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Hydrogenation of acetophenone in a pervaporative catalytic membrane reactor with online mass spectrometric monitoring

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Abstract

A pervaporative catalytic membrane reactor can afford chemical reaction and separation or concentration of the products in one step. The hydrogenation of acetophenone (AP) in diluted aqueous solution was investigated applying catalytically reactive polydimethylsiloxane (PDMS) and polyether-b-amide (PEBA) membranes in the pervaporative membrane reactor. A quadrupole mass spectrometer (QMS) was employed to follow online the hydrogenation reaction. Homogeneously distributed palladium clusters inside the polymeric membranes catalyze the hydrogenation of AP to 2-phenylethanol (PE) and the consecutive product ethyl benzene (EB) at low temperatures (30-70°C). The reaction depends strongly on the disposability of H_2 inside the membrane. Only by means of the online QMS analyser the availability of stoichiometric or excess amounts of H_2 at the catalyst with adjusted parameters such as temperature, hydrogen pressure, solute concentrations and membrane permeability could be detected. It could be shown, that the hydrogen level by bubbling at ambient pressure was not sufficient, however, at 4 bar H_2 pressure and 50°C conversions up to 83% in 6h were obtained. Efforts to quantify the measured intensities of the QMS were not successful; however, the relation of the organic compounds and the presence of excess H_2 were detected precisely with this method.

Keywords: Catalytically reactive polymer membrane, membrane reactor, pervaporation, online mass spectrometry, hydrogenation, acetophenone, palladium

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I.) Introduction

The coupling of mass spectrometry (MS) and pervaporation (PV) had been used first by Eustache and Histi [1]; nevertheless it is a rarely applied method for monitoring the PV process on-line. Schäfer et al. [2] investigated the PV of a model wine must on regard of transport phenomena. Changes of operating conditions were observable in real time and good resolution. Standard laboratory PV equipment was fitted with additional valves to allow a split like inlet to the mass spectrometer. Similar in operation and more common is the membrane introduction mass spectrometry (MIMS), a well known method to detect organic compounds dissolved in water in very low concentrations [3-5]. The pervaporative step may increase the concentrations of organics by factors of 100 to 10000 and amplifying the signal remarkably [6]. On the other hand, the method is applicable for measuring the diffusion of gases and vapours through different kind of polymers [7, 8]. Allen et al. [9] showed that MIMS could be a viable method to monitor simultaneously components of extreme different volatility.

In the presented work the PV-MS coupling is applied to a permeate vapour mixture that not only contains water and different organics of high boiling point, but also the permanent gas H_2, required for the hydrogenation reaction in the catalytically reactive membrane. The pervaporative catalytic membrane reactor combines the separation by pervaporation and a catalytic reaction within the same membrane [10], thus not only enriching a reactant from the feed solution but also concentrating it towards the catalyst and, if possible, separating the reaction product. Model system is the hydrogenation of acetophenone (AP) catalyzed by palladium. AP in neutral solution is reduced by palladium catalyst and molecular hydrogen either to the alcohol 1-phenylethanol (PE) or the aromatic hydrocarbon ethyl benzene (EB), (see Fig. 1) depending on the activity of catalyst [11]. Using a highly active supported Pd

catalyst and following the reaction profile showed that PE is the intermediate and EB the final product [12].

Low concentrations (in the range of 0.01 to 0.1%) of AP and PE in water are enriched by pervaporation till phase separation occurs with enrichment factors up to 200-300 by PEBA membranes [13]. The boiling point of PE (204 °C) is as high as that of AP (202 °C); the water solubility of PE is about 5 times higher than that of AP (see Tab. 1). In contrary, EB is much more volatile than AP and PE (bp. 136°C) and of very poor water solubility. EB is formed by the hydrogenation of intermediate styrene, originating from the dehydration of PE [14]. However, styrene is hydrogenated very fast and, therefore, maybe not detected as intermediate. [15].

Experimental

Membrane preparation: PDMS membranes were prepared by suspending a supported catalyst in a 14% solution of room temperature cross-linkable PDMS (Dehesive, Wacker Chemie) in THF. After adding a few drops of crosslinker, the solvent was evaporated at ambient temperature on a Teflon-plate. The supported catalyst was prepared by suspending silica (Aerosil OX 50, Degussa) in ethanol, adding polyvinylpyrrolidone (PVP) and palladium acetate and refluxing the suspension for 2 h to reduce the Pd salt and forming nanosized metal clusters. After evaporation of the ethanol the supported catalyst consisted of 5% Pd, 65% SiO2 and 30% PVP. The PVP layer is not soluble in THF used for PDMS catalytic membrane preparation. The final Pd concentration in the PDMS membranes was about 2%. Preparation of catalytic/non-catalytic PEBA (PEBAX®, grade 4033, Atochem) membranes is described in [16].

Pervaporation: The catalytic pervaporation setup is described in [10]. Membrane area is 100 cm², feed volume is 2L, permeate pressure <0.1 mbar, feed flow > 1L/min, feed concentration AP about 1000 ppm (mg/kg water). The permeate vapour was collected in a cooling trap by

liquid nitrogen over a certain time period (1 to 3h), then diluted with ethanol and subsequently analyzed by gas chromatography. GC: Hewlett-Packard 5890, Series II with FID; column: 30 m Supelcowax 10, 0.53 mm ID, film thickness 1µm; temperature program:120°C to 200°C at 40°C/min.

Online mass spectrometry: Coupling to PV is performed comparable to [2]. The permeate side of the membrane was connected by means of a valve and a heated tube (about 100°C; length 20 cm, diameter 2.5 cm) to the inlet valve of the mass spectrometer (QMS 200 quadrupole mass spectrometer "Prisma", Pfeiffer Vacuum). Via the heated inlet valve an appropriate part of the permeate vapour was continuously introduced to the ionisation chamber. The Quadstar software of the QMS was used in the single-ion mode to monitor online the masses m/z= 2 (H_2), 4 (He), 18 (water), 32 (O_2, leak indication), 77 and 105 (AP), 91 (EB), 79 and 107 (PE), 104 (Styrene) (see Fig.1) and m/z = 85 as blank value. The total internal pressure (IP) was set to about 10^{-6} mbar by adjusting the inlet valve, and was recorded, too. During the regular change of cooling traps in the pervaporation part the inlet to the QMS was closed.

Recording and calculation of apparent diffusion coefficients

The mass spectrometer was connected to the permeate side of the membrane cell and evacuated to below 0.1 mbar. Starting with a dry membrane and opening of the by-pass fed the membrane with a single or a mixture of compounds including solved gas (H_2) in water. After some seconds an increase of signals can be observed caused by the permeation of the compounds (e.g. Fig. 2). After some time a steady permeation is reached visible by a steady ion current. The time delay may last from a few to several 100 seconds depending on the compound and the membrane thickness. From these data the apparent diffusion coefficients D_a were calculated. Tanaka et al. summarizes the theoretical background [8] and gives the data treatment to yield the time lag (ϑ) as the intercept on the time axis. D_a is finally calculated using the thickness (l) by $D_a = l^2/6\vartheta$. During pervaporation time lags can be

determined in different ways: Starting with the dry membrane by suddenly contacting the membrane by opening of the by-pass or by increasing the feed concentration suddenly to measure apparent diffusion coefficients of the swollen membrane at PV conditions.

Results and discussion

Membranes

Two commercially available polymers, PEBAX® (Polyether-*b*-polyamide) grade 4033 and Dehesive (Polydimethylsiloxane) were selected as catalyst support and separation membrane. The first is characterized by high sorption selectivity for medium polar organic compounds and generally lower total flux, while PDMS has a lower selectivity for polar organics, but a considerably higher over-all flux density measured at comparable membrane thickness. Homogeneous membrane films were used to exclude support effects. Palladium nano clusters (2 to 10%) as catalyst were formed inside the membranes during preparation and provided with cluster sizes of 2-5 nm a high surface area of the catalyst. PEBA membranes were about 80 to 100 µm, PDMS 200 to 250 µm thick, to achieve almost similar flux densities of about 20 to 40 g/m²h at 30°C and 80 to 100 g/m²h at 50°C. These flux densities allow for low permeate pressure in pervaporation to evaporate the high boilers fast and completely. The enrichment for organics, however, is high, e.g. about 300, when starting with a diluted 0.1% AP solution (PEBA).

Mass spectrometry coupled to pervaporation

The recorded mass spectra of the compounds under consideration corresponded well to the literature [17] and suitable masses were detected without overlapping (see Fig. 1). Except for styrene (m/e = 104) the molecular mass peaks are of lower intensity and the base peaks (100%) are formed by molecular mass minus 15 (methyl group). The base peaks do not overlap and were used for all compounds. Additionally the masses m/z=77 (AP) and 79 (PE) were recorded too, to improve the quality of detection. To assay the applicability of the QMS

online coupling for high boilers in pervaporation a noncatalytic PDMS membrane was selected to test the basics. In Fig. 2 a run with a plain (non-catalytic) PDMS membrane at 30°C is shown at various operating conditions. A by-pass to the membrane allows setting up the feed solutions separately, e.g. changing of temperature and concentration. After recording the background with the dry membrane the first feed (2 min.) is pure water resulting in a steep increase of mass 18 (water). Because of the increase of the internal pressure all other masses show a small step, too. Opening the by-pass 10 min later disconnects the membrane from the feed, reduces the pressure and results, therefore, in a small signal decrease in all masses as seen for all following similar operations. The water is replaced by a 500 ppm AP-solution, the by-pass closed again (15 min.) and AP permeation causes a steep increase of the AP signal of three decades to $1x10^{-8}$ A (m/z = 105 (also of 77, not shown here). Masses 107 (PE), 104 (Sty) and 91 (EB) show also an increase, although not that steep. By gas chromatography could be shown that AP of reagent grade contains some minor amounts of these compounds, originating from an autolysis reaction, and are detected by QMS as well. Next, the AP concentration is increased to 1000 ppm (36 min.) accompanied by a further increase of the AP signal of about $1x10^{-8}$ A. After 10 min at these conditions the by-pass is opened and the solution bubbled with H_2 gas. Preceding experiments using a H_2 sensor had shown that the dissolution of H_2 in water is rather fast (within 1-2 minutes), therefore, the by-pass is closed after 52 min and the H_2-signal increases instantly about one order of magnitude. Before exchange of H_2 to He the membrane is disconnected from the feed by opening the by-pass. The feed is bubbled for about 5 min. by He to drive out the H_2 and at closing the by-pass a steep increase of the He-signal of 4 orders of magnitude was observed. To summarize the results presented in Fig. 2: AP and even traces of the hydrogenation products can be detected in accordance with their concentration all together and not influenced by H_2 or He. Moreover, the signals of He and the IP-signal are useful as markers for disconnecting the feed resp. opening of the by–pass. In Fig. 3 is depicted a similar run with a catalyst containing PDMS

membrane. AP is again added in two portions to finally 1000 ppm, forming identical steps in ion current for AP, PE and EB like in Fig. 2. After 80 min. reactive PV applying H_2 is started, causing an increase of the H_2-signal proceeding precisely with the rise of the EB, PE and Sty (not shown) signals, while AP is slightly decreasing. This finding confirms the applicability of the QMS detector for use in reactive pervaporation. Exactly with the start of H_2 as reducing reagent an instant appearance of the reaction products is observed also evidencing that the membrane bound nanosized Pd-catalyst is highly active and starts operation with first contact to H_2. The H_2-signal increases only with a delay of 1-2 min (compare Fig. 2 no delay for non-catalytic membranes). This delay time is caused by solution of excess-H_2 in the Pd-nanoclusters prior to break through the membrane thus verifying the high affinity of H_2 to the Pd-nanoclusters.

In Fig. 4 is depicted a run with a catalytic PEBA membrane. The order of events is similar: After the detection of the QMS background with evacuated membrane pure water is fed, followed by 500 and 1000 ppm AP. Next H_2 is started. Compared to the PDMS membrane a much longer induction period of 19 min. was observed to obtain a steady signal for the hydrogenation products EB, PE and Sty accompanied by a slight decrease of the AP-signal. A sparsely visible increase of the H_2-signal was also identified (see insert in Fig. 4). This increase was not finished after 40 min. and uncovers a slight excess of H_2 on stoichiometric conditions for hydrogenation inside the reactive membrane. To increase the reaction rate a temperature program was started, increasing the temperature uniformly from 30 to 70°C with 0.6°C/min. The temperature increase causes a higher permeation within the membrane, rising the water signal and consequently the internal pressure (not shown in Fig. 4). Permeation of AP increases too, measurable also in pervaporation flux, but hydrogenation products are slightly decreasing. Noteworthy is also a change of the relative intensities of the products. The relation of PE to EB (first and final hydrogenation product, see Fig. 1) is shifted in favor to EB thus indicating a change of the reaction conditions temperature, AP concentration, and H_2

availability. By following the H_2-signal shift it is not clearly visible if there is any more excess of H_2. It seems all H_2 is consumed at the higher temperature due the lower solubility of H_2, the faster permeation (lower contact time to the catalyst) of all educts and the expected higher reaction rate. Therefore, the reaction runs at H_2-deficiency at 70°C. To supply more H_2 for the reaction the concentration of H_2 during pervaporation was increased by applying a pressure vessel as feed reservoir. Either by simple H_2 pressure-build-up via a tube or by means of a hollow fibre module, a H_2 pressure corresponding to a defined H_2 concentration was set. The pervaporation process is only slightly sensitive towards feed pressure, of more importance is the pressure difference between feed and permeate for high boilers. In Fig. 5 an experiment is shown during which the hydrogen pressure was increased stepwise from 1 to 4.5 bar. The used PEBA membrane had a rather high content of Pd (15%). Start is at 1 bar H_2 for 20 minutes to obtain steady conditions. The feed solution is less than 100 ppm of AP. Within 30 min. the H_2 pressure was increased to 2 bar. With some delay the signal for EB and PE increased accompanied by a decrease of the AP signal thus demonstrating higher conversion with increasing presence of H_2. However, no change of the H_2 signal was detectable. All hydrogen is consumed completely by the catalyst and hydrogenation was started, visible after some delay by the increase of the products EB and PE and a decrease of the educt AP. Within half an hour at 2 bar H_2 no permeation of excess H_2 through the catalytic membrane was achieved. Hydrogen in detectable excess was reached after further increase of H_2-pressure to 3.2 bar within a delay time of about 10 min. The actual concentration of dissolved H_2 in the feed solution was measured by means of a WLD-sensor: In the beginning it's 1.4 ppm (1bar) and rising up to 5 ppm at 4.5 bar (depicted as grey dots in Fig. 5).

In Table 2 are summarized reactive pervaporation runs at 30°C and 50°C with either 1 or 4 bar H_2-pressure. As generally known, the reaction rate roughly doubles with 10K temperature increase. In addition, the flux density of organics and water increases with temperature

causing a decrease of contact time at the catalyst, and the H_2 supply to the catalyst also may decrease originated by lower solubility of H_2 at higher temperature in the feed solution. From the QMS signal in the permeate using PEBA membranes it is not clearly detectable if H_2 is still in excess during reaction at low H_2-pressure. However, from the reactive pervaporation results should be deducible if H_2 is supplied at least in stoichiometric amounts. Starting with 2 L feed solution and 1000 ppm AP the reactive pervaporation was run for 6 to 10 h and samples were collected from feed and permeate. The test at 1 bar H_2/30°C results in a steady decrease of AP in the feed such as with non-reactive pervaporation accompanied by a consequential decreasing concentration of AP (~400 ppm, 10 h) in the permeate. The reaction products PE and EB are found in similar low concentration in the permeate (1-2%), however, an increasing amount of PE is also seen in the feed by back diffusion from the membrane after generation. With increase of the H_2 supply to the reaction by applying 4 bar H_2 at 30°C the AP concentration in the feed decreases to a lower level (~200 ppm, 10 h). PE is detected in permeate only in low concentration (~0.1% after 4 h; negligible later), though EB is the main product in the permeate (10-15%). PE, on the other side, is concentrating in the feed up to 200 ppm, thus unveiling again the tendency of PE to diffuse in significant amounts to the feed side. PE staying inside the membrane and being hydrogenated further to EB, on the other hand, is found as reaction product EB exclusively in the permeate. EB driven by its much lower solubility in water has no driving force to accumulate in the water above its very low concentration limit. Rising the temperature to 50°C at same 4 bar H_2 pressure results in further, faster decline of the AP level in the feed (~140 ppm, 6 h). The PE concentration in the permeate diminishes quickly with decreasing AP feed concentration and is negligible after 5 h reactive pervaporation, thus disclosing that at 4 bar H_2, 50°C and feed concentration of AP ~300 ppm, PE ~400 ppm (as intermediate reaction product by back diffusion from the membrane) the exclusive product is EB in the permeate. The fractions of the components after 6 h of reaction at same reaction conditions as reported above are summarized in Table 3.

Increasing the H_2 pressure from 1 to 4 bar forces the conversion at 30°C within 6 h from 17% to 52%. Rising the temperature at 4 bar H_2 to 50°C doubles about the total flux to 95 L/m² h and increases the total conversion further to 83%. A considerable amount of product PE (44% of total products mass) is yet detected in the feed.

Attempts to calibration the QMS

Cooks [4] and Schäfer [2] claim a direct dependence of the peak area/detector signal on the concentration in permeate resp. feed via a known enrichment for non-reactive pervaporation. In addition, it is known that a large amount of permeating water may affect the mass transport of the organics to the QMS [18]. In our case we are using high boiling compounds (bp. ~200 °C) besides water concentration up to 90% of all components and the membrane thickness is selected to generate acceptable fluxes. Therefore, the permeate pressure is far away from below 10^{-4} mbar and condensation of at least one to several layers of water including the high boiling compounds at the wall of the permeate side is expected. This layer will cause and change by time a considerable background signal, thus impact the quality of the measured data. Moreover, calibration of the QMS by applying a known mixture of all components (H_2O, AP, PE, EB) is difficult because they do not form a homogeneous phase in liquid and are only stable in gas phase at pressures below 0.1 bar. In Fig. 6 are reported the permeate data of a reactive pervaporation run for 6 h at 4 bar H_2/50°C. A break in the signals indicate the change of the permeate collectors. There is detectable the increase/decrease of EB and PE and the decrease of AP as reported in Tables 2, 3. In addition, after about 200 min. of elapsed time the H_2 signal starts to rise considerably (not in correlation with the water signal). This visualizes the point where H_2 is in detectable excess as extracted at the permeate side of the membrane. The feed concentration of AP and PE (as back diffused first reaction product) are 470 (AP) and 360 ppm (PE) meaning at higher AP concentration there is eventually stoichiometric H_2 available or, more likely, at the beginning with 1000 ppm AP even a H_2

deficit. The correlation of the organics detected by QMS online and GC offline gives a different picture. In case of the low boiling, low water soluble EB a good correlation is seen (Fig. 7a) but for AP and PE, the high boiling, fairly good water soluble compounds there is no useful correlation. The QMS signal even increases with decreasing amount of these organics in the permeate as shown for PE in Fig. 7b. As pointed out above at the permeate side with relatively high total flow of ~80% water (~100 L/m² h) the pressure is relatively high and at the large area of walls a layer of surface liquid may buffer the mixtures composition and tamper the measured results. The low boiling, sparsely water soluble EB on the other hand can be calibrated satisfactorily.

Comparison of PEBA and PDMS as membrane material

PDMS is a hydrophobic material with high diffusion coefficients to gases, vapors and also in pervaporation, whereas the PEBA is more hydrophilic due to its polyether blocks. This is reflected by the diffusion coefficients to gases of the dry polymer being roughly an order of magnitude higher for PDMS (e.g., D_a H_2 = 6.8 x 10^{-5} cm²/s (PDMS) and 4.4 x 10^{-6} cm²/s (PEBA). With the pervaporation set-up diffusion coefficients of water, AP, PE and EB were calculated according to [8] for both catalytic and non-catalytic membranes. The catalytic membranes all contains silica supported catalysts and PVP, therefore, the filler is expected to slow down diffusion, to prolongate the path through the membrane and increase the contact time at the catalyst to improve conversion [16]. This was confirmed by all D_a data as shown in Fig. 8. The D_a for AP, PE and EB solved in water are generally about one order of magnitude higher for PDMS compared to PEBA. The under PV conditions (partly) swollen membranes affect the D_a only marginally. Pervaporation data with catalytic PDMS were not obtainable because of mechanical problems of the membranes in the 100 cm² cell. Several trials ended with the breakdown of the membrane. Reinforced membranes [19] may be made to solve this problem.

Conclusions

The coupling of a pervaporative catalytic membrane reactor with a QMS mass spectrometer was used to monitor online the hydrogenation of acetophenone to 1-phenylethanol and the consecutive product ethyl benzene. The reaction is catalyzed by supported palladium catalyst incorporated into the polymeric membranes. Two polymers were applied, PDMS and PEBA, whereas PDMS affords an order of magnitude higher diffusion coefficients for all compounds applied. The QMS detector allows for fast and direct control of the reactive pervaporation results. Changes of process parameters like concentration and temperature, as well as the progress of hydrogenation could be followed directly by changes of the QMS signals. In addition, the availability of excess H_2 was proved by the QMS during the reaction. Since conversion demands at least stoichiometric availability of H_2 at the membrane enclosed catalyst, PEBA membranes with a low H_2 permeability had to be operated at 4 bar H_2. Using a time lag method the apparent diffusion coefficients for water, AP, PE and EB were calculated from QMS signal increase. For both membrane materials the diffusivity decreased by incorporation of the silica supported Pd. Attempts to correlate the ion current intensities of the QMS signals with actual concentrations measured of permeates by GC were successful only with the more volatile, sparsely water soluble ethyl benzene.

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Figure

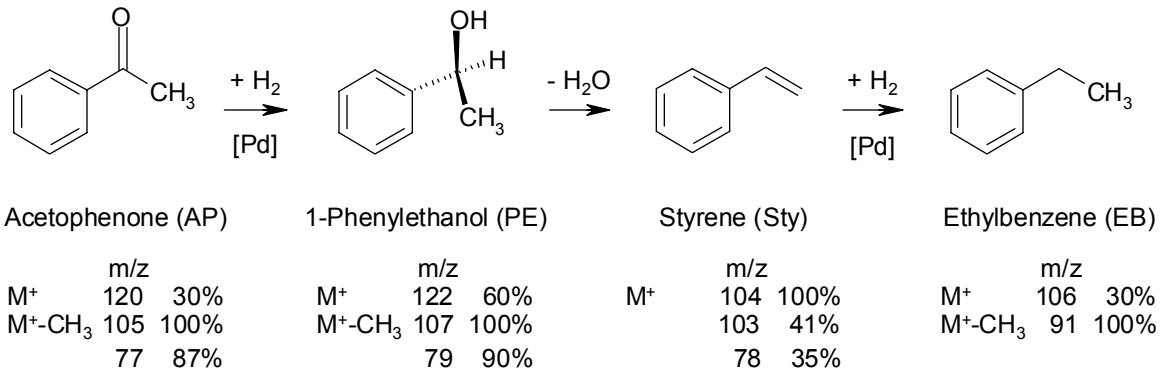

Fig. 1. Scheme of hydrogenation reactions. Mass intensities, as given in [17].

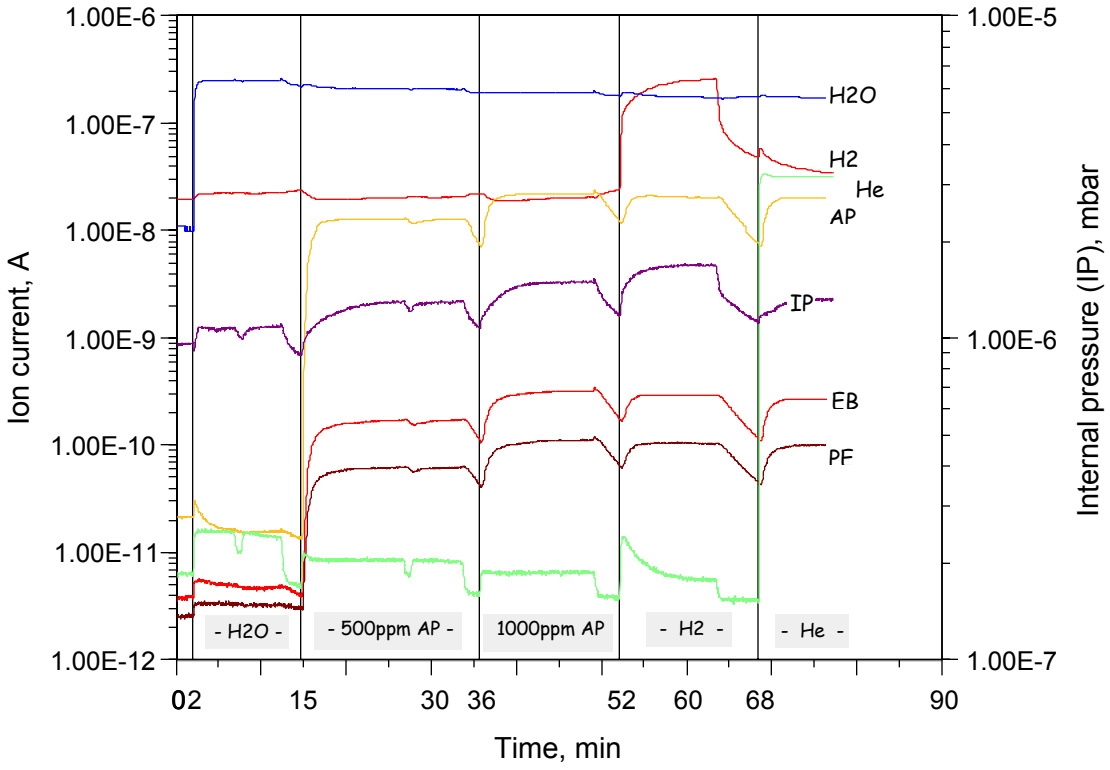

Fig. 2. Mass intensities recorded during pervaporation at 30°C. Started with a dry membrane. Membrane: 220µm PDMS (non-catalytic). H_2 , He by glass frit. Markers on the time axis indicate closing of the by-pass and re-starting of PV at changed conditions.

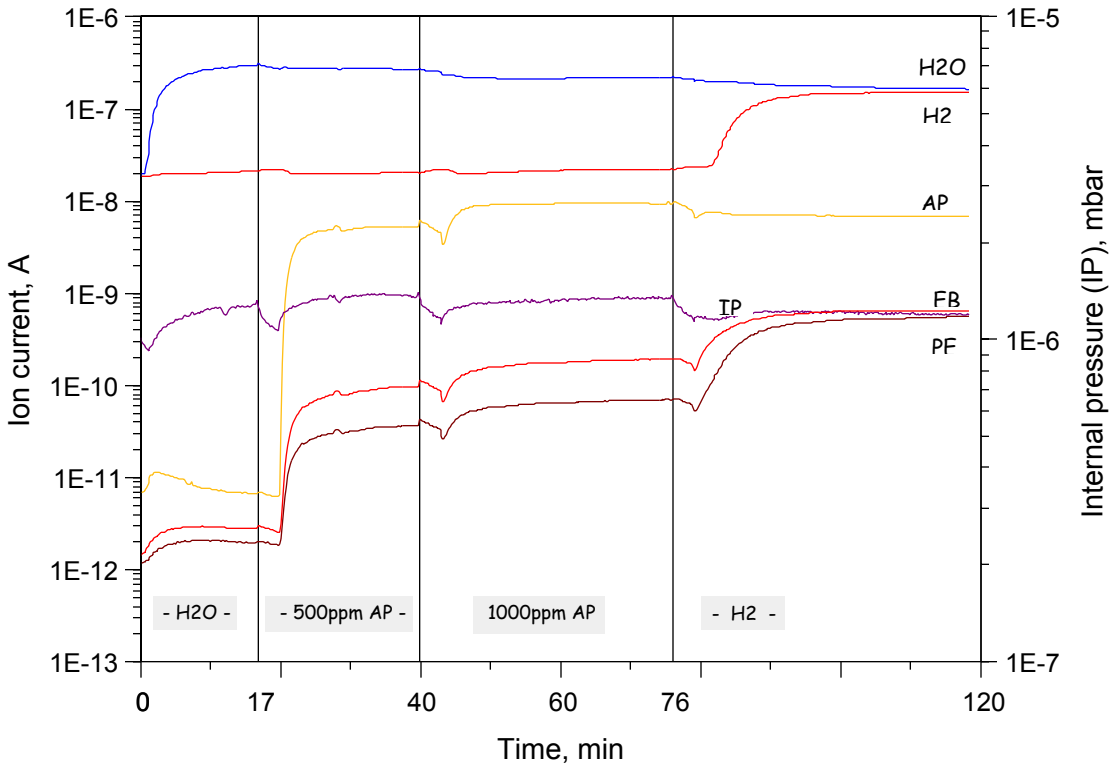

Fig. 3. Mass intensities recorded at reactive pervaporation of AP with a catalytic PDMS membrane (2% Pd, thickness 277µm). T= 30°C. H_2 by glass frit. Markers on the time axis show opening of the by-pass, thus indicating disconnection of the feed from the membrane.

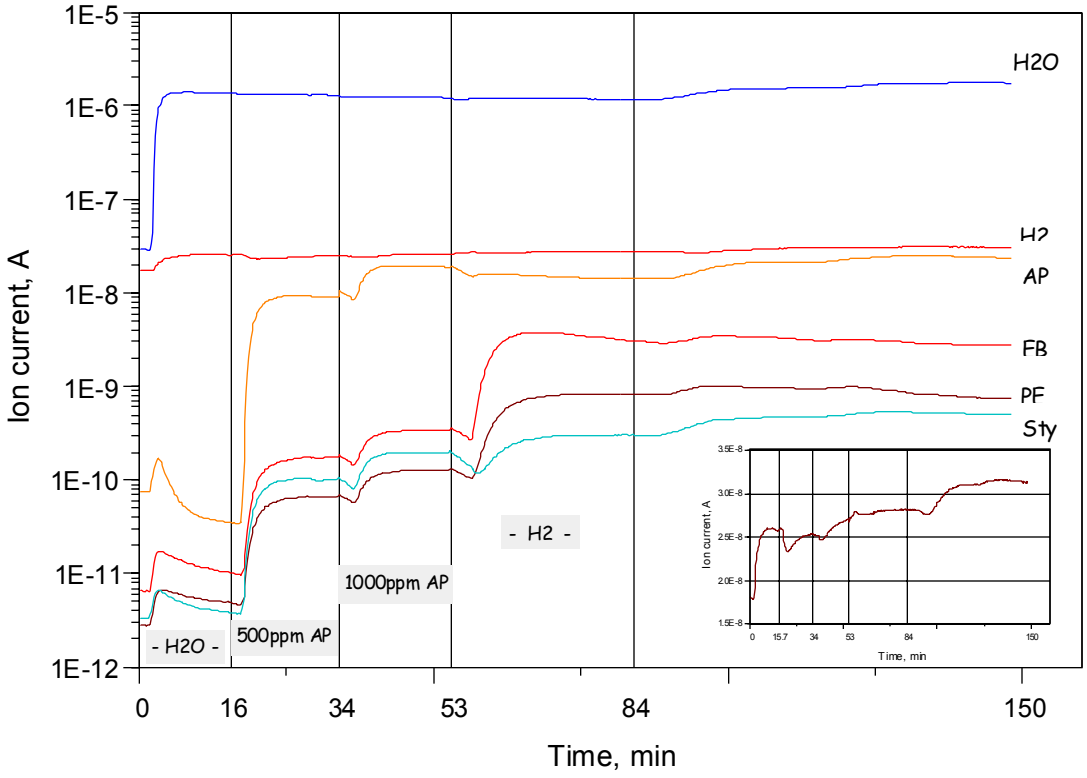

Fig. 4. Reactive pervaporation of AP with catalytic PEBA membrane (2% Pd, thickness 70µm). H_2 by glass frit. Start with dry membrane at 30°C. Linear temperature increase to 70°C with 0.6°C/min. starting at 84 min. Markers on the time axis show opening of the by-pass, thus indicating disconnection of the feed from the membrane. The insert shows the H_2 signal in non-log scale.

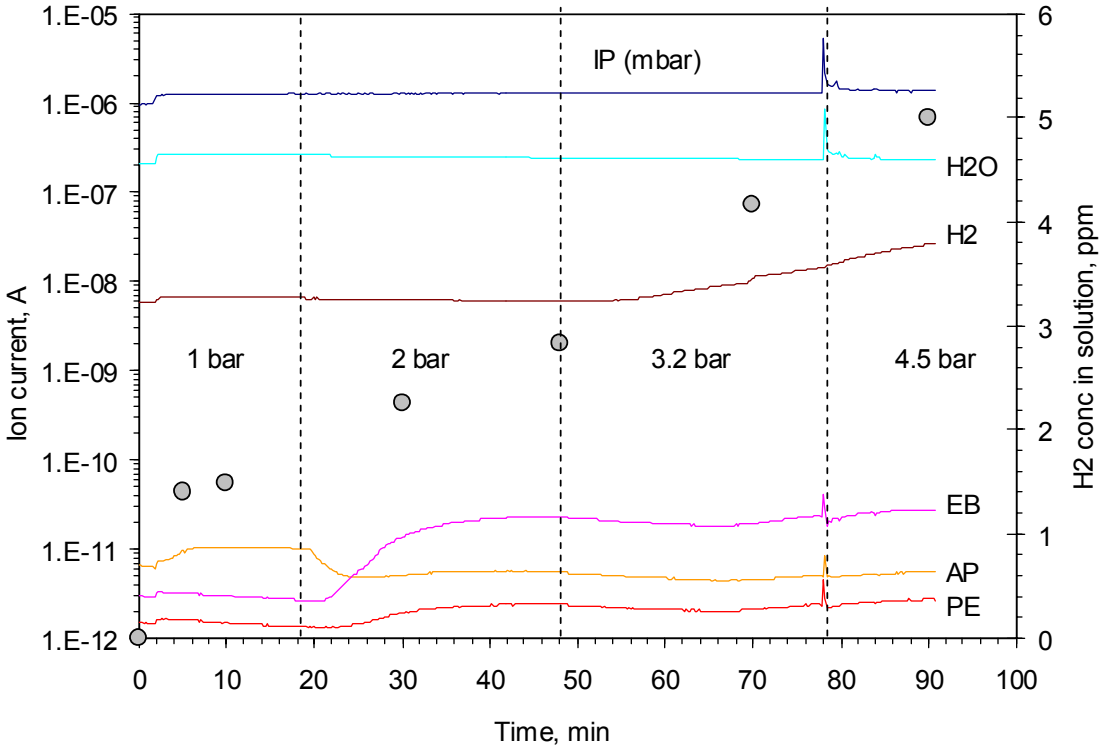

Fig.5. Reactive pervaporation of AP (>100ppm) with catalytic PEBA membrane (15% Pd) and stepwise increase of hydrogen pressure. Start: H_2O / AP, 1bar H_2, 30°C. IP = Internal pressure in QMS (mbar). Grey dots: H_2 concentration in solution (ppm).

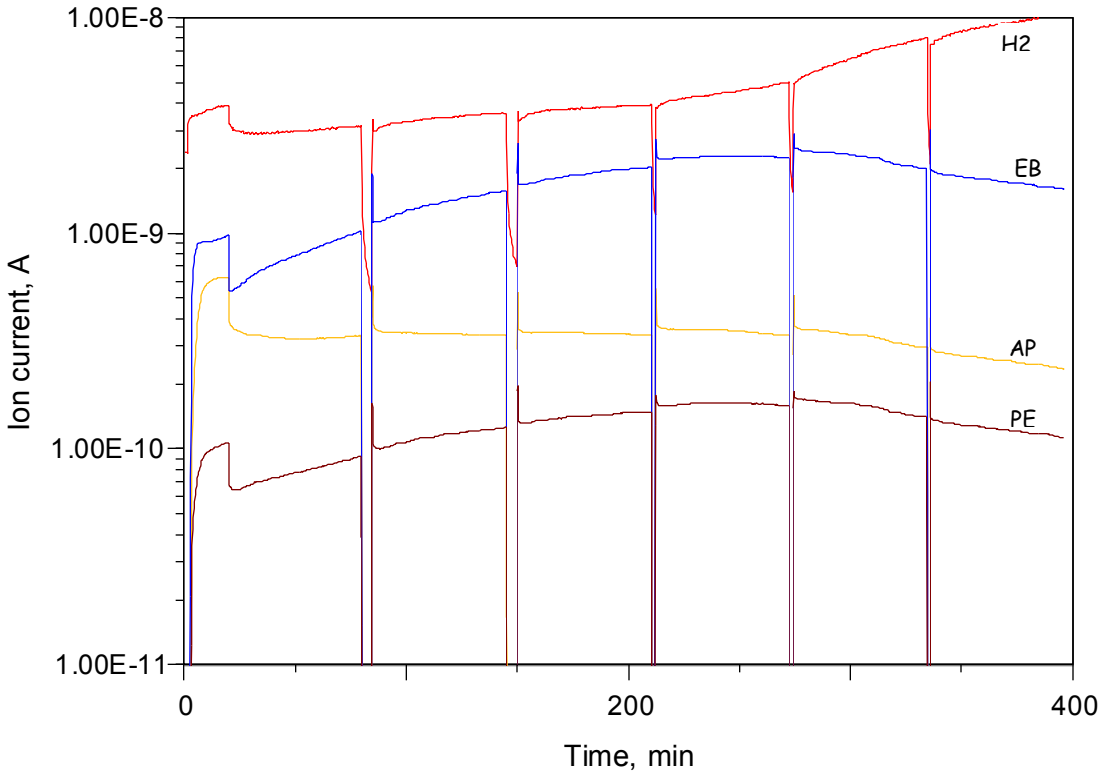

Fig. 6. QMS signals for correlation with GC data of permeate (see 7a, b)

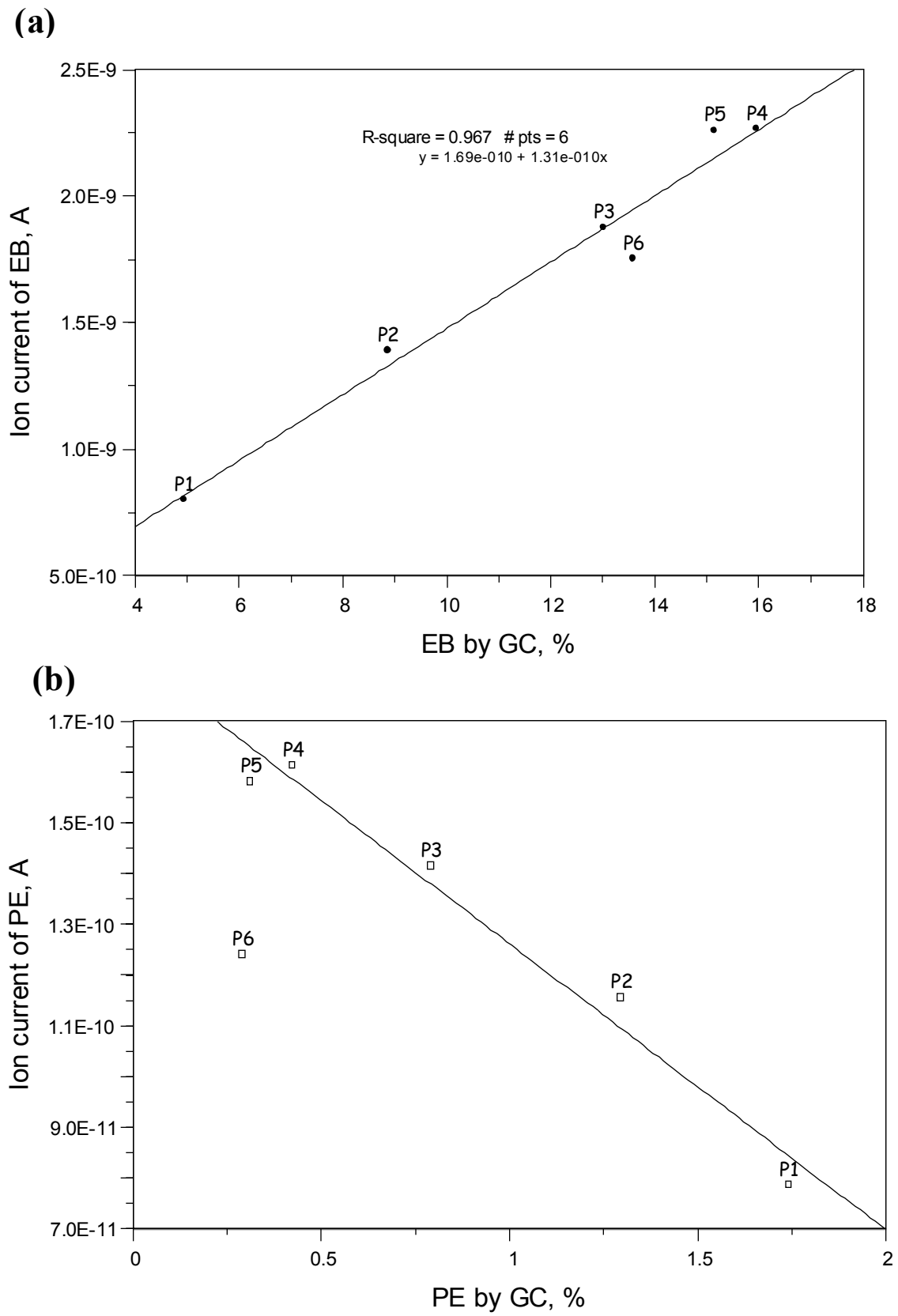

Fig. 7 Correlation of GC to QMS data. A: ethylbenzene (EB), b: phenylethanol (PE)

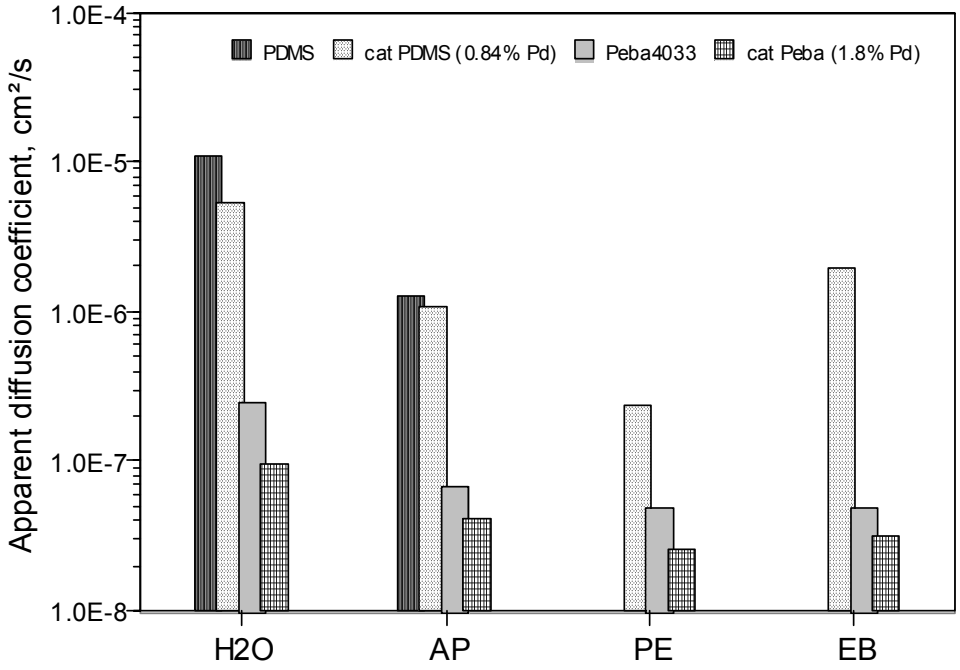

Fig. 8. Apparent diffusion coefficients of non-catalytic and catalytic PDMS and PEBA membranes

Table

	Acetophenone (AP)	**1-Phenylethanol (PE)**	**Styrene (ST)**	**Ethyl benzene (EB)**
Mol weight, g/mol	120.15	122.17	104.15	106.17
Mp, °C	20	21.5	-31	-95
Bp, °C	202	204	145	136
Solubility in water, g/L	5.5	29	0.24	< 0.1

Table 1. Summary of data of the educt and products.

Conditions		**2 h**	**4 h**	**6 h**	**8 h**	**10 h**
1bar H2, 30°C	*Feed, ppm*					
	AP	769	673	585	496	394
	PE	16	48	83	116	163
	EB	0	0	0	0	0
	Permeate, w-%					
	AP	11.4	9.0	6.8	5.7	4.2
	PE	1.1	1.4	1.6	1.9	1.6
	EB	0.9	1.1	1.6	1.5	2.3
4bar H2, 30°C	*Feed, ppm*					
	AP	675	520	356	270	210
	PE	80	160	196	205	220
	EB	0	0	0	0	0
	Permeate, w-%					
	AP	1.8	0.1	0.02	0.01	0.01
	PE	1.8	0.1	0.05	0.02	0.01
	EB	10	15	14.70	13	10
4bar H2, 50°C	*Feed, ppm*					
	AP	545	295	144		
	PE	290	413	361		
	EB	0	0	0		
	Permeate, w-%					
	AP	2.10	0.30	0.01		
	PE	3.40	0.90	0.1		
	EB	7.30	14.40	13.9		

Table 2. Pervaporation results at various H_2 pressures at 30°C (1 and 4 bar H_2) and 50°C (4 bar H_2) starting with 1000 ppm AP in the feed.

Conditions	Flux (average), L/m² h	Feed AP, %	Feed PE, %	Perm AP, %	Perm PE, %	Perm EB, %	Mass balance, %	Overall conversion, %	Reaction products in Feed, % a)
1bar H2, 30 °C	37	66.2	12.3	9.8	1.4	1.4	91	17	81
4bar H2, 30 °C	42	38.6	24.5	1.1	1.1	17.2	82	52	57
4bar H2, 50 °C	95	13.8	38.8	4.2	5.9	42.6	106	83	44

a) Related to the amount of products only (without unreacted AP).

Table 3. Distribution of educt and products in feed and permeate after 6 h of reactive pervaporation.