

# Microwave Enhanced Reactive Distillation

## THESIS ABSTRACT

The present abstract presents the relevant results and conclusions of the work conducted at the Process and Energy Laboratory at the Delft University of Technology in The Netherlands during the years 2007 to 2011. In this period several concepts of microwave (MW) heated multifunctional reactors were developed and tested, being the microwave enhanced reactive distillation process one of the most promising technologies studied. MW ( $f=2.45$  GHz) used as an alternative energy source for chemical syntheses (microwave chemistry) has been proven to provide clear advantages over conventional heating methods in terms of reaction time, yield and selectivity. Several applications using this technology have been effectively demonstrated in diverse scientific fields. In this work, the scope of microwave chemistry was further expanded to a conventional reactive distillation (RD) process with the primary objective to evaluate its use in view of possible process intensification (PI). The innovative and unique idea of combining electromagnetic radiation in form of microwaves to enhance the conventional process delivered important results that substantially improved the efficiency of one of the desktop examples in PI. In this context, a new integrated concept of a microwave enhanced reactive distillation (MWeRD) unit was proposed by separately researching (i) a conventional RD process, (ii) the effects of MW on a model homogenous and heterogeneous catalyzed esterification reaction and (iii) the effects of MW on molecular separation for application in vapour-liquid contactors. As a model system, the esterification reaction for the synthesis of *n*-propyl propionate (ProPro) was chosen. The ester can be obtained from the reaction of propionic acid (ProAc) with excess of 1-propanol (ProOH) catalyzed under acidic conditions. The state-of-the-art industrial scale production of ProPro involves the use of a RD process as the system core, with two downstream units for reactant recovery and product purification. By applying PI principles and approaches using MW the original process was improved to a more efficient one.<sup>1,2</sup> Perhaps the most interesting outcome of this thesis was the discovery that MW could improve molecular separation of mixtures while being irradiated. Our experiments have shown that molecular separation of certain binary mixtures can be enhanced only when microwaves interact directly with the vapour-liquid interface that is exposed to the electromagnetic irradiation. The mechanisms involved in this process are still unknown, and further research is required to gain additional insight into the interactions between MW and the vapour-liquid interface. Regarding distillation, this may be translated, in practical terms, into the design of smaller columns with fewer trays for a given separation efficiency, compared with conventional designs involving heat exchange only in the reboiler and condenser. On the reaction front, the synthesis of ProPro was investigated using various homogeneous and heterogeneous catalysts that could enhance the reaction rate under microwave heating conditions as compared with conventional heating methods. The baseline for catalyst screening was the reaction using the ion exchange resin Amberlyst 46, one of the best performing catalysts

used for the test system in conventional RD.<sup>3,4</sup> Several catalysts, including zeolites, MOFs, acidic clays, metal salts and triflates, were found to yield more ester under both heating methods with no by-product formation. From all catalysts tested, only the homogenous reaction using Zn triflate as catalyst was enhanced with the use of MW heating, producing 40% more ester. By taking into consideration all the experimental results, the concept of a fully integrated MWeRD column for the synthesis of ProPro was accordingly developed. Key aspects for technology integration, such as cavity design, scale-up and energy efficiency of magnetrons, were introduced and extensively discussed. The differences between the new and the conventional process were also clearly described. MWeRD has the potential to be much more efficient, not only because of the proven independent effects of MW on molecular separation and chemical reaction, but also because it takes advantage of the synergistic effects generated inside the column.

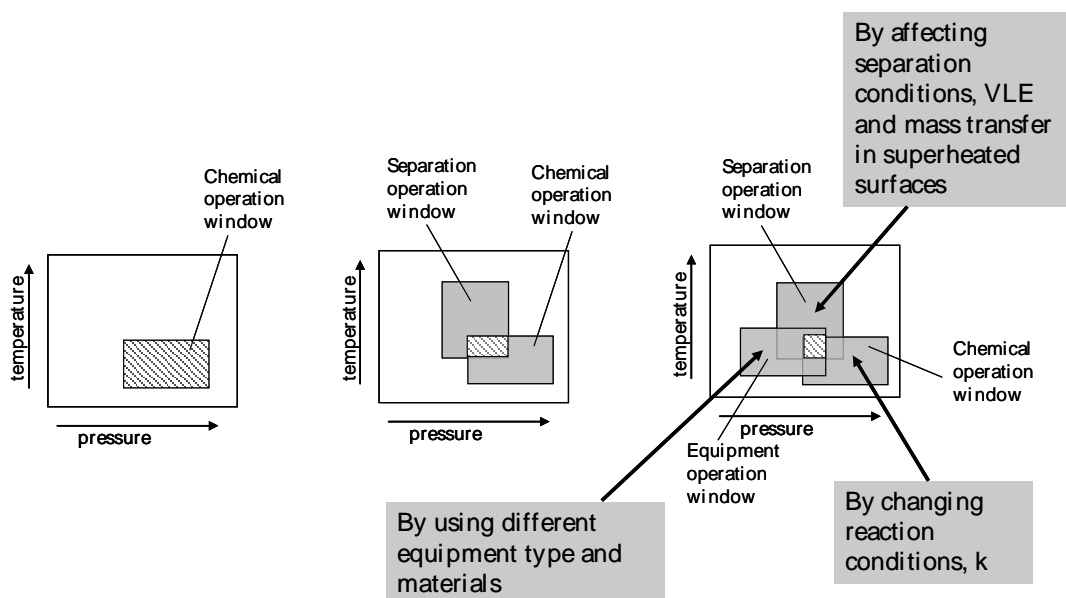
## 1. Originality of research and thesis outline

To the best of our knowledge, this thesis is the first attempt to investigate MW irradiation as a means to intensify reactive distillation processes. The nine chapters of the dissertation are compiled in four parts, each of which covers fundamental aspects of conventional RD processes and the effects of MW radiation on partial processes comprising RD, namely molecular separation and chemical reaction. Chapters 1 to 3 (Part I) form a comprehensive introduction to the thesis. Chapters 4 and 5 (Part II) cover state-of-the-art experimentation and modeling of conventional RD processes. Subsequently, in Part III, the effects of MW radiation on the two fundamental functions of RD, namely separation (chapter 6) and reaction (chapter 7), are studied separately. In the last two chapters (Part IV) bring together the proposed concept of a microwave-enhanced reactive distillation (MWeRD) process. The information generated in parts II and III of the thesis are used to discuss the general benefits of technology integration in *Chapter 8*. This chapter outlines the steps for further research and the type of hardware needed for the integration of both technologies. *Chapter 9* summarizes the highlights of the work and presents recommendations for follow-up research.

## 2. Problem Addressed

In recent years the chemical industry has had to address the growing global concern regarding energy availability, climate change, materials sourcing, safety and sustainability. Companies are forced to re-engineer the way they operate at different levels, striving to develop processes that are substantially more efficient. One possible way to achieve these developments is to apply a fundamental approach that can deliver innovative, radically different and avant-garde technologies, often with demonstrated feasibility at the pilot and industrial scales. The latter approach has been categorized by modern chemical engineering as process intensification (PI).<sup>5</sup> Perhaps one of the top examples of PI and one of the most relevant applications of the multifunctional reactor concept is reactive distillation (RD), also known as catalytic distillation where reaction, separation and enthalpy exchange take place in a single processing unit. There are a

number of obstacles that prevent the widespread application of RD, which could be further improved by different methodologies using PI; (a) **Fewer degrees of freedom**: The deliberate integration of several functions into one process may imply that the degrees of freedom would be higher than in the conventionally activated reaction followed by downstream separation. However, the opposite occurs. (b) **Reduced operational feasibility window**: Since both operations (reaction and distillation) are conducted simultaneously, overlapping of the operational window for reaction, distillation and equipment design occurs. Therefore, the temperatures and pressures of both processes must match, depending on a given hardware (column) configuration. (c) **Slow rate of partial processes (reaction, separation, or both)**: With slow reaction rates, expensive, large, and energy-inefficient equipment must be used (e.g. complex columns with side-reactors in heterogeneous systems) to provide sufficient residence time for the reaction to be completed. (d) **Optimal reaction conditions mean non-optimal separation conditions**: Process conditions at which the reaction optima or process feasibility occur will probably not correspond to the same conditions for optimum separation.<sup>6,7</sup>



**Figure 2.1** Superposition of operational windows reducing the process feasibility area.

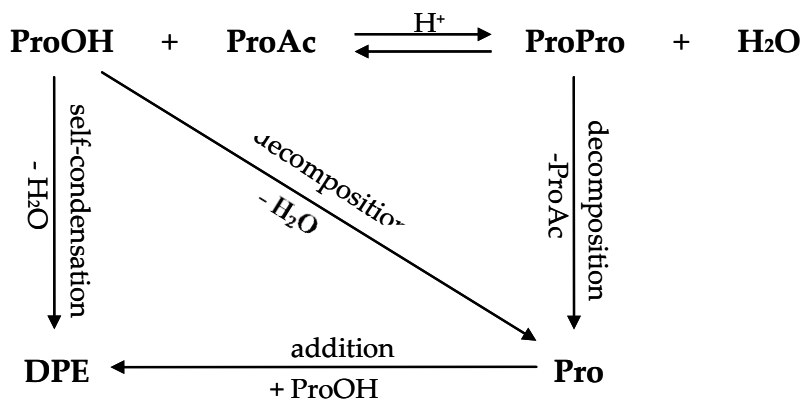
One way of overcoming these obstacles would be to apply the PI approach to the thermodynamic domain (energy), using alternative forms of energy that work at a meso-scale. The most important alternative sources include energy from electric, acoustic, and electromagnetic (MW and light) fields. Of these, the academia has paid special attention to the application of MW (dielectric) heating to improve yield and selectivity in chemical syntheses. Conditions for separation, mass transfer, heat transfer and reaction rate can be drastically different than those in conventional processes, possibly enlarging the operational feasibility windows and thereby augmenting the superposition area where the process is only possible. The challenge is to bring the aforementioned MW benefits into industrial practice. This study aimed to evaluate the use of MW as an alternative energy

source to intensify reactive distillation processes. The ultimate goal was to explore a novel concept of microwave-enhanced reactive distillation (MWeRD) based on demonstrated effects in partial processes (reaction and separation) and taking into account engineering challenges to achieve technology integration.<sup>8</sup>

### 3. State of the Art

#### 3.1. Esterification reaction

Esterification processes are in general, good test systems to prove concepts in RD. Most of the RD knowledge and design tools were developed for production of acetates with thermo-physical data including thermodynamic equilibria and kinetic models easily available for such systems. Esterification reactions are suitable for RD processes because: (i) As 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. In many esterifications, the reaction temperature coincides with the distillation temperatures. (ii) As the esterification reaction is reversible, the simultaneous withdrawal of the products shifts the equilibrium to the product side thus improving product formation. (iii) The possibility of RD to overcome azeotropes and avoid expensive downstream processing. Moreover, since the early stages of microwave chemistry when household equipment was used, esterification reactions were chosen as test systems.



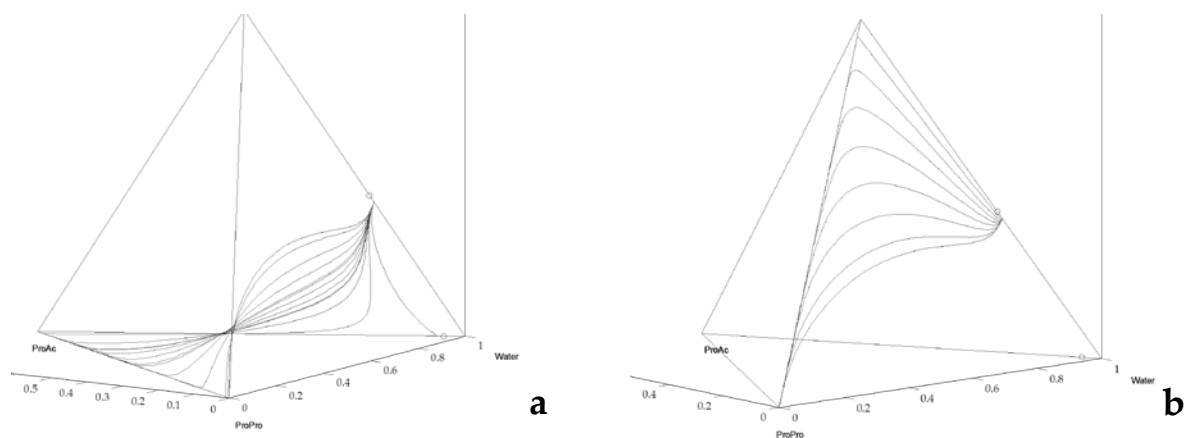
**Figure 3.1** Reaction scheme of *n*-propyl propionate synthesis.

Motives for this include: (i) Esters are very important products in the chemical industry accounting for a large production volume. Any improvement could have a direct impact in industrial operations. (ii) The time for the reactions to reach equilibrium could take several hours; large energy savings could be obtained if this time is drastically shortened. (iii) Reactions usually take place in excess of one reactant that has to be separated downstream. (iv) The reagents and products present in esterification reactions form highly non-ideal systems with several azeotropes present and by-product formation, causing difficult and expensive separation. This may be avoided by targeted selectivity.

Although the reaction occurs under acidic conditions, it is not self-catalyzed and addition of a strong acid catalyst, either homogeneous or heterogeneous, is needed. The complete reaction scheme is depicted in Figure 3.1. Since the dependence of the dielectric parameters with temperature was not known, the properties of the pure components were determined experimentally and published.

### 3.2. Process feasibility

Residue curve maps (RCMs) are thermodynamic diagrams that cover the whole composition space and give valuable information for the design of separation processes especially in RD. Their importance lies in the possibility to explicitly see in a visual representation the existence of distillation boundaries (separation constraints) and thus assess the separation feasibility of any given equilibrium-based process. RCMs can be considered as a prerequisite before any attempt is made in reactive distillation experimentation. They are constructed based on phase equilibrium data (vapor-liquid, liquid-liquid, and solid-liquid equilibria) and the system's physical properties thus being suitable for commonly used separation methods. As the case system chosen is a four component mixture ProOH/ProAc/ProPro/Water, a three-dimensional tetrahedron is used. ProPro was chosen as the reference component to calculate the transformed composition space. Figure 3.2 shows the RCMs when the chemical reaction takes place. All the reactive residue curves start at a new binary reactive azeotrope and end in either the pure ProAc vertex or the pure ProPro vertex. The trajectory of the lines depends on the initial composition of the feed. For feeds close to equimolar conditions (Figure a), the RCs will end in pure ProAc. For feeds with an excess of alcohol (Figure b), the RCs will end in pure ProPro.



**Figure 3.2.** RCM for the quaternary system with equilibrium reaction, trajectories ending in pure ProAc (a) and in pure ProPro (b)

### 3.3. Conventional Reactive Distillation

Using the results obtained from the RCMs in combination with some heuristic rules it is possible to propose a feasible process for the synthesis of ProPro in a single RD column. The information gathered from the RCMs show that: (a) By using the correct concentration of reagents in the feed composition (e.g. excess of ProOH) the process in a single RD unit will yield pure ProPro at the bottom and an azeotropic mixture of water and ProOH at the column top (Figure 3.2.b). If no excess of alcohol is used, then the bottom product will be a mixture of unreacted ProAc and ProPro. (b) The three binary azeotropes are “reacted away” when the chemical reaction occurs. The boundary plane from the non-reactive case is not visualized in the RCMs with chemical reaction. (c) The reactive azeotrope is a stable node. (d) The ternary azeotrope is likely to occur under certain process conditions and if the concentrations of ProPro/Water/ProOH and temperature are adequate. It is very important to know the phase split in the ternary diagram and its dependence with temperature to avoid two liquid phases inside the column. The previous statements are not enough to materialize the concept of a RD process. They determine however the feasibility of the process for a certain range of conditions. By using heuristic rules the conceptual design can be complemented as follow: (a) Due to the difference in boiling points of the reagents, it is not possible to have only one feed flow to the column. If they were to come together in a single feed, most of the ProOH ( $T_b=97.78^\circ\text{C}$ ) will evaporate and be distilled while most of the ProAc ( $T_b=141.16^\circ\text{C}$ ) will fall down to the bottom. Two feed flows shall mark the reactive section of the column, the acid being fed at the top and the alcohol being fed at the bottom thereby ensuring extensive countercurrent contact of both reactants. (b) The maximum operating temperature of the ion-exchange resin catalyst is  $120^\circ\text{C}$ . Above this temperature the catalyst is inactivated. In order to protect the catalyst, there should be a safe zone between the reboiler and the reactive section of the column. (c) The azeotropic mixture obtained at the column top contains valuable ProOH that did not react. A downstream process is needed (e.g. decanter, membrane or distillation column) to recover the alcohol. (d) Above the reactive section and depending on the column operating conditions a ternary mixture of ProPro/Water/ProOH may exist. The number of stages must be such that mixture is rectified to recover as much as possible ProPro that was distilled. According to the thermodynamic information regarding liquid-liquid equilibrium, it would be possible to recover part of the excess of alcohol in an economic way by using the big immiscibility gap of the ternary mixture ProPro/Water/ProOH using the phase split. Consequently a reactive distillation process in a single column coupled with a decanter on top is proposed for the synthesis of ProPro. To prove experimentally the concept, the pilot-scale reactive distillation column installed in the laboratory facilities at the Technical University of Dortmund was used and experimental results extensively discussed and published. The pilot-scale column (DN-50) is equipped with two types of structured packings (Sulzer BX and Katapak-SP 11). In addition, a non-equilibrium stage model (NEQ model) for the column was used. Model predictions were compared to experimental results showing good accuracy. Theoretical investigations of the most important operating parameters

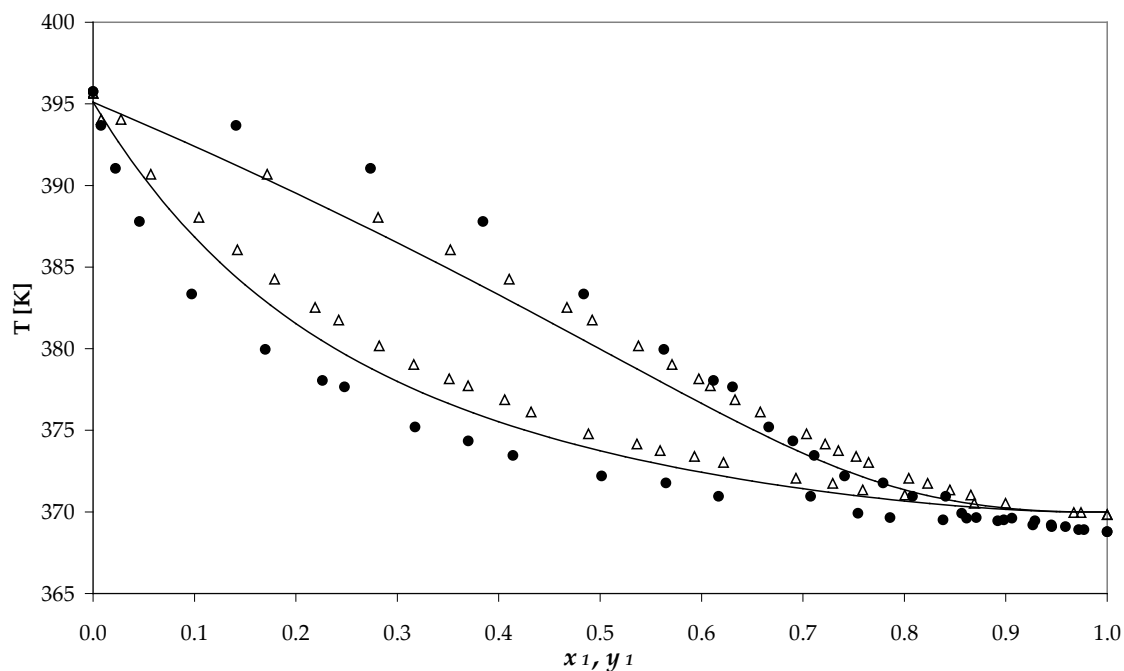
(total feed, molar feed ratio, reflux ratio and heat duty) and their effect on the overall process performance were presented.

## **4. Key Innovations - Microwave experiments**

### **4.1. The application of microwaves to vapour-liquid separations**

We have experimentally explored the effect of microwaves on separation of binary mixtures by comparison with conventional thermodynamic equilibrium experiments. Although, the effects of electromagnetic radiation on boiling and evaporation have been studied for more than three decades, the underlying physics are not yet universally agreed upon, as they are difficult to verify experimentally.<sup>9,10</sup> Different theories have been proposed to explain why the boiling points of polar liquids are higher under MW irradiation; these include surface hydrodynamic instabilities (Marangoni and Hickman), superheating, non-equilibrium conditions at the evaporating interface and pressure increase at the interface. In this work, we first performed conventional vapor-liquid equilibrium (VLE) experiments with binary mixtures of components involved in the case esterification reaction. 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. For determination of MW effects on the binary separations, two different setups were used.<sup>11-13</sup> The main difference between the two was the position of the vapor-liquid interface of the mixture with respect to the cavity where the electromagnetic field was applied. MW irradiation exerts an effect on separation of binary mixtures only when both, the bulk liquid and the V-L interface are irradiated. The experimental data obtained via MW irradiation differ from conventional VLE data in that the vapor phase is richer in the high volatile component for different 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 non-equilibrium state originating from the direct interaction of MW with the VL interface; it is likely that higher temperatures developed locally at the top liquid surface result in enhanced mass transfer from the liquid to the vapor phase (more pronounced for the component with the lower boiling temperature). This qualitative picture, though, is difficult to verify experimentally due to the difficulty in measuring temperature at the interface with the equipment used and due to the liquid being stirred. The experimental results show that the higher the difference in the boiling points of the mixture, the stronger the separation effect. A secondary dependence on the dielectric properties of the mixture was found. The effect of power supplied on separation was studied by heating samples with the same initial concentrations using different power inputs. 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 VL interface is under on-going investigation. Nonetheless, we believe that the reported observations herein are of

importance in the field of vapor-liquid separations. Figure 4.1 shows the  $T_{xy}$  diagram constructed for the system ProOH (1) / ProPro (2) with improved separation.<sup>14-17</sup>



**Figure 4.1**  $xy$  and  $T_{xy}$  graphs obtained with the Discover single-mode microwave oven and the custom designed distillation head. System ProOH (1) / ProPro (2); (-) UNIFAC, ( $\Delta$ ) data set from the literature and ( $\bullet$ ) experimental values. Temperature reported is the vapor temperature above the interface.

## 4.2. The application of microwaves to the model esterification reaction

The reaction was studied under microwave and conventional heating conditions using a variety of homogeneous and heterogeneous catalysts looking for possible rate enhancement.<sup>18-20</sup> Direct evaluation of the heating methods was done by comparing the ester yields after 30 min of equimolar reaction at 100°C which are the ideal reaction conditions inside the RD column avoiding the excess of alcohol. Several catalysts were found to produce more product than the ion-exchange resin Amberlyst 46 under both heating methods and the same catalyst loading. For the test system, the use of microwaves does not improve the conversion of the esterification reaction catalyzed by heterogeneous catalysts possibly because microwaves are dissipated in the liquid phase before they interact with the catalyst particles. From all the catalysts tested, the homogenous Zn triflate proved to be more effective under microwave heating conditions producing 40% more ester compared to the conventionally heated experiment during the short reaction as seen in detail in Figure 4.2. Metal triflates ( $M(\text{CF}_3\text{SO}_2)_n$  or  $M(\text{OTf})_n$ ) have received attention for this application and fall into an interesting category of catalysts for green



chemistry due to enhanced Lewis acidity, high water tolerance and the possibility to fix them on supports.

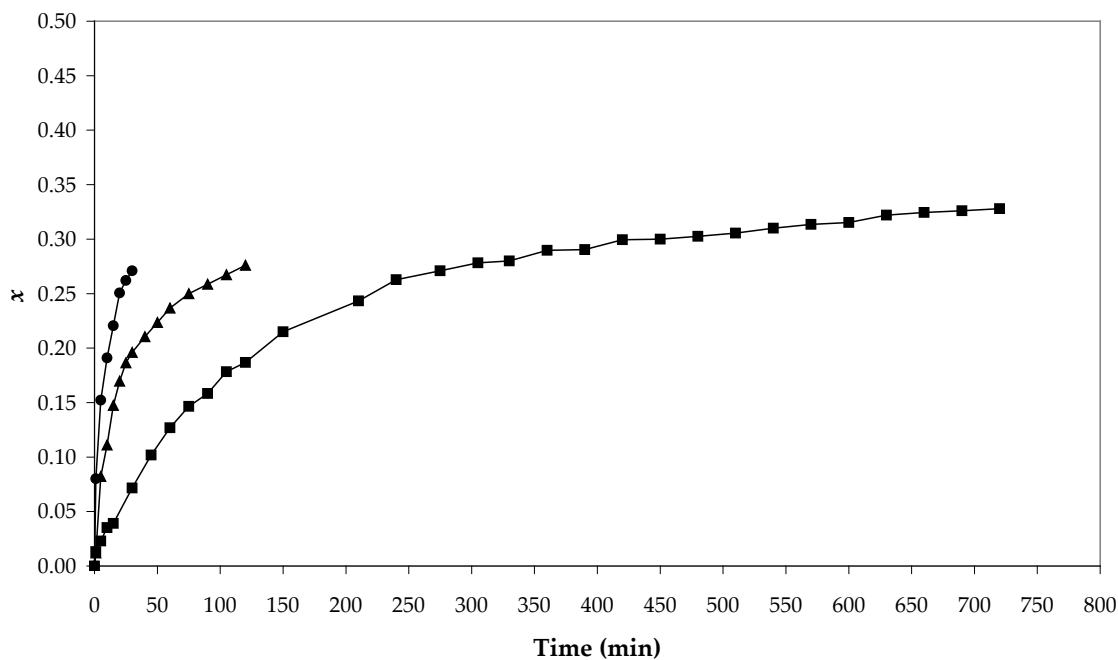


Figure 4.2 Catalysts and heating mode comparison, equimolar reaction at 373.15 K with 2% w/w catalyst loading. (●) reaction with Zn triflate catalyst using MW; (▲) reaction with Zn triflate catalyst conventionally heated; (■) reaction with Amberlyst 46 catalyst using MW.

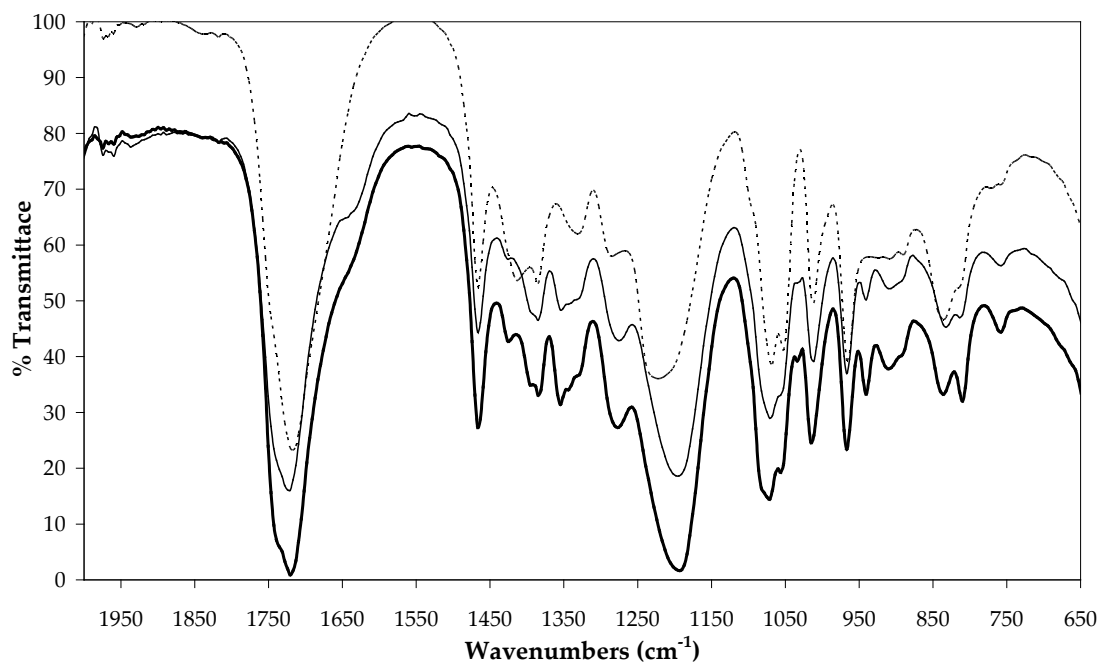


Figure 4.3 FT-IR spectra of the reacting mixtures. --- mixture without catalyst at 100°C, – conventionally heated reaction after 30 min, – MW heated reaction after 30 min.

Elucidation of the phenomena is difficult since the nature of the zinc triflate-MW interaction is actually unknown. In general, rate enhancements are rationalized in three ways; (a) superheating of one of the reactants and/or the catalyst to higher temperatures than the bulk one, associated with increase in the reaction rate constant (pure thermal effect), (b) changes in chemistry due to the superheating effect (e.g. decomposition) and (c) selective interaction of the electromagnetic field with specific molecules in the reacting mixture (known as non-thermal or microwave effect). Scientists working actively in the field should aim to discriminate the existence of a non-thermal effect.<sup>21-24</sup> Another way to compare results between conventional and MW heating and discriminate between the above mentioned effects is via in situ spectroscopic techniques. Three methods have been used (yet not extensively) by researchers to follow chemical reactions; X-ray scattering, Raman spectroscopy and FT-IR spectroscopy. We have used FT-IR to verify whether there was a change in chemistry particularly in the Zn(OTf)<sub>2</sub> catalyst either by thermal decomposition or other side reactions. Thermal decomposition of triflic groups occurs at 540°C, as measured experimentally which is unlikely to happen under the conditions used in this study and considering the dielectric properties measured. On the contrary, a secondary chemical reaction between hydroxyl groups to form ZnO and CF<sub>3</sub>SO<sub>3</sub>H (triflic acid) would be more likely to happen and could explain the boost in reaction conversion. Triflic acid is one of the strongest acids known. To determine the Zn(OTf)<sub>2</sub> spectra we used the spectra of a solution of the catalyst in ProOH and subtracted it from the one of pure alcohol. Characteristic peaks for triflic acid as compared to the Zn(OTf)<sub>2</sub> spectra are found at 1280, 1000 and 959 cm<sup>-1</sup>. Pure component spectra were obtained and recorded as background. Intense characteristic peaks for ProOH were detected at ca. 967 cm<sup>-1</sup>, for ProAC at 1414 and 847 cm<sup>-1</sup>, and for ProPro at 1355 cm<sup>-1</sup>. We then monitored the conventional reaction in situ. The progress of the reaction can be followed by the growth of peaks over time. Ester formation can be traced in the peak at 1355 cm<sup>-1</sup>. In order to compare the two heating modes and verify the possible catalyst reaction, IR spectra obtained from solutions after 30 minutes of reaction along with spectra from the mixture without catalyst are plotted together in Figure 4.3. It can be concluded from the IR spectra that the chemistry of the components in the reaction mixtures is the same for the two heating modes and that hydrolysis of Zn triflate into triflic acid is not likely to occur.<sup>25</sup>

In conclusion, MW can potentially enlarge the operational feasibility window of a RD process by enhancing the molecular separation of components in a mixture, accelerating the chemical reaction and by using equipment materials that can interact with the electromagnetic field (e.g. structured packings made of silicon carbide thus heating surfaces to temperatures higher than the surrounding liquid). The limited overlap between the reaction and the separation windows can then be magnified so that the required match in process conditions occur. As clearly evidenced by the work conducted, to establish whether a given system can benefit from MW heating, extensive experimentation have to be performed determining if enhanced molecular separation and increased reaction yields take place prior to conducting experiments in the integrated MW<sub>e</sub>RD system.

## 5. References

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