidic cation exchange resins [11] have been used for the  $\alpha$ -pinene alkoxylation.

Recently, sulfonic-modified mesoporous silica was used as catalysts in the  $\alpha$ -pinene methoxylation [12]. However, lower catalytic

activity of the PMO-SO<sub>3</sub>H and MCM-41-SO<sub>3</sub>H than beta zeolite and exchange resins was observed.

In order to improve the catalytic activity or selectivity, thanks to environment created by the polymeric matrix around the catalyst, homogenous and heterogeneous catalysts could be immobilized in polymeric matrix [13,14].

Hydration of olefin, dehydration of alcohol, alkylation of phenols, etherification and ester hydrolysis has been carried out over polymers with sulfonic acid groups [15–21].

In a previous work, it was observed that poly(vinyl alcohol) (PVA) membranes with  $-SO_3H$  groups have catalytic activity in esterification of acetic acid by isoamyl alcohol [22].

In the present work, we report the  $\alpha$ -pinene methoxylation over poly(vinyl alcohol) containing sulfonic acid groups. These groups were introduced by the direct reaction between  $-OH$  of PVA and sulfosuccinic acid (SSA).

## 2. Experimental

### 2.1. Catalysts preparation

PVA (Merk, average molecular weight: 72000) was dissolved in water at 80 °C, during 24 h. Aqueous 10 wt.% PVA solution were

\* Corresponding author. Tel.: +351 266745311; fax: +351 266744971.  
E-mail address: [jefc@uevora.pt](mailto:jefc@uevora.pt) (J.E. Castanheiro).

**Table 1**

Polymeric catalytic characteristics.  $Q_{\text{methanol}}$ ,  $Q_{\text{pinene}}$ : swelling degree for methanol and  $\alpha$ -pinene, respectively;  $De$ :  $\alpha$ -pinene diffusivity calculated from data collected in the two-chamber apparatus, by applying the second Fick's law; acidity calculated as base uptake.

Polymeric catalysts <sup>a</sup>	Thickness (mm)	Acidity (meq/g <sub>poly</sub> )	$Q_{\text{methanol}}$	$Q_{\text{pinene}}$	$De \times 10^9$ (m <sup>2</sup> /h)
PVA_SSA5	0.112	0.50	0.329	0.054	12.31
PVA_SSA20	0.104	2.02	0.223	0.044	9.12
PVA_SSA40	0.108	4.00	0.114	0.029	4.28

<sup>a</sup> The code PVA\_SSAx means a PVA matrix with x% of its –OH groups esterified.

mixed with the appropriate amounts of sulfosuccinic acid 70 wt.% solution (Fluka) and them vigorously stirred at room temperature for 24 h [23,24].

The solutions were poured and cast on a Teflon plate. The polymeric matrixes were allowed to dry at 60 °C during 24 h. In order to complete the esterification reaction, the dried polymeric matrixes were heated at 120 °C, during 24 h, under vacuum. The obtained samples were denoted as PVA\_SSAx, where  $x = 5$  or 20 or 40 means a PVA matrix with  $x\%$  of its –OH groups esterified.

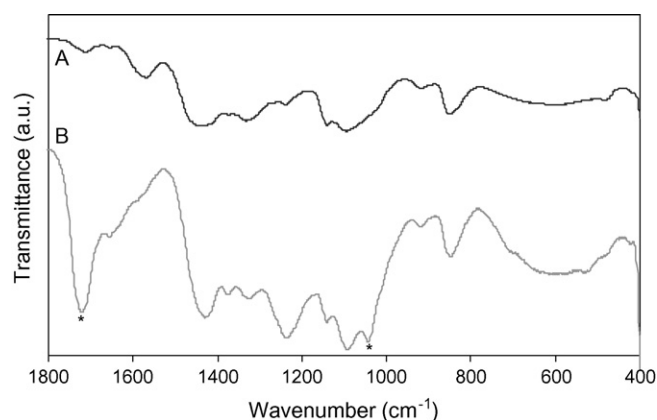
## 2.2. Catalysts characterization

FTIR spectroscopy in KBr pellets was carried out on a Bio-Rad FTS 155 spectrometer. The spectra were taken with a resolution of 4 cm<sup>-1</sup> in the range of 400–4000 cm<sup>-1</sup>, by running 1000 scans.

The amount of acid groups in the PVA\_SSA catalysts was measured by using a classic titration with 0.1 M NaOH.

The swelling degree ( $Q$ ) was measured by immersing the polymeric catalysts in the pure component (methanol or  $\alpha$ -pinene) at 60 °C for 24 h. Then, the samples were taken out, wiped with tissue paper and weighted. For calculations was used  $Q = (m - m_0)/m_0$ , where  $m$  is the mass of the swollen sample and  $m_0$  is its initial mass.

$\alpha$ -Pinene diffusivity in the polymeric catalytic matrixes was evaluated by using a two-chamber apparatus. The two chambers separated by the composite were filled with methanol.  $\alpha$ -Pinene was added to one chamber and its concentration increase in the other chamber was followed. For calculations, the second Fick's law

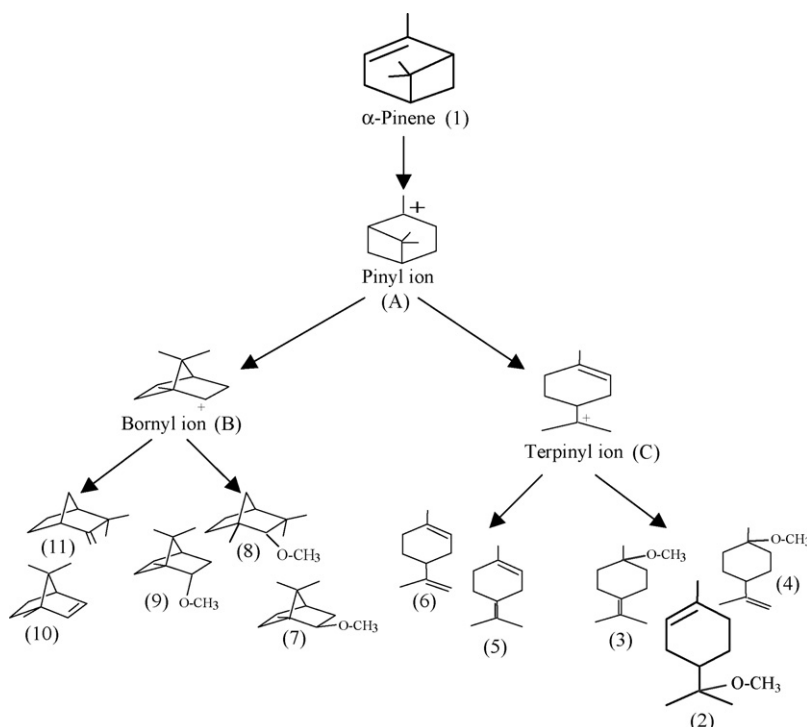


**Fig. 1.** FTIR spectra of PVA matrixes. (A) Pure PVA; (B) PVA\_SSA40.

was used. Table 1 summarizes the polymeric matrixes characteristics.

## 2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at 60 °C. In a typical experiment, the reactor was loaded with 50 mL of methanol and 0.2 g of catalyst. Reactions were started by adding 3 mmol of  $\alpha$ -pinene.



**Scheme 1.**

Stability tests of PVA.SSA20 catalyst were carried out by running four consecutive experiments, in the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by filtration, washed with methanol and dried at 100 °C overnight.

Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column.

### 3. Results and discussion

#### 3.1. Characterization of catalysts

Fig. 1 shows the FTIR spectra of PVA (Fig. 1A) and PVA crosslinked with SSA (PVA.SSA40) (Fig. 1B). The adsorption band at  $\sim 1730\text{ cm}^{-1}$  appearing in the spectra of PVA.SSA40 (B), usually assigned to the ester group ( $-\text{CO}-\text{O}-$ ), suggests that crosslinking was succeeded. The adsorption band at  $1040\text{ cm}^{-1}$ , usually assigned to the  $\text{O}=\text{S}=\text{O}$  symmetric vibrations [25,26], which are present in spectra B, are a strong indication of the presence of sulfonic acid groups in the polymeric matrix.

The swelling of the polymeric catalysts obtained for the pure components,  $\alpha$ -pinene and methanol, decreases when the SSA content increases (Table 1). The swelling degrees decreased due to the decrease of the free volume, even though the polymeric catalysts bears a higher content of hydrophilic functional groups, as observed by other [23].

The acidity of polymeric catalysts was calculated as the base (NaOH) uptake divided by the weight of dry polymer (Table 1). As expected, it increases with the PVA crosslinking, since the number of sulfonic acid functions introduced in the polymeric matrix also increases.

Table 1 shows also the  $\alpha$ -pinene diffusivity through PVA polymeric catalysts. A decrease of  $\alpha$ -pinene diffusivity from the PVA.SSA5 to PVA.SSA40 was observed. This behaviour can probably be explained due to the increase in the restrictions to molecules motion, which are expected to occur with the increase of crosslinking. In a previous work [22], we observed that the isoamylic alcohol diffusivity decreases with the increases of crosslinking degree.

#### 3.2. Catalytic experiments

The main product of  $\alpha$ -pinene (1) methoxylation was  $\alpha$ -terpinyl methyl ether (2) being also formed  $\gamma$ -terpinyl methyl ether (3),  $\beta$ -terpinyl methyl ether (4), terpinolene (5), limonene (6), endo-bornyl methyl ether (7),  $\beta$ -fenchyl methyl ether (8), exo-bornyl methyl ether (9), bornylene (10) and camphene (11) as by-products (Scheme 1). Several reaction products are associated with irreversible rearrangements of the pinyl ion (A). The pinyl ion can rearrange into the bornyl ion (B), which it is further isomerised into bornylene and camphene, and after methanol addition, endo-bornyl methyl ether,  $\beta$ -fenchyl methyl ether, exo-bornyl methyl ether are formed. The pinyl ion can also rearrange into the terpinyl ion (C), which it is further isomerised into terpinolene, limonene, and after methanol addition,  $\alpha$ -terpinyl methyl ether,  $\gamma$ -terpinyl methyl ether and  $\beta$ -terpinyl methyl ether are formed (Scheme 1).

Fig. 2 shows the concentration profiles obtained over PVA.SSA5, PVA.SSA20 and PVA.SSA40 catalysts, in the  $\alpha$ -pinene methoxylation. In Fig. 2, ME, BE, MH and BH represent all the monocycle ethers, all the bicycle ethers, all monocycle hydrocarbons and all the bicycle hydrocarbons formed, respectively. The solid lines represent the model fitted to the data points.

The  $\alpha$ -pinene concentration profile over PVA.SSA5, PVA.SSA20 and PVA.SSA40 catalysts are shown in Fig. 3. It was observed that the catalytic activity of polymeric catalysts increases with the amount

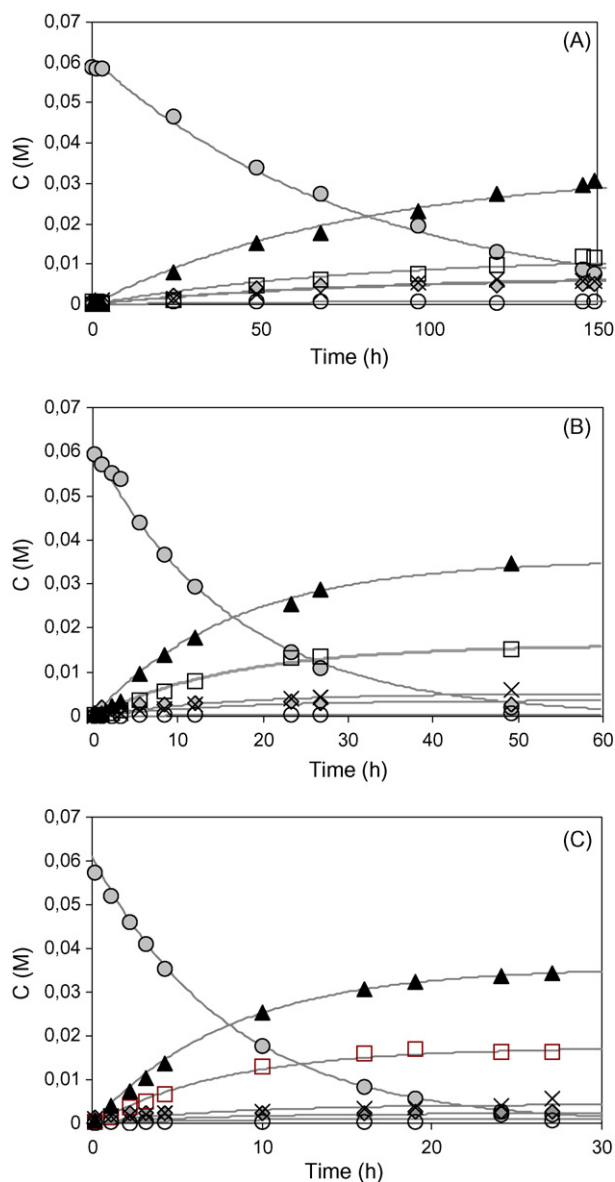


Fig. 2. Methoxylation of  $\alpha$ -pinene over PVA with sulfonic acid groups. Concentration vs. time. (A) PVA.SSA5; (B) PVA.SSA20; (C) PVA.SSA40. (●)  $\alpha$ -Pinene; (▲)  $\alpha$ -terpinyl methyl ether; (□) MH lumps all the monocycle hydrocarbons formed; (○) ME lumps all the monocycle ethers formed; (×) BE lumps all the bicycle ethers formed; (◇) BH lumps all the bicycle hydrocarbons formed. The solid lines represent the model fitted to the data points.

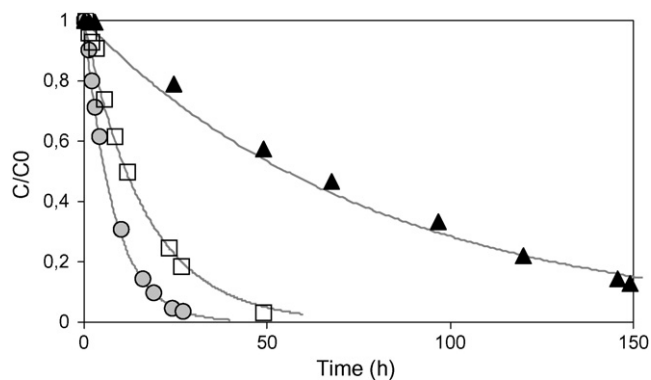
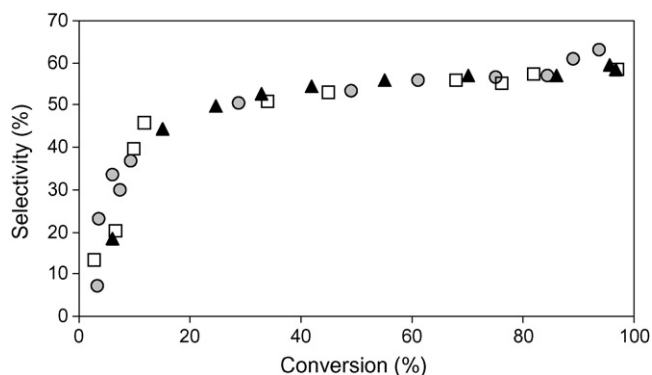


Fig. 3. Methoxylation of  $\alpha$ -pinene over poly(vinyl alcohol) with sulfonic acid groups. Effect of crosslinking degree of PVA on the concentration profiles of  $\alpha$ -pinene. (▲) PVA.SSA5; (□) PVA.SSA20; (●) PVA.SSA40. The solid lines represent the model fitted to the data points.

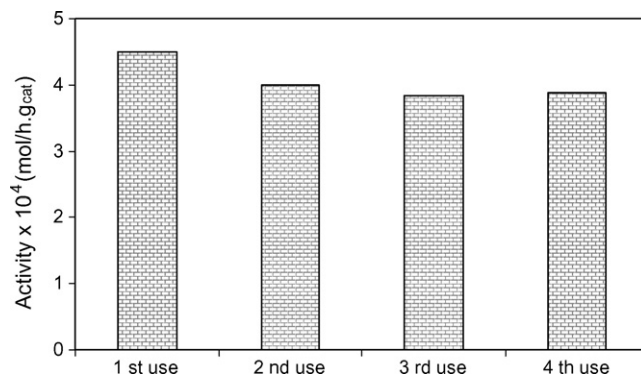


**Fig. 4.** Methoxylation of  $\alpha$ -pinene over poly(vinyl alcohol) with sulfonic acid groups. Selectivity to  $\alpha$ -terpinyl methyl ether: (●) PVA.SSA5; (□) PVA.SSA20; (▲) PVA.SSA40.

of sulfonic acid groups of the PVA. However, with high crosslinking degree of polymeric matrix, a slight increase of activity was observed. This behaviour could be explained not only due to the high mobility restriction of  $\alpha$ -pinene molecules in the PVA due to the decrease of diffusivity of the  $\alpha$ -pinene through the polymeric matrix, but also due to the decrease of the swelling degree for methanol and  $\alpha$ -pinene (Table 1).

The dependence of selectivity to the  $\alpha$ -terpinyl methyl ether with the  $\alpha$ -pinene conversion, for PVA.SSA5, PVA.SSA20 and PVA.SSA40 catalysts is shown in Fig. 4. It was observed that all of the catalysts tested on  $\alpha$ -pinene methoxylation exhibited good selectivity to  $\alpha$ -terpinyl methyl ether (about 60% near complete conversion).

In order to study the catalytic stability of the PVA.SSA20, consecutive batch runs with the same catalyst sample were carried out. It was observed a decrease of the catalytic activity from the first to the third use. However, after the third batch it was observed a stabilisation of the initial activity (Fig. 5).

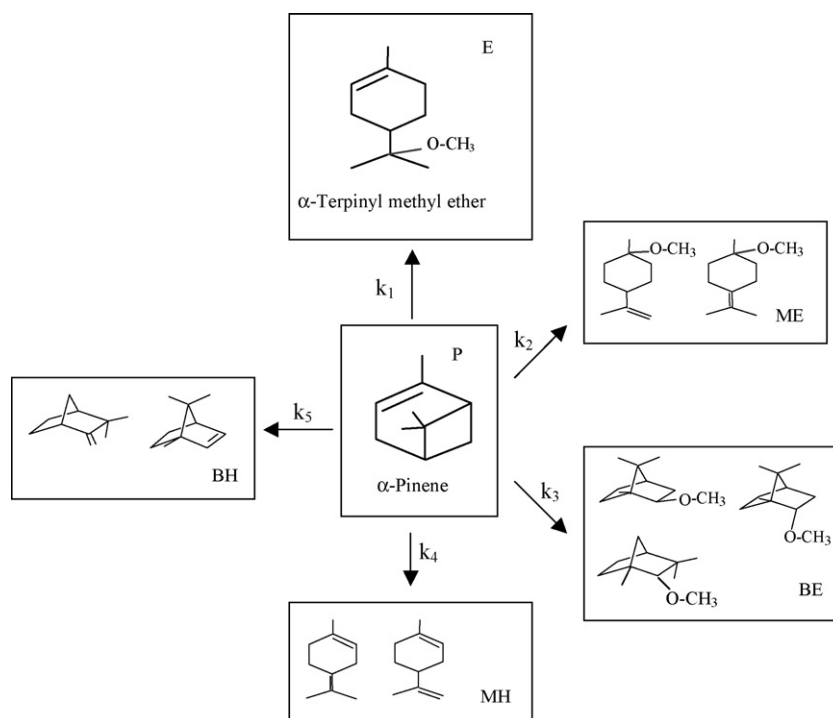


**Fig. 5.** Stability studies on PVA.SSA20 catalyst sample. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the  $\alpha$ -pinene kinetic curve.

### 3.3. Kinetic modelling

A kinetic model can be established based on the following assumptions:

1. Isothermal and isobaric reaction conditions.
2.  $\alpha$ -Pinene is consumed according to the parallel reaction network shown in Scheme 2, where P represents  $\alpha$ -pinene, E represents  $\alpha$ -terpinyl methyl ether, ME represents all the monocycle ethers formed, BE represents all the bicycle ethers formed, MH represents all monocycle hydrocarbons formed and BH represents all the bicycle hydrocarbons formed.
3. As in the present case  $\alpha$ -terpinyl methyl ether seems not to be consumed, is not necessary a more complex reaction network.
4. The concentration profiles of the reagent and products do not exhibit any pronounced initial inductive period (Fig. 2). The external and internal diffusion of the reagents and products on the catalyst were not considered.
5. First order kinetics is assumed.



**Scheme 2.**

**Table 2**  
Model parameters obtained by fitting the model to experimental data.

Polymeric catalysts	$k_1$ (dm <sup>3</sup> /h g <sub>cat</sub> )	$k_2$ (dm <sup>3</sup> /h g <sub>cat</sub> )	$k_3$ (dm <sup>3</sup> /h g <sub>cat</sub> )	$k_4$ (dm <sup>3</sup> /h g <sub>cat</sub> )	$k_5$ (dm <sup>3</sup> /h g <sub>cat</sub> )
PVA_SSA5	0.00175	0.00005	0.00035	0.00062	0.00037
PVA_SSA20	0.00880	0.00010	0.00130	0.00400	0.00090
PVA_SSA40	0.01800	0.00060	0.00220	0.00880	0.00120

The reaction rates of these five pseudo elementary reaction are expressed as:

$$r_1 = k_1 C_p \quad (1)$$

$$r_2 = k_2 C_p \quad (2)$$

$$r_3 = k_3 C_p \quad (3)$$

$$r_4 = k_4 C_p \quad (4)$$

$$r_5 = k_5 C_p \quad (5)$$

For batch reactor the mole balance equations may be written as

$$\frac{dC_p}{dt} = -\frac{W}{V}(r_1 + r_2 + r_3 + r_4 + r_5) \quad (6)$$

$$\frac{dC_E}{dt} = \frac{W}{V}r_1 \quad (7)$$

$$\frac{dC_{ME}}{dt} = \frac{W}{V}r_2 \quad (8)$$

$$\frac{dC_{BE}}{dt} = \frac{W}{V}r_3 \quad (9)$$

$$\frac{dC_{MH}}{dt} = \frac{W}{V}r_4 \quad (10)$$

$$\frac{dC_{BH}}{dt} = \frac{W}{V}r_5 \quad (11)$$

The software package Scientist™, from Micro-Math® Scientific Software (USA), was used to perform the non-linear regression calculations. This software includes the capability to perform non-linear fittings and simultaneously to solve differential equations. The least squares and the simplex algorithms were used. Initial estimates of parameter values are required as starting values.

The fitting of the model to data points is shown in Figs. 2 and 3. It was observed that kinetic model fits experimental concentration data quite well. The effect of the PVA crosslinking degree on the model parameters is shown in Table 2. It was observed that the apparent kinetic constants increase with the crosslinking degree, i.e. with the amount of sulfonic acid groups presents in the polymeric matrix (Table 1).

#### 4. Conclusions

The  $\alpha$ -pinene methoxylation yields  $\alpha$ -terpinyl methyl ether as main product being also formed bornyl methyl ether, fenchyl methyl ether, limonene and terpinolene as by-products.

Poly(vinyl alcohol) crosslinked with succinic acid containing sulfonic acid groups, was used as catalysts in the methoxylation of  $\alpha$ -pinene.

The conversion increases when the amount of sulfosuccinic acid used in the polymer crosslinking is increased from 5% to 20%. However, when crosslinking degree increases from 20% to 40%, the conversion of  $\alpha$ -pinene increases only slightly.

All of the catalysts tested on  $\alpha$ -pinene methoxylation exhibited good selectivity to  $\alpha$ -terpinyl methyl ether.

After the third batch, it was observed a stabilisation of the activity of the PVA\_SSA20.

A kinetic model, assuming that the  $\alpha$ -pinene is consumed according to the parallel reaction network and the external and internal diffusion of the reagents and products on the catalyst are despised, has been developed. The kinetic model fits experimental concentration data quite well.

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