

Process Intensification of Reactive Distillation for the Synthesis of *n*-Propyl Propionate: The Effects of Microwave Radiation on Molecular Separation and Esterification Reaction

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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 irradiation (MW) ($f = 2.45$ GHz) is studied. In this frame, the fundamental research performed is divided in two parts comparing reaction conditions and equilibrium curves under MW and conventional heating, looking for possible improvement in process efficiency. For the test system, the use of microwaves does not improve the conversion of the esterification reaction catalyzed by selected zeolite catalysts possibly because microwaves are dissipated in the liquid phase before they interact with the zeolites. Concerning molecular separation, however, it was found that when the vapor–liquid interface is exposed to microwaves, the system can be disturbed from conventional equilibrium conditions and a positive deviation in phase composition can be achieved, as the vapor phase becomes richer in the component with the lower boiling temperature; the extent of separation improvement depends on the boiling points and the dielectric properties of the mixture components. This finding may have significant practical impact as it implies smaller columns with a lower number trays for a given separation efficiency, compared to conventional designs involving heat exchange in the reboiler and the condenser only. It is stressed, though, that the effect is present only when the vapor–liquid interface is exposed to microwaves; no effect is observed when solely the bulk liquid volume is irradiated.

1. Introduction

In the last decades, the application of electromagnetic radiation in the 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 Currently, microwave (MW) technology is being successfully applied in industrial operations like metal and ceramic sintering, food thawing, and wood drying. Although the literature regarding intensification effects of MW on chemical reactions is remarkably rich (only since 2009 to date more than 400 publications in reviewed journals were published), no successful commercial implementations in chemical plants have been reported. This may be partly due to the poor understanding of the interaction mechanisms between chemical media and electromagnetic waves, the ongoing debate on thermal and nonthermal effects posed by microwaves, and the biases and contradictions found when comparing operating conditions to conventional heating. Moreover, most of the results have been published by chemists and physicists; therefore, little attention has been paid to the engineering aspects of microwave reactors, applicators, modeling, and control. In addition to reactions, distillation processes could possibly benefit from MW. Several concepts of microwave-assisted laboratory distillation have been developed.^{2,3} Their implementation at industrial scale though is hindered by the scale up issue of microwave applicators. In this project, the novel concept of a microwave heated reactive distillation (RD) column is addressed in view of possible PI. Considering the scale and importance of distillation and reactive distillation in the process

industry, any improvement in the reaction and/or separation functions could have a wide application and direct impact on large scale operations. In this context, two research questions are addressed namely, the effect of microwave irradiation on (1) the physics governing the separation of components and (2) heterogeneous liquid phase reactions.

First, we experimentally explore the effect of microwaves on the separation of binary mixtures by comparison with conventional thermodynamic equilibrium experiments. Albeit, the effects of electromagnetic radiation on boiling and evaporation have been studied for more than three decades (e.g. refs 4 and 5), the underlying physics driving these effects are not yet universally agreed upon, as they are difficult to verify experimentally. Different theories have been proposed to explain (at least partially) why pure polar liquids can be disturbed from equilibrium boiling conditions under MW irradiation and increase their temperatures above their normal boiling points to temperatures referred to as nucleation limited boiling points (NLBP); these include surface hydrodynamic instabilities (Marangoni and Hickman),^{6,7} superheating,^{8–10} nonequilibrium conditions at the evaporating interface,¹¹ and pressure increase at the interface.¹² In any event, if the boiling point of pure components can be affected by microwaves, then this may be taken as an advantage to improve the separation efficiency of mixtures. In this work, we first performed conventional vapor–liquid equilibrium (VLE) experiments of some constituent binary mixtures involved in the quaternary reactive system of *n*-propyl propionate (details of the process are given in section 1.1). Then, we executed the same experimental protocol under microwave heating to investigate potential changes in phase composition as compared to conventional VLE due to selective heating of some compounds that are better MW absorbers than others or due to possible superheating. The conventional and

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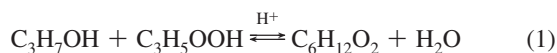
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MW equipment used as well as the relevant experimental procedures adopted are thoroughly described in the following sections so that the findings can be reproduced by other researchers active in the field.

In the *second part* of the paper, we discuss the zeolite-catalyzed esterification reaction performed under conventional and microwave heating. Normally, commercial esterification reactions performed in RD columns are heterogeneously catalyzed using acidic surface-sulfonated ion exchange resins.^{13–15} It has been reported that microwaves cannot enhance heterogeneous reactions using ion-exchange resins because their building block (in this case, styrene divinylbenzene copolymers) is transparent to them^{16,17} and therefore no superheating of catalytic sites can be produced. On the other hand, it has been proven that zeolites can catalyze esterification reactions acting as solid acid catalysts.^{18,19} Besides, experiments have shown that it is possible to selectively heat catalyst particles and functional groups in zeolites (silanols and other metal oxides present in the framework).²⁰ Furthermore, it has been demonstrated that, in heterogeneous gas–solid reaction systems, the use of MW to selectively superheat catalysts may enhance reactions. Following the same approach, a liquid–solid system with the liquid phase being a low MW-absorber can be benefited by MW heating in that the bulk liquid temperature remains lower than the solid catalyst temperature ($T_{\text{zeolite_metal_oxides}} > T_{\text{bulk_liquid}}$). This temperature decoupling implies energy savings in RD since most of the energy is used to heat the catalyst and not the bulk liquid. Different types of commercial zeolite catalysts, all having a silica/alumina framework in different morphologies, were studied. Catalyst selection was based on their dielectric properties and their performance under MW heating conditions.

1.1. *n*-Propyl Propionate Synthesis. Esterification reactions, in general, are good test systems to prove concepts in RD. Most of the RD knowledge and design tools were developed for production of acetates after the introduction of the Eastman process in 1980.²¹ There are three main reasons for this: (a) Since both operations are conducted simultaneously in a RD column, an overlap between the operational windows for reaction and distillation exists and consequently the process conditions are required to match. (b) As the esterification reaction is reversible, the simultaneous withdrawal of the products shifts the equilibrium to the product side thus improving product formation. (c) The possibility of RD to overcome azeotropes. In this study, the synthesis of the *n*-propyl propionate ester (ProPro) has been chosen as exemplifying reaction. ProPro is a broadly used solvent with diverse applications ranging from paints, coatings, and industrial cleaners to flavors. The ester is obtained from the esterification reaction of propionic acid (ProAc) and 1-propanol (ProOH) (eq 1). The reaction can be both homogeneously and heterogeneously catalyzed.



Parameter properties of the reactants and products were extracted from ASPEN Properties Plus and compared to data from the literature showing good agreement. Dielectric properties were taken from the literature.²² The parameters used are given in Table 1.

Aside from the boiling points, which are key parameters in distillation, in the case of a MW heated column, the interaction of the electromagnetic radiation with the reagents, products, catalysts, and column materials must be considered. Microwave absorption and propagation in materials is described by two parameters: one related to the electric field of the electromag-

Table 1. Property Data of Pure Components

property	propionic acid	1-propanol	<i>n</i> -propyl propionate	water
<i>M</i> (g/mol)	74.08	60.10	116.16	18.01
<i>T</i> _b (1.013 bar) (°C)	140.90	97.20	122.90	100.00
Δh_v (20 °C) (kJ/mol)	31.14	41.44	35.54	40.66
ϵ'' (20 °C) (–)	1.000 ^a	15.216	0.200 ^a	9.889

^a Approximated values.

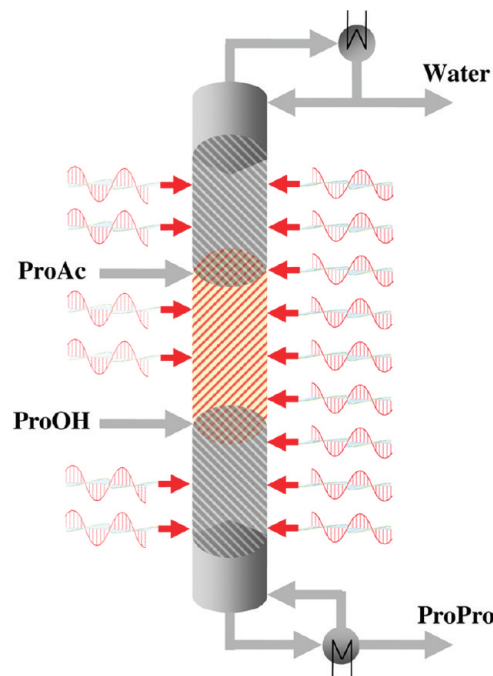


Figure 1. Envisioned reactive distillation column for the esterification of ProPro irradiated with microwaves.

netic spectrum, the complex permittivity ϵ^* (–), and the other related to the magnetic field, the complex permeability μ^* (–). Since the materials involved in this research are not magnetic, the complex permeability μ^* (–) is not considered. The complex permittivity parameter ϵ^* (–) is both temperature and frequency dependent and comprises a real and an imaginary part as shown in eq 2.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2)$$

The imaginary part of eq 2 is the dielectric loss ϵ'' (–). This parameter represents the ability of a material to absorb microwaves and dissipate them into heat. Therefore, a system containing materials of considerably different dielectric losses can be treated with MW so that the different components absorb MW selectively.

Three potential ways to achieve energy savings in RD processes with use of MW have been identified. (1) Use of a diabatic column. Diabatic columns exchange heat in all segments along the column height and are known to have higher energy efficiency than adiabatic ones which only exchange heat at the reboiler and the condenser.²³ Diabatic operation can be achieved with conventional as well as with MW heating (Figure 1). (2) Use of a reaction system in which the low boilers (heavier components) are also low MW absorbing materials (ProAc and ProPro), whereas the light components are good MW absorbers (water and ProOH). This could result in a more effective and reasonable use of energy by heating the components that need to be evaporated and distilled while leaving the heavy components sink at the bottom of the column. (3) Decoupling the bulk

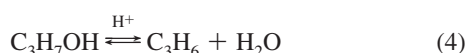
Table 2. Azeotropic Data

type of azeotrope	temperature (°C)	mass fraction (g/g)			
		ProOH	ProAc	ProPro	water
homogeneous	87.6	0.432			0.568
homogeneous	99.9		0.050		0.950
heterogeneous	90.0			0.350	0.650
heterogeneous	86.2	0.350		0.130	0.520

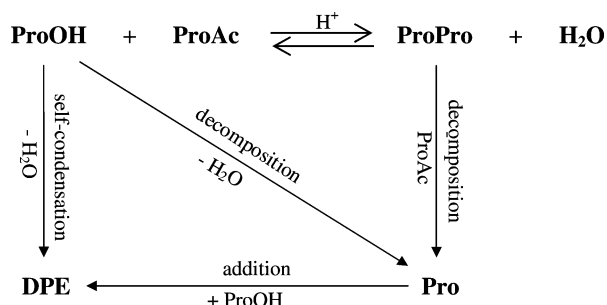
liquid from the catalyst temperature implying that temperature can be higher at the catalyst acidic sites resulting in faster reaction rates, lower energy demand, shorter residence times, and smaller equipment. It must be noted that the foreseen process can only generate energy savings if the overall process performance can overcome the energy efficiency of the magnetron transforming electrical into microwave energy (typical magnetron efficiencies range from 60 to 70%).^{24–26} Applicator efficiencies should always be close to 100% if the cavity is well designed.

1.2. RD Process Design: Thermodynamics and Kinetics.

Kinetic and thermodynamic parameters are needed for conceptual process design of RD systems. For the present quaternary mixture, the thermodynamic properties are built on the information of six constituent binary systems. The complete set of binary interaction parameters for the VLE calculation can be found in the literature.²⁷ The system is characterized by strong liquid phase nonidealities with several azeotropes present. The azeotropic data is shown in Table 2. Pilot scale experiments for this reaction have been performed in RD columns using the acidic surface-sulfonated ion-exchange resin Amberlyst 46 from Rohm and Haas. This catalyst has proven to be very effective for the production of esters, suppressing important side reactions such as the dehydration of 1-propanol to propene and the self-condensation of 1-propanol to di-*n*-propyl ether (DPE) for the system under investigation.¹³ The complete reaction scheme is depicted in Figure 2 and described by eqs 1 and 3–6.



The main drawback of ion exchange resins is their poor thermal resistance limiting them from a broader application in industry. Due to the ion-exchange resins being inert to MW, other solid acid catalysts, including various metal oxides and

**Figure 2.** Reaction scheme of *n*-propyl propionate synthesis.

zeolites, were considered. These catalysts not only exhibit good thermal resistance and offer the possibility of custom preparation controlling to a certain extent Lewis and Brønsted acidity but also can be coated over structured packings for RD distillation. Six commercial zeolite samples all having a framework of silica and alumina with different morphologies were investigated. The catalytic activity of a catalyst is determined considerably by its acidity. The latter is a combination of the concentration of acid sites (directly correlated to the amount of alumina) and the acid strength (associated to the morphology) of the sites. Besides acidity and morphology, understanding of the interaction of electromagnetic radiation with the catalyst is crucial as it can determine the thermal effects. Two types of experiments were carried out to investigate MW–catalyst interactions. First, several beds of dry catalysts were irradiated with low MW power in a monomode Discover (CEM corp.) cavity to see how the standalone powders behave. Then, each catalyst was evaluated in the reaction mixture to check whether the catalyst particles could be heated selectively, even when surrounded by high dielectric media. The successful temperature decoupling of the catalyst from the bulk liquid was proven when comparing the temperature that blank samples of the reagent mixtures reached compared to the ones containing catalyst. The latter reached higher temperatures (data not shown). Finally, two BEA type zeolite catalysts were chosen and used in the reaction experiments.

Different kinetic models, such as the Langmuir–Hinshelwood–Hougen–Watson (LHHW) and the Eley–Rideal (ER), have been proposed for esterification reactions catalyzed by zeolites. Nijhuis et al.²⁸ has modeled the esterification of hexanoic acid and 1-octanol with a BEA zeolite using a LHHW mechanism; it is assumed that both acid and the alcohol molecules are adsorbed to the catalyst surface; they react to form ester and water, which subsequently desorb from the catalyst surface. The reaction between the adsorbed reactants is thought to be the rate-limiting step. ER differs from LHHW in that it postulates that only one reactant molecule adsorbs to the catalytic surface and then reacts with a molecule in the bulk liquid. The reaction only occurs when one specific reactant (acid) is adsorbed; if the other reactant (alcohol) adsorbs to the surface, reaction with bulk acid does not occur. This yields two ER models, that is, with and without competitive alcohol adsorption. Kirumakki et al.^{19,29} modeled the esterification of alcohols with acetic acid over zeolites with a competitive ER model. Kinetics for zeolite catalyzed ProPro synthesis has not been put forward in the literature.

2. Experimental Section

2.1. Chemicals and Zeolite Characterization.

ProOH, ProAc, and ProPro were purchased from Sigma-Aldrich. The reagents were degassed with an ultrasound bath and dried over molecular sieves from Sigma-Aldrich. The purities of these components were reported to be more than 99.5% for ProOH and more than 99.0% for ProAc and ProPro. The commercial zeolite catalysts were purchased from Zeolyst International (The Netherlands). The complete list of catalysts including the manufacturer's reported properties can be found in Table 3. In addition, zeolites were characterized using X-ray fluorescence (XRF) and their compositions are presented in Table 4. Crystal size distribution (CSD) was determined using trilater diffraction (Microtrac S3500), and the water content was measured by loss on ignition using a thermogravimetric analyzer (TGA) with an SDT 2960 thermobalance; the temperature control program set the sample at 120 °C for 1 h and then ramped it to 600 °C for

Table 3. Specifications of Zeolite Catalysts

zeolite type	commercial name	SiO ₂ /Al ₂ O ₃ mole ratio ^a	nominal cation form	unit cell size ^a (Å)	surface area ^a (m ² /g)	crystal size (μm)
FAU	CBV 712	12	ammonium	24.35	730	1.38
BEA	CP 814C	38	ammonium		710	0.82
BEA	CP 811C	300	hydrogen		620	0.82
FER	CP 914	55	ammonium		400	7.78
FER	CP 914C	20	ammonium		400	4.62
MOR	CBV 21A	20	ammonium		500	0.97

^a Data from manufacturer.

Table 4. Composition of Zeolite Catalysts

metal oxide (wt %)	CP 814C	CP 811C	CP 914	CP 914C	CBV 712	CBV 21A ^a
SiO ₂	95.4300	99.3100	96.5100	91.4000	87.2000	92.2
Al ₂ O ₃	4.3300	0.4990	3.3300	8.3600	12.6000	7.8
Na ₂ O	0.0217	0.0056	0.0326	0.0299	0.0142	
P ₂ O ₅	0.0130	0.0106	0.0073	0.0086	0.0074	
K ₂ O	0.0133		0.0064	0.0109		
TiO ₂	0.0182	0.0184	0.0270	0.0306	0.0280	
Fe ₂ O ₃	0.0727	0.0686	0.0438	0.0567	0.0213	
ZrO ₂	0.0302	0.0200	0.0063	0.0077	0.0079	
MgO	0.0360	0.0104				
CaO	0.0190	0.0096	0.0198	0.0061		
SiO ₂ /Al ₂ O ₃ mole ratio	37.40	337.72	49.18	18.55	11.75	20.0

^a Ratio calculated.

2 h. Acidity was measured by ammonia desorption (NH₃-TPD) using a TPD/TPR Micromeritics 2900 setup. Approximately 30 mg of zeolite sample (H⁺) was used for all experiments. For desorption of absorbed water, the sample was heated to 573 K at a rate of 10 K/min under a flow of helium and kept at that temperature for 1 h. The sample was then cooled down to 393 K, and three successive pulses of ammonia were injected with subsequent desorption for 30 min at 393 K. TPD was achieved under helium flow by increasing the temperature to 1073 K. Finally, the surface morphology was examined using a Jeol JSM 5400 scanning electron microscope (SEM).

2.2. Apparatus. For determination of MW effects on the binary separations, two different setups were used. *The main difference between the two is the position of the vapor–liquid interface of the mixture with respect to the cavity where the electromagnetic field is applied.* More specifically, in the first set of experiments, a modified glass Fischer LABODEST vapor–liquid equilibrium apparatus model 602/D, (Fischer Labor), shown in Figure 3A, was employed to study separation effects using the system ProOH/ProPro. In these experiments, only the bulk liquid was irradiated with the *vapor–liquid interface lying outside the MW cavity.* The original heating resistance used for the so-called conventional heating experiments was removed, and instead, a 50 mL glass flask (containing the liquid binary mixture) was placed in a Discover single-mode microwave oven (CEM corp.) and was connected to the glass body. The apparatus is a dynamic recirculating still equipped with a Cottrell circulation pump; it is inside the Cottrell tube where the phase equilibrium is reached (Figure 3A). Two temperatures were measured: one outside the cavity with a digital PT-100 thermometer placed inside the Cottrell pump and one inside the MW cavity using a microwave transparent fiber optic (FO) temperature probe (FISO Technologies). Online temperature monitoring was performed using a TMI temperature signal conditioner (FISO Technologies).

A second MW irradiated apparatus, shown in Figure 3B, was built to study the effect of MW *when not only the bulk liquid but also the vapor–liquid interface is directly irradiated.* A 50-mL glass flask with tubing was inserted into a Discover single-mode microwave oven and connected to a custom-made distillation head with two valves for condensers connection and

a polytetrafluoroethylene (PTFE) cap from BOLA. Heating was controlled by a built-in power controller inside the MW. A magnetic stirrer was used to mix the reagents. The distillation head and the reaction flask were insulated with insulation foam to minimize heat losses. Three FO temperature sensors were introduced through the PTFE cap. Online temperature monitoring was performed using a TMI temperature signal conditioner. The cooling liquid circulation through the two condensers was done using a cooling thermostat.

For the reaction experiments, a 500 mL three-neck flask with glass tubing was used. The total amount of reagents was 450 g. For experiments under MW conditions, a MARS (microwave-accelerated reaction system) multimode cavity (CEM corp.) was used. The microwave was controlled via programmable software SynergyPrep (up to 1600 W). Temperature feedback control of the microwave cavity is achieved with a microwave transparent FO temperature probe. Temperatures were recorded online. Experiments were carried out under open reflux conditions using a condenser with circulating cooling liquid. For experiments under conventional heating conditions, the same glass setup was used in combination with a heating plate equipped with a magnetic stirrer.

2.3. Composition Analysis. Vapor and liquid phases obtained in the separation experiments as well as products and reactants from the kinetic experiments were measured by gas chromatography with a Varian 3900GC instrument equipped with a flame ionization detector. The column used was CP-Wax 58 FFAP CB (50 m, 0.25 mm, 0.2 μm/CP7727) and helium was used as carrier gas. Injector, detectors, and oven temperature were set at 473.15, 503.15, and 423.15 K, respectively. The column temperature profile started at 80 °C kept constant for 5 min, followed by a 60 °C/min ramp to 130 °C, where it remained constant for an additional 1.5 min. Finally, Karl Fischer titration was used to determine the water content in the product samples from the kinetic experiments.

2.4. Experimental Procedure. In the first type of experiments, where only the bulk liquid (and not the interface) is irradiated, 100 mL of the sample mixture were loaded inside the glass body of the modified Fischer LABODEST unit. Isobaric experiments at atmospheric pressure were conducted at a constant MW power of 100 W. Recording of the temperature inside the MW cavity was done with an optical fiber and compared with the temperature reading of the thermometer inside the Cottrell tube. When the temperatures remained constant for 30 min or longer, steady state was assumed; liquid and vapor samples were taken, and the experiment was stopped.

For separation experiments using the custom distillation head, 50 mL of the sample mixture were charged in the glass flask inside the MW cavity. Isobaric experiments at atmospheric pressure and total reflux conditions were performed at a constant MW power of 100 W. Two FO temperature sensors were placed inside the cavity: one ~0.5 cm below the liquid interface to monitor and record liquid temperature and the other one ~0.5 cm above the interface to monitor and record vapor temperature. When the temperatures remained constant for 20 min or longer,

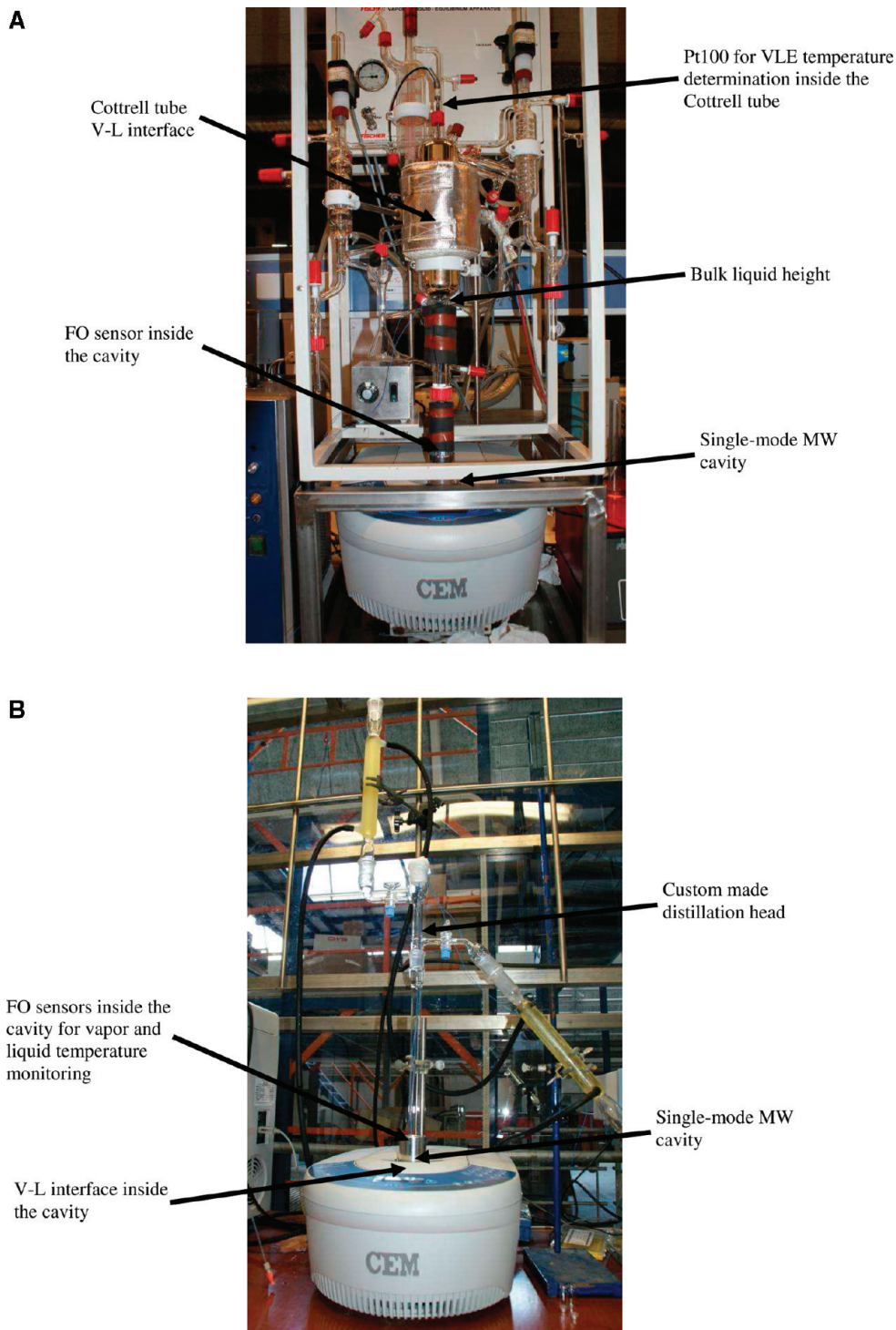


Figure 3. (A) Modified Fischer LABODEST unit used for isobaric vapor–liquid equilibrium experiments of the binary system ProOH/ProPro under microwave heating (*only part of the liquid volume is irradiated, whereas the vapor–liquid interface is established higher than the microwave cavity*). (B) Equipment used for vapor–liquid equilibrium experiments of the binary systems ProOH/ProPro, ProOH/ProAc, and ProPro/ProAc under microwave heating (*contrary to part A, both the liquid volume and the vapor–liquid interface are irradiated*).

steady state was assumed and condensed vapor samples together with the corresponding liquid samples were collected from the condenser and from the bottom of the flask, respectively.

In the experiments for powder catalyst heating, a 10 mL glass tube containing a catalyst powder bed was inserted into the Discover single-mode microwave oven. Then, power of 10 W was supplied for 35 min. The temperature was monitored using one FO temperature probe placed in the middle of the catalyst bed (with respect to the horizontal plane) and introduced 5 cm deep (total height 8 cm). Online temperature monitoring was

performed using the TMI temperature signal conditioner. For the catalyst heating experiments in the solution of reagents, the same equipment used to run reactions was employed. The oven was power controlled and set to 100 W. Experiments were carried out for 35 min with continuous stirring.

For the reaction experiments, catalysts with ammonium cations were calcinated to have the H^+ protonated form and run acidic catalyzed reactions. The zeolites were activated in a conventional oven at 400 °C for 6 h according to the TGA analysis. Catalysts with already protonated cations were air-

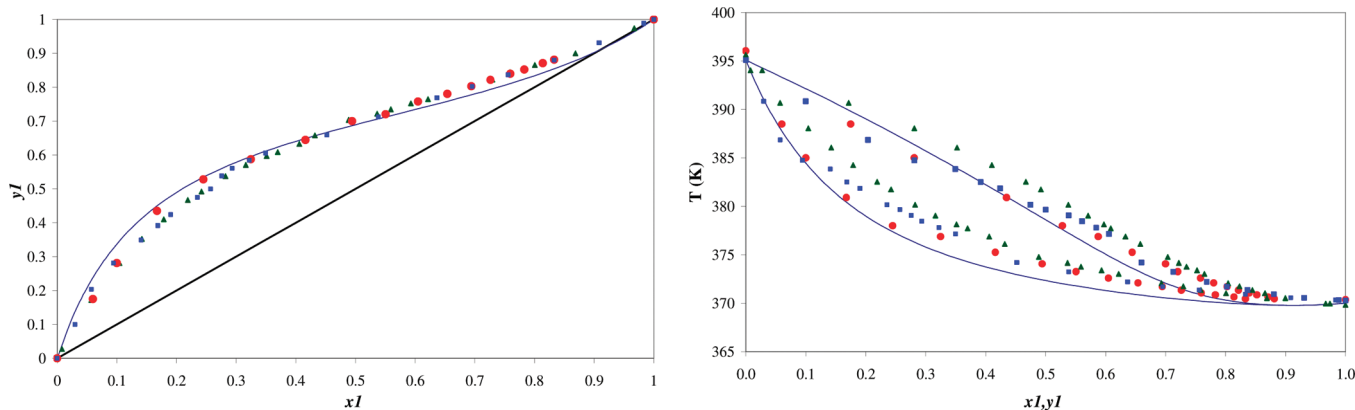


Figure 4. Isobaric VLE experimental results for the binary system ProOH (1)/ProPro (2) obtained in the modified glass Fischer LABODEST apparatus (Figure 3A) with the Discover single-mode microwave oven at 1 bar. (—) UNIFAC, (\blacktriangle) data set from the literature, (\blacksquare) experimental values without MW, and (\bullet) experimental values with MW. The temperature reported is the equilibrium temperature inside the Cottrell tube.

dried for 24 h at 100 °C and then used. The 500 mL three-neck flask was loaded with a measured amount of acid mixed with the catalyst and placed inside the MARS MW oven and heated up to the reaction temperature. In a separate flask, a measured amount of alcohol was heated up to the reaction temperature. When the reaction temperature was reached in both flasks, the reactants and catalyst were mixed together, and timing was started. Reactions were performed under total reflux conditions. Every 15 min, a sample from the reaction mixture was taken using a syringe for subsequent GC and Karl Fischer analysis; the sampling interval was increased as the experiment progressed. The reaction runs were stopped after 10 h.

3. Results and Discussion

3.1. Effects of MW Radiation on Separation. As explained in section 2, two types of experiments were designed and carried out in two different setups. In the first set of experiments, only the bulk liquid was irradiated by MW, whereas in the second set of experiments not only the bulk liquid but also the V–L interface was irradiated.

3.1.1. Part I. Effects When Only the Bulk Liquid Is Heated. These experiments were designed to resemble what would be the effect of exchanging a conventionally heated reboiler with a MW irradiated one with the motivation of studying the effects that electromagnetic radiation may have on thermodynamic equilibrium. One could expect that if selective heating of molecules in the bulk liquid occurs (according to the difference in dielectric properties), that should reflect in the concentrations of the high MW-absorbing component in the vapor phase. Consequently, the same equipment that is normally used for determination of vapor–liquid equilibrium curves was modified with a monomode MW oven. In Figure 4, the experimental results for the binary system ProOH (1)/ProPro (2) are presented. On the left, the xy diagram outlines the liquid phase mole fraction, x_1 , on the horizontal axis and the vapor phase mole fraction, y_1 , on the vertical axis. On the right, the corresponding Txy diagram outlines the equilibrium temperature (T) vs the liquid and vapor phase mole fractions (x and y , respectively) of the lighter component (in this case, ProOH). The Txy diagram comprises two lines. A lower line corresponding to the saturated liquid line or bubble point curve and an upper line corresponding to the saturated vapor or dew point curve. All data was taken at a constant pressure of 101.3 kPa. Initial experiments were performed in the conventional setup with no MW (\blacksquare). The data obtained was compared with at least one data set from the literature³⁰ (\blacktriangle), and data generated

using the UNIFAC group contribution method from ASPEN Properties Plus (—); as seen in Figure 4, all these data were found in good agreement. Then, MW experiments were performed and the output (\bullet) was compared with the conventional curves to check how much it deviated. It can be seen that the experimental data obtained using the modified apparatus with the MW heater show no significant difference from the data obtained using the conventional equipment. This is most likely because equilibrium conditions are achieved inside the Cottrell tube (above the microwave cavity), where vapor and liquid have a unique temperature.

Apart from the ProOH/ProPro system, the ProOH/toluene system was also investigated. In the latter, ProOH is a very good MW absorber ($\epsilon'' = 15.216$), whereas toluene is a very poor one ($\epsilon'' = 0.096$). The result was the same as in conventional VLE with the exception that a minimum concentration of ProOH was needed in order to make the mixture boil (the highest power level of 300 W for the Discover microwave oven was used).³¹ This shows that selective interaction of MW with molecules does exist. However, MW energy is dissipated rapidly into heat, and in combination with stirring, the liquid temperature becomes uniform. *The underlying message from this set of experiments is that molecular separation is not affected when only the bulk liquid is irradiated.*

3.1.2. Part II. Effects When the Bulk Liquid and the V–L Interface Are Heated. A second set of experiments was planned and conducted in the custom-made distillation head (Figure 3B). In this case, not only the bulk liquid but also the vapor–liquid interface is irradiated by microwaves, representing the case of the hybrid MW-irradiated RD column depicted in Figure 1. Experimental results from three binary pairs (system A ProOH (1)/ProPro (2), system B ProPro (1)/ProAc (2), and system C: ProOH (1)/ProAc (2)) were obtained and are presented in Figure 5 in terms of xy (left) and the corresponding Txy (right) diagrams with liquid phase mole fractions x_i and vapor phase mole fractions y_i at the corresponding equilibrium temperature T . The following symbol convention is used: (\bullet) for experimental data, (\blacktriangle) for reference data, and (—) for UNIFAC modeled data. Reference data from the literature³⁰ was also used for comparison in the case of system A. For system B, no data was published before, but results were compared to own data produced under conventional heating conditions, and for system C, a data set from the literature³² was used. It can be clearly seen in Figure 5 that MW irradiation exerts an effect on the separation of binary mixtures only when both the bulk liquid and the V–L interface are irradiated. The experimental

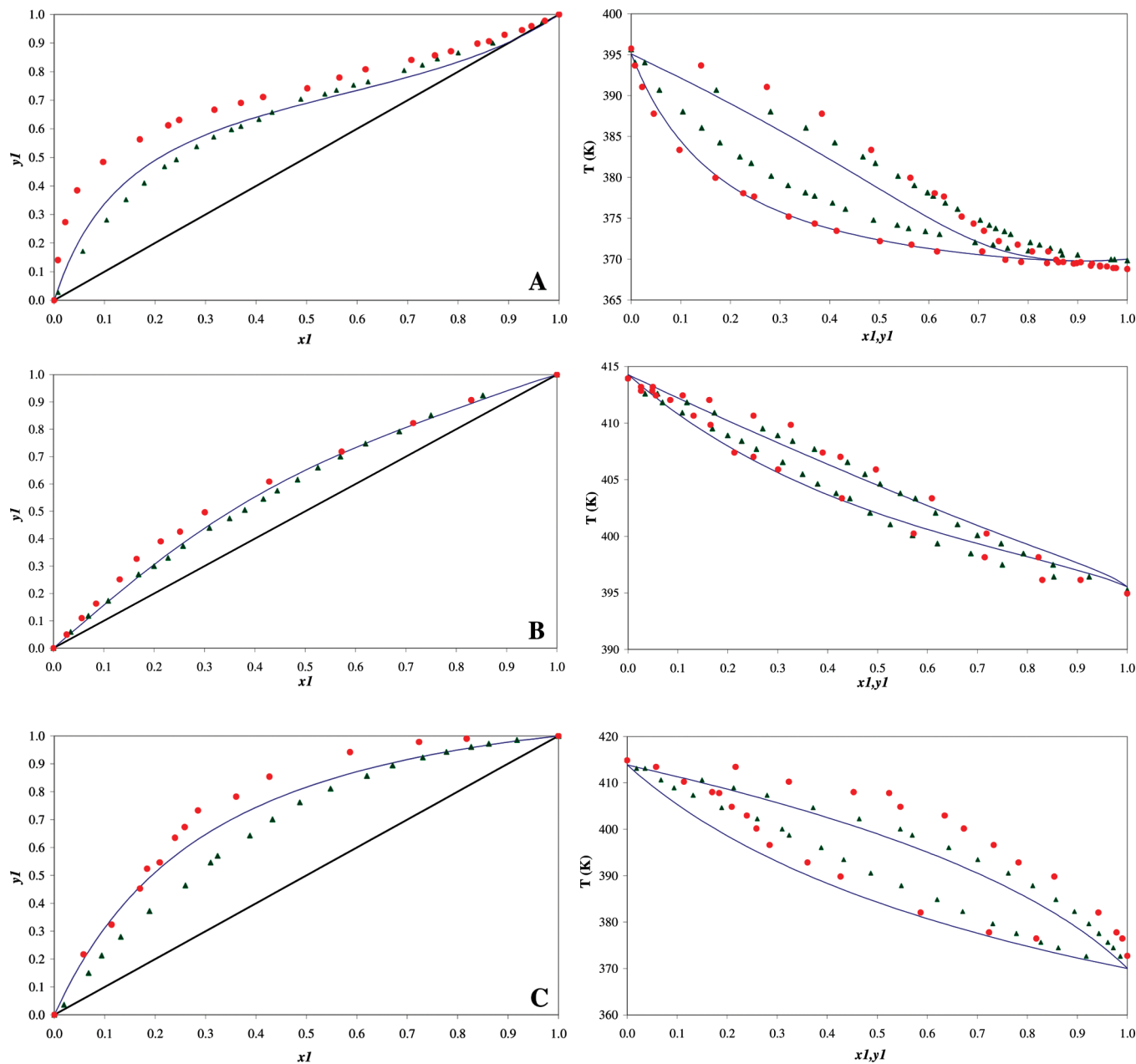


Figure 5. xy and T_{xy} graphs obtained with the Discover single-mode microwave oven and the custom-designed distillation head (Figure 3B): system A ProOH (1)/ProPro (2), system B ProPro (1)/ProAc (2), and system (C) ProOH (1)/ProAc (2); (—) UNIFAC, (\blacktriangle) data set from the literature, and (\bullet) experimental values. The temperature reported is the vapor temperature above the interface.

data obtained via MW irradiation differ from conventional VLE data in that the vapor phase is richer in the high volatile component for the three systems. It is noted here that the thermodynamic laws governing phase equilibria are well-established and hold both for conventional and microwave heating. We believe that the experimental observations presented herein are a consequence of a nonequilibrium state originating from the direct interaction of MW with the V–L interface associated to different phenomena linked together such as superheating, enhanced mass transfer, and hydrodynamic instabilities. When the mixture is superheated, a change occurs not only in the boiling point but also in the partial vapor pressures of the constituent components (for pure components, a higher boiling point results in a lower vapor pressure). Furthermore, higher temperatures developed locally at the top liquid surface may result in enhanced mass transfer from the liquid to the vapor phase (more pronounced for the component with the lower boiling temperature). This increase in surface

activity can also generate turbulence allowing molecules to set off easier into the vapor phase. This qualitative picture is difficult to verify experimentally and quantify due to the difficulty in measuring temperature at the interface with the equipment used and due to the liquid being stirred. Further investigations are currently performed and focus on rationalization of the results using local composition models such as the NRTL model and vapor pressures of superheated pure components under microwaves.

The experimental results in Figure 5 also show that the MW effect is more pronounced in system C followed by systems A and B. This can be related to the difference in boiling points (ΔT_b) of the binary components in each system (A $\Delta T_b = 25.7$ °C, B $\Delta T_b = 18.0$ °C, and C $\Delta T_b = 43.7$ °C). More specifically, the higher the difference in the boiling point, the stronger the separation efficiency, which points out a strong thermal effect. However, the difference in ΔT_b between systems A and B is not big, whereas the difference in the separation efficiency is considerable indicating that a secondary dependence on the

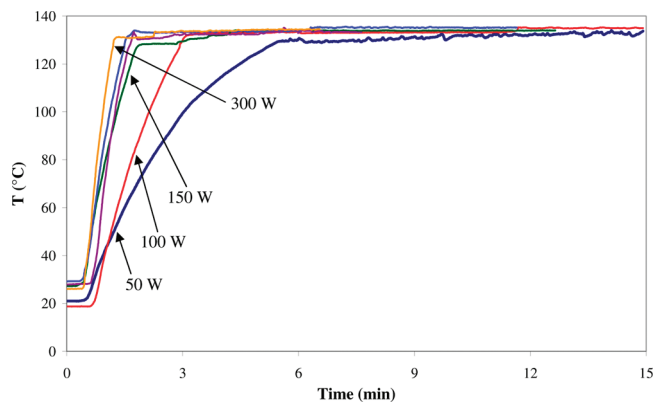


Figure 6. Temperature vs time during heating of system B ProPro (1)/ProAc (2) with different MW power inputs. Initial liquid mole fraction: $x_{\text{ProPro}} = 0.36$. Vapor mole fraction: $y_{\text{ProPro}} = 0.58$.

dielectric properties of the mixture might exist. In this frame, system B (ProPro/ProAc) is of particular importance as its low boiling component (ProAc) is the higher MW absorber ($\epsilon'' = 1.0$ vs 0.2). If only a thermal effect existed, the separation effect should have been more pronounced meaning that the concentration of ProPro in the vapor phase should have been higher for each measured data point. In contrast, Figure 5B shows that the positive difference in separation when using MW is very little and the MW data are close to the thermodynamic equilibrium curve most likely due to the counterbalancing effect of dielectric properties (i.e., the component with the higher boiling temperature in this case ProAc is the high MW absorber).

The effect of power supplied on separation was studied by heating samples with the same initial concentrations using different power inputs. Figure 6 shows the results of a sample from system B having an initial ProPro mole fraction of $x_{\text{ProPro}} = 0.36$. The effect on steady state temperatures and x , y concentrations (mentioned in caption) is the same except for the required time to reach the steady-state temperature implying that the effect is not power dependent. Getting more insight into the interaction of MW with the V–L interface is under ongoing investigation. Nonetheless, *we believe that the reported observations herein are of importance in the field of vapor–liquid separations. In practical terms, the improved separation under MW nonequilibrium conditions may be translated into design of smaller columns with a lower number trays for a given separation efficiency, compared to conventional designs involving heat exchange in the reboiler and condenser only.*

3.2. Catalyst Selection and Reaction Experiments. The selection of a catalyst is crucial for the correct operation of any RD column. Pressures and temperatures for reaction and distillation are required to match thus reducing the operational window over which the process is feasible as well as the degrees of freedom to control the process. By the use of MW irradiation, this window can be enlarged especially due to selective MW interaction with certain materials. MW heating enables some reactions to occur at much higher rates in the presence of a suitable heterogeneous catalyst thus enabling processes that would otherwise be infeasible due to the low yields or the long time needed to reach high conversions. Consequently, RD technology used so far only in petrochemical and commodities production could be taken to new industrial frontiers in combination with MW irradiation. Kappe et al.³³ discuss more than 700 reaction schemes performed under MW heating conditions that could serve as suitable reactions for RD processes. As in heterogeneous gas phase reactions, where the use of MW radiation has been demonstrated to enhance reaction

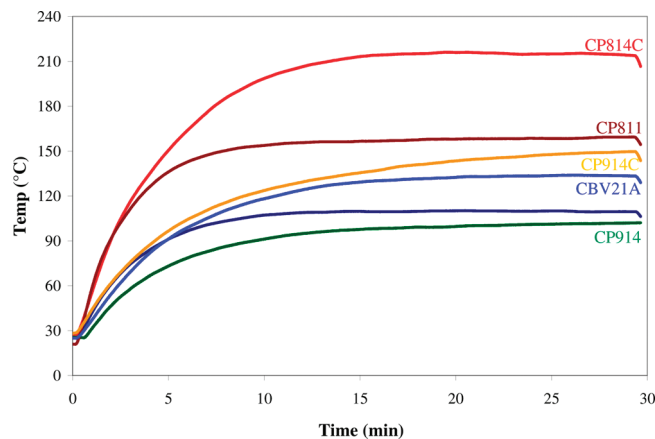


Figure 7. Temperature vs time in different zeolite powder beds irradiated in a Discover monomode microwave oven. Power is 10 W.

rates,³⁴ heterogeneous liquid phase reactions could benefit from the technology in the same way. The objective is to selectively heat zeolite particles with high dielectric properties (metal oxides and silanol groups present in the framework) raising their temperature to a higher value than that of the bulk liquid surrounding them. In gas phase reactions, this can be more easily accomplished since gases are known to be very bad MW absorbers, whereas in liquid phase reactions the electromagnetic waves must overcome the absorbing liquid surrounding the catalyst and hit the particle.

In Figure 7, the interaction of microwave irradiation with six different commercial zeolites is shown. The catalysts were heated under the same constant power profile (10 W) showing different heating rates. It was initially expected that selective heating would be dictated by the metal oxide concentrations and the corresponding dielectric properties: Al_2O_3 ($\epsilon'' \approx 9$), TiO_2 ($\epsilon'' \approx 50$), ZrO_2 ($\epsilon'' \approx 25$), Fe_2O_3 ($\epsilon'' \approx 9$). According to this hypothesis and looking to the XRF results presented in Table 4, the best heating catalysts should have been in the order $\text{CBV712} > \text{CP914C} > \text{CBV21A} > \text{CP814} > \text{CP914} > \text{CP811C}$ following the concentrations of the high dielectric oxides. Rather, the rank from the best heated catalyst to the worse heated one is $\text{CP814} > \text{CP811C} > \text{CP914C} > \text{CBV21A} > \text{CBV712} > \text{CP914}$. According to these results, it can be deduced that it is not only the metal oxides determining the interaction of MW radiation with zeolites but also the silanol groups of the silica. Turner²⁰ indicates that the concentrations of silanol groups in zeolites may be large. The value can be calculated by dividing the total amount of $-\text{OH}$ by the BET surface area. Silanol $-\text{OH}$ groups have a substantial dielectric loss thus governing the zeolite heating when exposed to microwave radiation. When the zeolites are heated together with the reaction mixture, the BEA type zeolites perform again better than the rest (results not shown). Overall, the best heated catalysts were the zeolites CP814C and CP811C, which were therefore selected for the reaction experiments. The latter were carried out to compare reactions under MW and conventional heating, looking for possible reaction yield improvement.

The results of reaction experiments performed are summarized in Table 5. The reported values are steady state conversions. The performance of zeolite CP814C was better, yielding more acid conversion under conventional heating conditions. This can be rationalized by the stronger acidity of this zeolite reported in Table 6. When comparing the heating modes, MW did not yield conversion improvement. At low to moderate alcohol/acid ratios, the conversions with MW are comparable to those with conventional heating. Unlike the gas–solid systems where

Table 5. Conversions with Selected Zeolite Catalysts under Conventional and Microwave Heating

commercial name	reaction temperature (°C)	heating mode	ProOH/ProAc (mol/mol)	ProAc conversion
CP 811C	100	MW	1.5:1	49.60%
			1:1	46.4%
		conventional	1.5:1	49.06%
			1:1	42.91%
CP 814C	100	MW	2:1	58.73%
			1:1	53.98%
		conventional	2:1	67.76%
			1:1	56.56%

Table 6. Measured Acidity for Zeolites CP811C and CP814C

zeolite	acidity (mmol g ⁻¹) NH ₃		
	weak (A)	medium (B)	strong (C)
CP 811C	0.12	0.28	0.41
CP 814C	0.47	0.41	0.10

^a Desorption temperature: (A) 400–650 K; (B) 650–800; (C) 800–1000 K.

there is direct MW–catalyst interaction, it is possible that MW are dissipated in the liquid phase (under the experimental conditions studied) and then the temperature is homogenized via stirring, yielding the same conditions as in conventional experiments. Only at high alcohol/acid ratios (2:1), the conversion with conventional heating becomes clearly better (Table 5). This may be related to adsorption–desorption mechanisms at the catalyst acidic sites; by selectively heating more alcohol molecules in the mixture, the adsorption of alcohol to the active site may be hindered lowering the possibility to react. Besides, both zeolite catalysts yielded acid conversions ~10% lower compared to the commercial ion exchange Amberlyst 46¹³ under the same reaction conditions. In addition, they produced the byproduct DPE in very low concentrations (0.05–0.20 wt %). It is most likely that the DPE is formed inside the porous structure of the catalyst by self-condensation of the alcohol. Previous studies of side reactions of the *n*-butanol esterification showed that fully sulfonated ion-exchange resins produced byproducts, whereas surface-sulfonated resins produced only ester and water.³⁵ Further investigation of MW-assisted esterification is currently performed and focuses on screening of additional acid (solid) catalysts including metal oxides. The appropriate catalyst for the new process should have the following desired characteristics: (a) Be selectively heated by MW so that the dielectric properties of the particles are able to overcome the dielectric properties of the surrounding liquid. (b) Give comparable or higher conversions at the same reaction temperature compared to the currently used ion-exchange resin. (c) Do not produce byproducts.

4. Conclusions

In this work, we discuss a new integrated concept of a microwave-assisted reactive distillation process in light of process intensification. In this context, the effects of microwave irradiation ($f = 2.45$ GHz) on a model esterification reaction (synthesis of *n*-propyl propionate from 1-propanol and propionic acid) and molecular separation (distillation) are investigated. Our experiments show that *microwaves can improve binary separation of mixtures only when they interact directly with the vapor–liquid interface*. In practical terms, this may be translated into design of smaller columns with a lower number trays for a given separation efficiency as compared to conventional designs involving heat exchange only in the reboiler and condenser. On the other hand, vapor–liquid equilibrium experi-

ments with microwave–bulk liquid interaction only (the interface was not exposed to microwaves) yielded compositions that did not differ from those in conventional vapor–liquid equilibrium experiments. On the reaction front, microwave-assisted esterification (catalyzed by selected zeolites) did not improve conversion. At low to moderate alcohol/acid ratios, the conversions with MW are comparable to those with conventional heating most likely because the microwaves are dissipated in the liquid phase before they reach the zeolite catalyst. Better conversion obtained with conventional heating at high alcohol/acid ratios (2:1) may be due to enhanced desorption of alcohol molecules from the catalytic surface thus lowering the possibility to react. Ongoing research involves screening of more zeolite and metal catalysts. Relevant results will be presented in a forthcoming communication.

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Nomenclature

Greek Letters

ϵ^* = complex permittivity (–)

ϵ'' = dielectric loss factor (–)

μ^* = complex permeability (–)

μ_N = chemical potential of component *N*

Subscripts

ProAC = propionic acid

ProOH = 1-propanol

ProPro = *n*-propyl propionate

DPE = di-*n*-propyl ether

Pro = propene

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