PROCESS INTENSIFICATION OF REACTIVE DISTILLATION: MICROWAVE EFFECTS ON ZEOLITE CATALYZED ESTERIFICATION REACTIONS

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Summary

An envisioned reactive distillation (RD) process for the esterification reaction of n-propyl propionate (ProPro) from 1-propanol (ProOH) and propionic acid (ProAc) using microwave radiation (MW) is studied. Selection tests and analysis concerning five commercial zeolite catalysts are presented. First, the interaction of microwave radiation ((*f*) 2.45 GHz) with the zeolites in different bulk liquid media looking for selective heating in the form $T_{zeolite\ metal\ oxides} > T_{bulk\ liquid}$ is studied. Kinetic experiments are performed with the selected catalyst to establish the reaction mechanism and to compare reactions under MW and conventional heating, looking for possible reaction enhancement.

Keywords

Microwaves, reactive distillation, esterification, *n*-propyl propionate, zeolites.

Introduction

In the last decades, the application of electromagnetic radiation in form of microwaves for chemical syntheses (microwave chemistry), has gathered the attention of the scientific and industrial communities in view of possible process intensification (PI) of commercial operations. [1] Microwave (MW) technology is being successfully applied in industrial operations like food, wood, metal and ceramic processing. Although the literature regarding intensification effects of MW on chemical reactions is remarkably rich (only in 2009 to date more than 400 publications in reviewed journals were published) no successful commercial implementations in chemical plants have been reported. In addition to reactions, distillation processes could possibly benefit from MW. In this project, a novel concept of a microwave heated reactive distillation column is addressed in view of possible PI. In figure 1, the envisioned reactive distillation radiated process is shown. Two fundamental questions are raised regarding the effective combination of the MW energy field with the current technology. What are the effects of an electromagnetic field on thermodynamic equilibrium and what are the effects on reaction kinetics? Commercial esterification reactions performed in RD columns are heterogeneously catalyzed using acidic surface-sulfonated ion exchange resins. It has been reported that microwaves cannot enhance heterogeneous reactions using ion-exchange resins because the building block of the catalyst (in this case styrene divinylbenzene copolymers) is transparent to them. [2] On the other hand, zeolites have been proven to catalyze esterification reactions acting as solid acid catalysts.

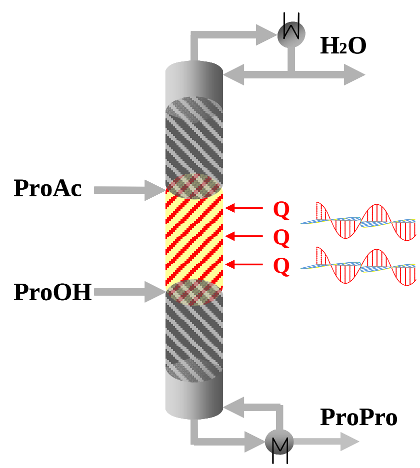

Figure 1. Envisioned reactive distillation column for the esterification of ProPro radiated with microwaves.

Experiments have shown that it is possible to selectively heat catalyst particles in the zeolites (silanols and other metal oxides present in the framework). [3] In heterogeneous gas phase reactions the use of superheated catalysts selectively heated by MW has been proven to enhance reactions. Following the same approach, a low absorbent liquid can be benefited from the selective MW

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heating in the form $T_{zeolite\ metal\ oxides} > T_{bulk\ liquid}$. The successful temperature decoupling can lead to energy savings in RD since most of the energy can be used to heat the catalyst and not the bulk liquid.

Materials and Methods

As a test system, the heterogeneously catalyzed synthesis of n-propyl propionate (ProPro) from 1-propanol (ProOH) and propionic acid (ProAc) is proposed. Different types of commercial zeolite catalysts (all having a silica and alumina framework in different morphologies) were studied. Selection was based on the material dielectric properties, absorption of electromagnetic radiation and reported reaction results under conventional heating conditions. The catalysts were characterized by XRF, CSD, TGA, NH_3-TPD and SEM. Zeolite screening experiments were performed in a Discover mono-mode microwave cavity from CEM corporation. For the kinetic experiments a MARS multimode cavity from CEM was used. Experiments were carried out in open reflux conditions. Temperature inside the MW cavities is measured with fiber optic probes FISO Technologies.

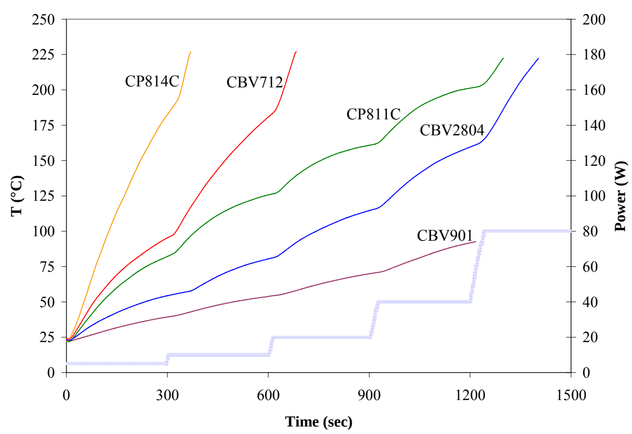

Figure 2. Heating experiments of 5 different commercial zeolite samples in a mono-mode microwave cavity. Different heating rates are observed after the application of the same power.

Results and discussion

In figure 2, the interaction of microwave radiation ((*f*) 2.45 GHz) with the zeolites showing selective heating can be seen. Five different commercial zeolite samples were heated under the same power profile showing different heating rates that depend on the metal oxide concentration in the framework and their corresponding dielectric properties. When the zeolites are heated mixed with other liquid media the profiles change, yet again depending on the dielectric properties of the bulk liquid. A sound method is being developed for the selection of a catalyst that can deliver the successful temperature decoupling. Once the catalyst has been selected, kinetic experiments are performed to establish the reaction mechanism and to compare reactions under MW and conventional heating, looking for possible reaction enhancement. Information on the mechanisms and kinetics of esterification reactions of carboxylic alcohols with acids over zeolites are scarce. The two proposed mechanisms; a dual site Langmuir–Hinshelwood (LH) or a single site Eley–Rideal (ER) appear to be dependent on the catalysts and the reactants. In figure 3, experimental results can be seen for the reaction using the Beta type zeolite powder BEA (CP811C) purchased from Zeolyst international. In order to obtain the highest product purity inside the column, conversion of the acid must be the highest possible. Therefore an excess of alcohol is used.

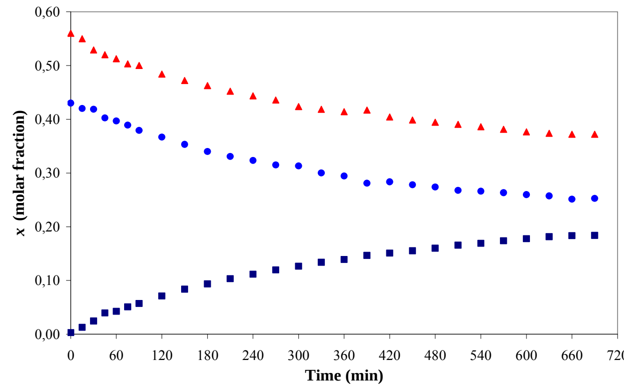

Figure 3. Experimental results for 2:1 molar ratio using (CP811C) (SiO_2/Al_2O_3 ratio 300). Δ- ProOH, ○ – ProAC and □ – ProPro.

Conclusions

In this work, an enhanced RD process for the esterification reaction of ProPro from ProOH and ProAc using MW radiation is proposed. Energy savings can be achieved in this process by successfully decoupling the bulk liquid temperature and the catalyst temperature in the reaction. Several zeolite catalysts are screened and a sound method for the selection is proposed. Kinetic experiments are performed to establish the reaction mechanism under MW radiation in comparison to conventional heating.

References

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