

LIMONENE HYDROGENATION IN HIGH PRESSURE CO₂: EFFECT OF FLOW

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INTRODUCTION

Hydrogenation in supercritical fluids has been presented as a typical case of advantageous use of these fluids as solvents for chemical reaction. Härröd et al. [1], for instance, developed extremely fast and selective hydrogenation processes of fatty acid methyl esters in supercritical propane.

However, fast hydrogenations of liquids were also obtained for high pressure CO₂-based systems that were clearly biphasic. It can be argued that subcritical mixtures of CO₂ + a liquid, just below the critical pressure, exhibit many of the advantages claimed for supercritical systems, such as reduced viscosity and increased diffusion rates, as well as a high content of gaseous reactants, such as hydrogen, due to increased solubility brought by the large quantities of carbon dioxide dissolved in the liquid. These conditions have been exploited for chemical reaction in what has been termed as “CO₂-expanded solvents”. For instance, a detailed study of homogeneous catalysis in expanded acetonitrile has been published by Wei et al.[2]

Previous studies from our laboratory [3-5] on mixtures of carbon dioxide + a terpene (α -pinene, or limonene) compared hydrogenation rates between biphasic (liquid + gas) reaction conditions and supercritical, monophasic ones. The results were highly dependent on the catalyst used, but no neat advantage of supercritical conditions over biphasic ones were registered.

In the present work, we report the effect of the flow on limonene reduction using a palladium catalyst in dense CO₂ atmosphere, at constant pressure of hydrogen (2.5 MPa) and total pressure 12.5 MPa at 323.15 K. In all the conditions used, the reaction mixture remained in two fluid phases (gas + liquid), that is, this pressure was always lower than the critical pressure of the limonene + CO₂ + H₂ system. As CO₂ is highly soluble in limonene at pressures close to the critical pressure, the liquid phase always contained more than 80 mol% of carbon dioxide.

Structures of limonene and formed terpenes are shown in Figure 1.

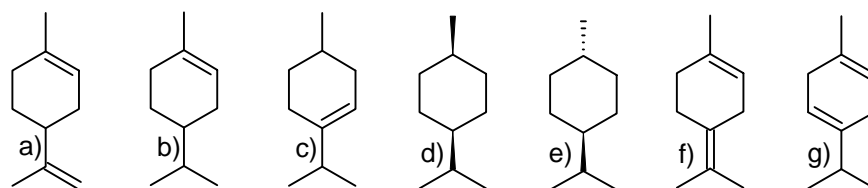


Figure 1. Limonene and other terpenes: a) limonene, b) *p*-menth-1-ene, c) *p*-menth-3-ene, d) *cis-p*-menthane, e) *trans-p*-menthane, f) terpinolene, g) γ -terpinene.

MATERIALS AND METHODS

Materials

Hydrogen and carbon dioxide were supplied by Air Liquide, with a stated purity of 99.998 mol%. R-(+)-limonene (purity: 98 %), (+)-*p*-menth-1-ene (purity: \geq 97 %), (+)-*p*-menth-3-ene (purity: \geq 97 %), terpinolene (purity: \geq 97 %), γ -terpinene (purity: \geq 98.5 %) and nonane (purity: \geq 99 %) were

supplied by Fluka. *cis-p*-menthane (purity: $\geq 97\%$) and *trans-p*-menthane (purity: $\geq 97\%$) were supplied by Fluorochem Limited. 1 wt % Pd SKN catalyst was prepared using a similar procedure to the one presented in literature.[4]

Reaction experiments and methods

The hydrogenations were performed with an apparatus consisting of one sapphire-windowed cell connected by a pump to a tubular reactor – short tube that encloses a catalyst bed. This apparatus was described by Bogel-Lukasik et al.[5] The hydrogenation of limonene was carried out in the presence of 0.2 g of catalyst and 1 ml of limonene at 323.15 K. 2.5 MPa of hydrogen was first loaded into the sapphire cell. The fixed total pressure of experiment after charged the reactor with CO₂ was 12.5 MPa. Due to that reactions were carried out at conditions where both a gas and a liquid phases are present. The reactions were performed at four various 1.3, 3.3, 5.3 and 7.3 mL/min flows. The reactants were withdrawn from the bottom of the view cell, circulated through the catalyst bed, and sent back to the upper entrance of the cell. Throughout the reaction time, stirring in the view cell continued, so that the feed would continuously be liquid in equilibrium with its vapour.

A Rheonik RHM 015 GNT flowmeter, equipped with an electronic transmitter RHE 11, was used to measure the flow in the tubular reactor, with repeatability better than 0.05 % of rate and accuracy better than 0.23 %. Samples have been taken at regular intervals through a HPLC valve with a 100 μ l sampling loop, at the top of the tubular reactor. CO₂ in the loop was carefully vented to the atmosphere. The liquid products were identified by GC-MS followed by quantitative analysis using GC (HRGC-3000C gas chromatograph, CP-Sil 8 CB column from Varian Inc. with flame ionization detector). Oven temperature program: 87-91 °C ramp at 0.5 °C min⁻¹, and 91-240 °C ramp 20 °C min⁻¹. Injector and detector temperature was 250 °C. Nonane in hexane (1.5 mM) was used as external standard for GC analysis (response factor for *R*-(+)-limonene: 1.42, (+)-*p*-menth-1-ene: 1.26, (+)-*p*-menth-3-ene: 1.26, terpinolene: 1.44, γ -terpinene: 3.76, *cis-p*-menthane: 1.44, and *trans-p*-menthane: 1.43; precision of the method: better than 10%).

RESULTS

The effect of flow has been examined at a constant temperature (313.15 K), fixed hydrogen and total pressures 2.5 MPa, 12.5 MPa, respectively.

Hydrogenation of limonene occurs in the liquid phase. Concentration of hydrogen present in the liquid phase under reaction condition equals 5.8 mol%, ratio H₂/limonene equals 2.3 as we presented earlier.[5, 6] Hydrogenation of limonene leads to the formation as final products of *cis*- and *trans-p*-menthane, in 1:2 ratio, obtained through hydrogenation of both C=C double bonds of limonene (Figures 2 and 3). The hydrogenation proceeds through intermediate *p*-menthenes, which are formed by the initial partial reduction of the exocyclic C=C double bond.

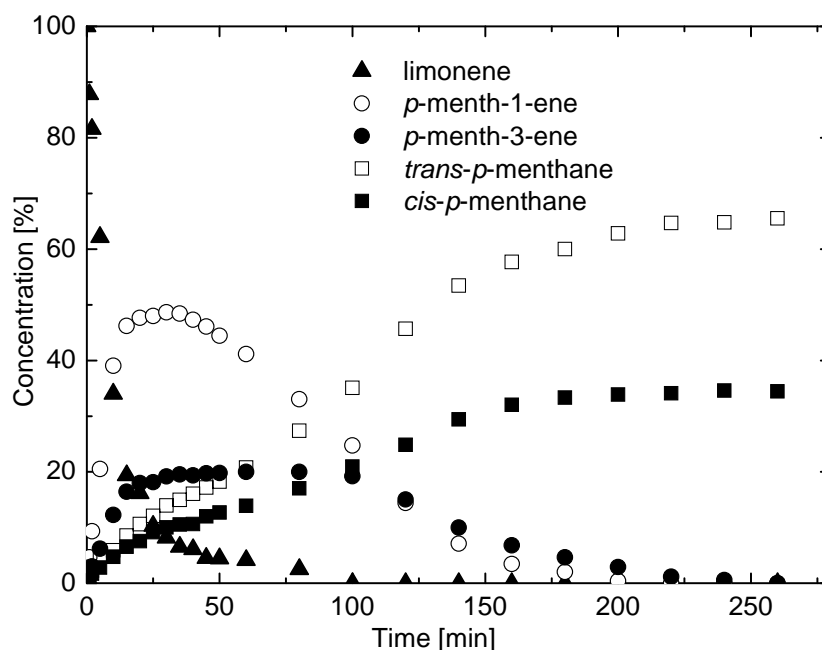


Figure 2. Concentration profile of limonene and hydrogenation's products at 1.3 mL/min flow.

Isomers of limonene were consumed throughout the progress of the reaction in the reactions with the lowest overall flows. Intermediates: *p*-menth-1-ene and *p*-menth-3-ene were detected in the measurable quantities in the reactions when flow was 1.3, 3.3 and 5.3 mL/min.

The speed of limonene consumption is remarkably different for investigated flows. Analysing the profile of limonene disappearing it can be concluded that limonene is consumed faster at lower flow what can be recognised as a curiosum. But from the microscopic point of view this unusual phenomenon could be explained by the fact that at higher flow, residence time - time for reaction act between limonene and hydrogen on the surface of the catalyst is too short. Due to higher flow the liquid layer surrounding the catalyst is refreshed few times faster than at lower flow and because of that lower amount of limonene is able to go through all steps of process including adsorption of limonene and hydrogen to the surface, reaction between them and desorption of products. Noteworthy is fact that for 1.3 and 3.3 mL/min overall flows, there is no significant difference in the speed of limonene consumption. That means that even at higher flow (3.3 mL/min) there is enough time to perform all steps of hydrogenation process on the catalyst surface. Furthermore, considered flows are sufficiently slow that do not reduce the mass transfer resistance allowing for formation of all partially hydrogenated products and isomers of limonene. The analogous conclusions could be done for reaction performed with 5.3 mL/min flow. At 5.3 mL/min flow consumption of limonene is slower than at 3.3 mL/min but the refreshing of the liquid layer where reaction occurs is supposed to be faster but not sufficiently effective to avoid completely the limitation such as mass transfer of hydrogen from the gas to the liquid phase through the interphase boundary.

Two effects, great solubility of hydrogen in limonene due to presence of dense CO₂ and limitation in a form of mass transport through the phase boundary which is driven by the flow, play in the opposite direction. High hydrogen solubility in limonene leads to faster hydrogenation and during the consumption of hydrogen, the force to equilibrate the temporary lack of hydrogen is created. This driving force increases the speed of hydrogen migration from further level of the liquid phase and from a gas phase to the layer which is in the direct contact with the catalyst. In this stage the mass

transport limitation starts to play a key role. The mass transport limitation is determined by the flow. For 5.3 mL/min flow and lower the transport is bounded what affects the presence of partially hydrogenated products in the analysed samples, but higher flow reduced the limitation, so the fresh hydrogen can go easily to the liquid layer. At the highest investigated flow, during reaction, due to introducing of fresh hydrogen ready to react, intermediates are consumed as fast as they are formed, so the mass transport limitation does not occur in this case.

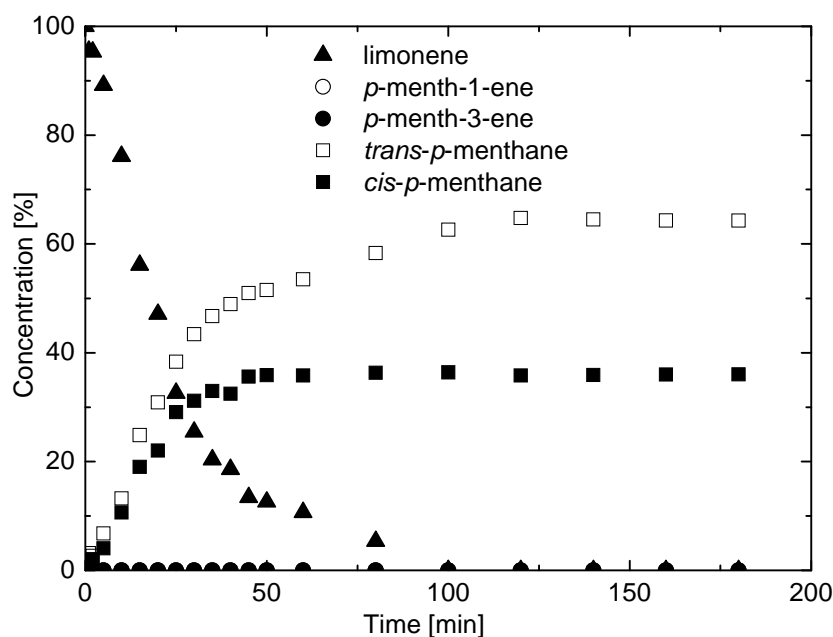


Figure 3. Concentration profile of limonene and hydrogenation's products at 7.3 mL/min flow.

As it was mentioned earlier higher flow introduces fresh hydrogen faster but at the same time the residence time undergoes reduction what affects the lower speed of reaction.

Performed reactions with different flows could be considered as a simulation of the batch and continuous systems. The highest flow (7.3 mL/min) could simulate the process carried out in the batch due to very fast circulation of the feed mixture and because of the large changes in the feed composition during reaction. As a proof we can quote the fact that at evaluated flow only fully hydrogenated products were observed in the analysed samples. The slowest flows (1.3 and 3.3 mL/min) allow us to conclude that these systems are close to continuous processes. Lower flow disturbs the feed minimally as it takes place in continuous processes.

CONCLUSION

Obtained results indicate that with different flows the systems could be considered as a simulation of the batch and continuous modes. The highest flow (7.3 mL/min) could simulate the process carried out in the batch due to very fast circulation of the feed mixture and because of the large changes in the feed composition during reaction. The slowest flows (1.3 and 3.3 mL/min) allow us to conclude that these systems are close to continuous processes. Lower flow disturbs the feed minimally as it takes place in continuous processes.

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