Electronic Supporting Information

Fate of monoterpenes in near-critical water and supercritical alcohols assisted by microwave irradiation

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Generation of near-critical water

The microwave oven Synthos 3000 (Anton Paar, Austria) was used to perform high-pressure experiments using near-critical water as solvent for the transformation of constrained monoterpenes α- (**1**) and β-pinene (**2**). Due to the fact that water becomes more transparent for microwave irradiation at elevated temperatures it is necessary to dope water with small amounts of ionic additives to maintain the good absorption capacity. *Kremsner* and *Kappe* investigated the heating behaviour of a NaCl-solution in comparison to deionized water, observing that the former results in better and more stable reaction conditions, which was verified by some basic heating experiments summarized in *Figure 1*.[1] Due to ion-conductivity mechanisms, the sodium and chloride ions in the reaction media are able to convert microwave irradiation into kinetic energy very effectively even at high temperatures (*Figure 1*).[2] The presence of ions results in shorter heat-up times and significantly improved pressure- as well as temperature-stability during the reaction, leading to a more homogeneous and controllable environment for reactions carried out under these prerequisites.

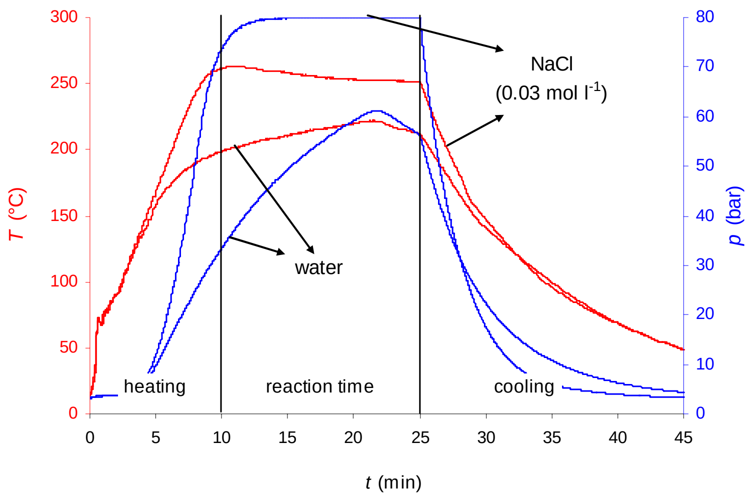

Figure 1. Temperature-time-chart for heating of water and 0.03 M NaCl-solution (15 ml solvent, 80 ml quartz vessel, heating: 10 min, reaction time: 15 min, cooling: 20 min, P_{max}: 1.2 kW, microwave: Synthos 3000)

Generation of supercritical alcohols

Regarding to *Table 1* (*cf.* manuscript text) the generation of the supercritical state of all applied alcohols should be realizable using the above mentioned microwave system. Regarding to the dielectric loss factor *tan* δ and penetration depth lower alcohols (*i.e.* methanol or ethanol) absorb microwave irradiation in a better way than pure water.[1] However at higher temperatures a total loss of microwave absorption can be recognized during the experiments due to the loss of absorption capacity while changing the state of aggregation from liquid to supercritical / gaseous. In case of water theses phenomena can be suppressed by the addition of small portions of ionic material to the solution (absorption through ion conductivity mechanism).[1,3] Another option to overcome this problem is the application of passive heating elements (PHE), which are typically made of a strong microwave absorbing material (*e.g.* SiC).[4] The energy is than be transferred by classical heating mechanisms (conduction, convection) to the bulk material.[5] This later route was applied herein to establish a stable and reproducible reaction environment for the performance of reaction in supercritical phase. The improved heating behavior is demonstrated for the heating of ethanol under closed-vessel conditions in *Figure 2*.

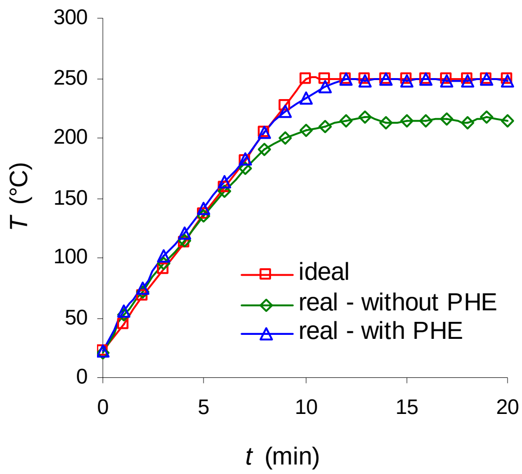

Figure 2: Heating behavior of ethanol under microwave irradiation (P_{max}: 1.2 kW, Synthos 3000) using closed-vessel conditions (30 mL; V_{vessel}: 80 ml; 3 PHE = passive heating element).

References

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