

# LIQUID PHASE REACTION WITH INTEGRATED SEPARATION IN CONTINUOUS CHROMATOGRAPHIC AND MEMBRANE REACTORS

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### 3. Abstract

#### *LIQUID PHASE REACTION WITH INTEGRATED SEPARATION IN CONTINUOUS CHROMATOGRAPHIC AND MEMBRANE REACTORS (INTREASEP)*

Many chemical reactions cannot be run to complete conversion of the reactants into products as conversion is limited by equilibrium or selectivity. The separation and reactant recycle requires vast amounts of energy and often generates a significant amount of waste products that can create an environmental problem. Novel reactor-separators, both membrane and continuous chromatographic systems, and their associated catalytic materials have been developed for partial oxidations and esterification reactions.

Esterification reactions are traditionally carried out in the presence of a strong acid, but can also be catalyzed by ion exchange resins such as polystyrene divinylbenzene copolymers cross-linked with sulfonic groups. The water formed is then preferentially sorbed in the resin and the reaction, normally limited by equilibrium, can now run to completion. Epoxides can be produced by oxidation with hydrogen peroxide on TS-1 in turn embedded in a hollow fiber polyimide / PDMS membrane as a catalyst, and solvent free operation can be obtained.

The main tasks in the project are:

- the identification of a number of classes of reactions that can benefit from such operation; the development of suitable catalyst and membrane materials
- the development of integrated heterogeneously catalysed reaction / separation units for liquid phase reactions limited by equilibrium or by selectivity and homogeneously catalysed in traditional processes
- the application of this methodology to two well chosen and industrially important model cases such as given above
- collection of data for technical, economic, energetic and environmental evaluation of such integrated reactor/separation units; in the case of the chromatographic separation, a pilot unit will also be used.

The tasks were successfully completed and generated 3 TIP results in the field of esterifications and chromatography:

- A monolithic column for reaction with integrated separation and for chromatography
- Esterification process in Simulated Moving Bed Reactors (SMBR) with commercial exchange resins
- Modified cation exchange resins as acid catalyst

In the field of oxidations, a hollow fiber membrane reactor was successfully operated in solvent-free conditions, but the expected run length and conversions could not be reached. All tried catalysts and reactions showed problems due to inactivation of the catalyst by the products formed. The project has however yielded a wealth of insight in the phenomena involved, not previously available in literature.

The partners are actively pursuing the exploitation of some of the results, both by offering licenses and implementation in their own production.

**Keywords:** reaction, separation, integration, oxidation, esterification

#### **4. Partnership**

This project is executed by the following partners:

VUB: Vrije Universiteit Brussel, BE (Coordinator)

POLIMI: Politecnico di Milano, IT

SISAS: Societa Italiana Serie Acetica Sintetica S.p.A., IT

DUPONT: DuPont de Nemours Belgium N.V., BE

TUCL: Technische Universität Clausthal, DE

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## Partner IV

### **5. Objectives of the project**

Many chemical reactions cannot run to complete conversion because of equilibrium or selectivity limitation. In these cases, the reactants and products have to be separated and recycled to the reactor. This requires large energy consumption and generates vast amounts of waste products (environmental problem). Our objective was to avoid some of these problems by integrated operation.

#### ***5.1 Objectives of the POLIMI/SISAS-groups***

Esterification reactions, traditionally carried out in the presence of a strong acid as homogeneous catalyst, represent a classical example of reversible reactions, where a chromatographic separation integrated with the reaction can lead to important economic benefits.

The main objectives in these projects are:

- The identification of a number of esterification reactions that can benefit from such integrated process;
- Replacing homogeneous acid catalysis by a heterogeneous catalyst and milder operation conditions;
- Developments of novel materials as catalyst/sorbent for esterification reactions;
- Development of integrated reaction/separation unit;

Collection of data for technical, economic, energetic and environmental evaluation of such integrated reaction/separation systems.

#### ***5.2 Objectives of the TUCL-group***

Active catalysts for esterification reactions are acids. Commonly, strong liquid acids like sulfuric acid are used in homogeneous processes. The disadvantage of this method is that the remaining catalyst in the reaction product has to be removed or neutralized. This additional technical effort can be avoided by the use of solid acid catalysts. As solid acid catalysts ion exchange resins are well suited for the esterification of organic acids with alcohols. So far ion

exchange resins are only available as small spheres with dimension ranging from 0.2 to 2 mm. This material does not fit the requirements for chromatographic or membrane reactor applications. The main objective was to develop an acid ion exchange resin inside carrier materials with a shape that is adapted to the above mentioned processes.

### **5.3 Objectives of the VUB/DUPONT-groups**

The VUB / DUPONT group wanted to investigate if it was possible to replace the conventional stoichiometric or homogeneous type catalysis methods for partial oxidation by novel membrane based catalytic systems. This appeared feasible from literature and preliminary experiments. Two systems were selected and after elimination of one, the focus was on epoxide production from alfa-alkenes by oxidation with hydrogen peroxide over TS-1 catalyst. The ultimate goal was to develop a scaleable technology for such reactions, say hollow fiber modules for use on large scale but only through tests on small scale. So a catalyst, reaction had to be selected, a catalytic membrane developed, a small reactor constructed, and finally many different characterizations and analysis had to be performed. As this had not yet been attempted in the liquid phase in such harsh conditions, it was indeed a formidable task with high risk and no certainty of success, even partial, but then this was the aim.

## **6. Scientific and technical description of the project**

### **6.1 Development of an SMB reactor process (POLIMI/SISAS)**

The esterification reactions (between an organic acid and an alcohol) represent a classical example of reversible reactions.

In order to achieve a conversion higher than the equilibrium one, the reaction must be shifted towards the formation of the products. This result can be obtained, for example, by removing water from the reaction site. This operation can be performed by distillation, but in this case the separation may be difficult because of the formation of an azeotropic mixture and therefore requires very high energetic costs.

The second problem related to the esterification reaction is a kinetic problem. The reaction rate is high enough only if catalysed by strong acids (or strong bases). A typical esterification catalyst is sulphuric acid that, on the other hand, being a homogeneous catalyst, causes several separation and purification problems in the downstream processes.

The first objective has been the identification and the systematic inventory of liquid phase esterification reactions that present industrial interest and are suitable candidates for heterogeneous catalysis and chromatographic separation.

The following 4 esterification reactions in liquid phase that present a potential interest for application in the integrated reaction and separation technology, have been identified:

- 1) n-butyl alcohol + acetic acid  $\rightarrow$  n-butyl acetate + water
- 2) Phthalic anhydride + 2 (2-ethylhexanol)  $\rightarrow$  Dioctyl phthalate + water
- 3) Phthalic anhydride + 2 Ethyl alcohol  $\rightarrow$  Diethyl phthalate + water
- 4) Glycerol + acetic acid  $\rightarrow$  Glycerol acetate (acetin) \* 1 water  
Glycerol + 2 acetic acid  $\rightarrow$  Glyceroldiacetate (diacetin) \* 2 water



These four reactions have been chosen both for their industrial relevance and for the difficulty that arises if we want to obtain total conversion and to minimise the formation of by-products.

We have identified a suitable material to use as catalyst in the esterification reaction and to selectively adsorb the products. Ion exchange resins, that are acid by the presence of sulfonic groups, have been used frequently as catalyst for reactions that are usually catalysed with mineral acids.

These resins seem to be able to play the double role of catalyst and water remover. From the catalytic point of view, resins are very attractive since they offer the benefits of homogenous catalysis together with the physical and mechanical ones of the heterogeneous catalysis.

Sulfonic groups on this material provide catalytic properties similar to those shown by sulphuric acid in homogeneous catalysis and they present the typical advantages of heterogeneous catalysis.

The selective swelling process during the reaction is of fundamental importance to realise a liquid solid chromatographic reactor. Only solvents with appropriate properties are sorbed into the matrix. This process is correlated with sulfonic groups too.

The cation exchange resin considered (up to now) in this work, is a commercial macroporous resin constituted of cross-linked polystyrene-divinylbenzene functionalised with sulfonic groups (Amberlyst 15). Concentration of acid sites is 4.7 meq/g, particle size 0.5-1.2 mm and 20 % of DVB.

First of all, we studied the thermodynamic equilibria of mono- and bi-components in the system including the chemical species involved in the reactions with Amberlyst 15.

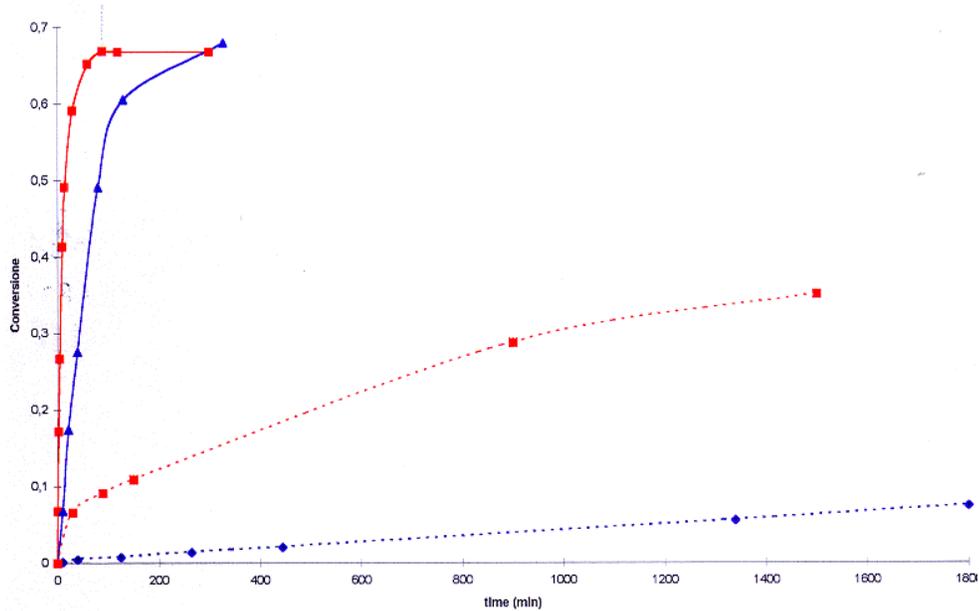
We measured the efficiency and the affinity toward the resin of all reagents and products involved in each reaction. In the case where the liquid phase is constituted by a multicomponent mixture, each component is sorbed to a different extent. This selective swelling and the possibility of predicting the partitioning ratio of each component between the two phases is very important if resins are used as heterogeneous catalyst.

Then we have defined the efficiency of the resins for the chosen esterification reactions and in some cases we compared these results with other catalysts.

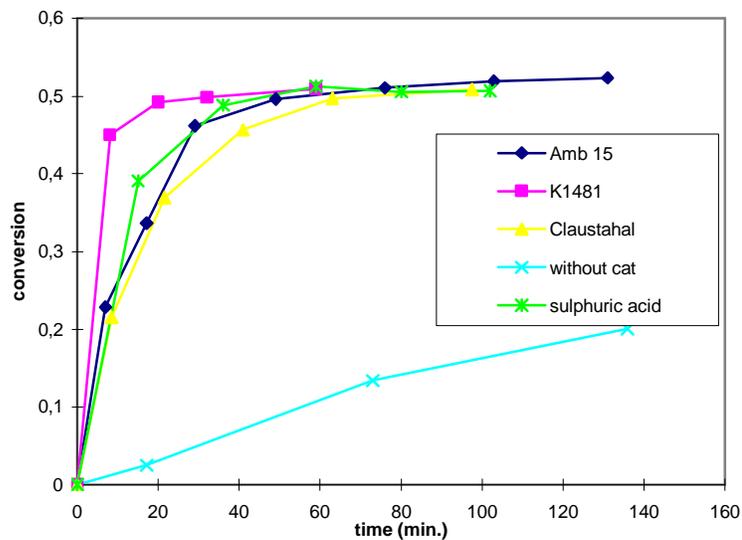
At first, the rate of the chemical reaction has been studied through experimental runs, conducted in an isothermal well-stirred batch reactor.

The first reaction tested, among those before mentioned, is acetic acid and butyl alcohol to yield butyl acetate and water and acetic acid and glycerol to give glyceroltriacetate.

Batch experiments have been performed with and without catalyst. These confirmed the remarkable catalytic activity of the acid resins (**Figure 1a** and **Figure 1b**).



**Figure 1a.** Batch experiments with and without catalyst for butylacetate (40°C and 70°C)



**Figure 1b.** Glyceroltriacetate (Triacetin) batch reactions

In order to study the kinetics of the esterification reactions of glycerol with acetic acid and to examine the effect of mass transport resistances, a series of experimental runs were made in a batch reactor.

The reaction rate is expressed in terms of concentrations in the adsorbed phase (i.e. the polymeric phase) by the mass action law, where the reaction rate is proportional to the deviation from equilibrium:

$$r_k = k_k \prod_{ir=1}^{n_{reag}} \Gamma_{ir,k}^{n_{ir,k}} \left( 1 - \frac{\prod_{i=1}^{NC} (\Gamma_i)^{n_{i,k}}}{K_{EQ,k}^\Gamma} \right)$$

- with:
- $\mathbf{r}_k$  (mol/s g cat.) is the rate of the  $k^{\text{th}}$  esterification reaction;
  - $\mathbf{k}_k$  (g.cat. /s mol) is the kinetic constant of the  $k^{\text{th}}$  reaction;
  - $\mathbf{v}_{i,k}$  is the stoichiometric coefficient of the  $i^{\text{th}}$  species in the  $k^{\text{th}}$  reaction;
  - $K_{EQ,k}^\Gamma = \prod_{i=1}^6 (\Gamma_{EQ,i})^{n_{i,k}}$  is the equilibrium constant of the  $k^{\text{th}}$  reaction and is experimentally evaluated at the desired temperature.

The batch reactor model has the objective of estimating the kinetic constant of the three esterification reactions involved in the synthesis of triacetin.

The range of temperatures investigated is 60-100°C. The Arrhenius parameters have been estimated using as objective function the minimisation of the square weighted deviations between the molar fractions calculated by the model and those measured experimentally.

The esterification reaction to DOP (dioctylphthalate) and DEP (diethylphthalate) are the two most interesting reactions, because of the increasing demand of the market and the intrinsic synthesis problems.

For the reaction to DEP, we have operated at higher temperature (110°C) and with a light pressure (2-3 bar), to preserve the ethanol in liquid phase. As we see in **Figure 2a**, the batch reaction with Amb. 15 shows a lower monoester conversion as a function of time, but a larger amount of ethyl ether (**Figure 2b**), compared to the reaction catalyzed by sulfuric acid (with an equal amount of acid equivalents). This is due to the larger steric hindrance of the anhydride with respect to ethanol. This favors the ethanol condensation reaction which leads in fact to about 2.5% ether formation at the end of the reaction.

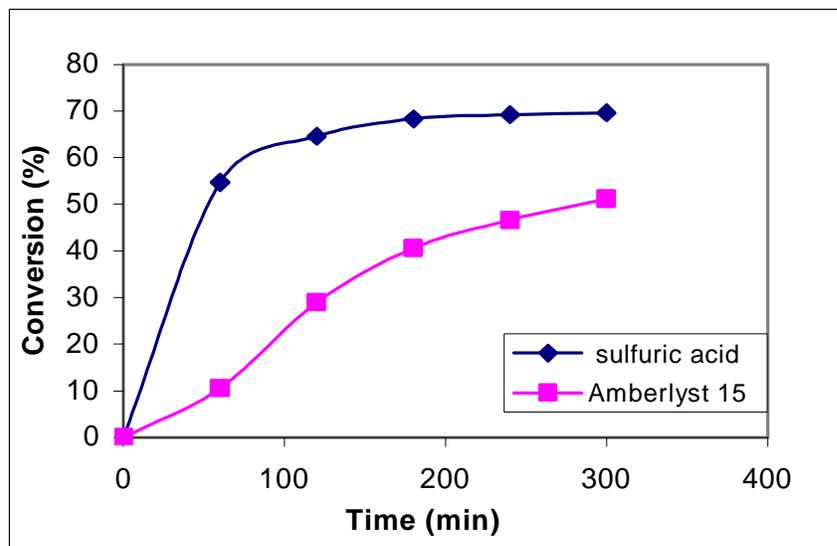


Figure 2a

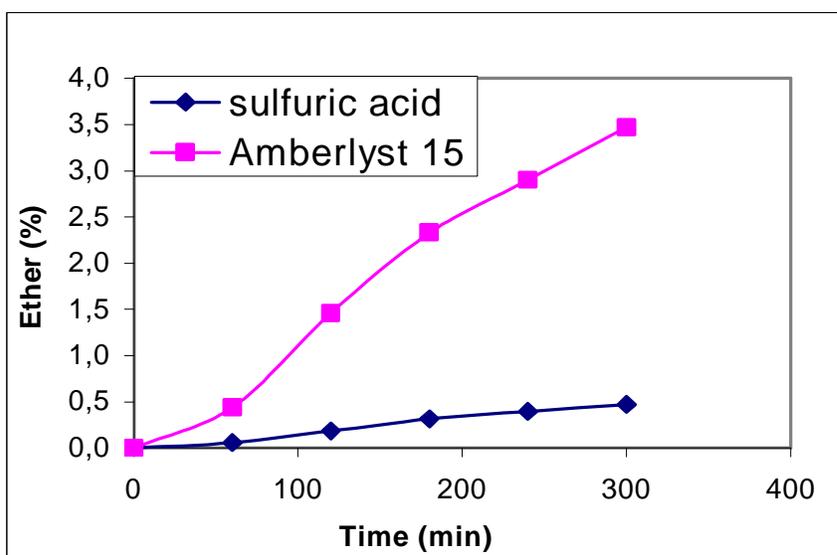


Figure 2b

For DOP the experiments have shown that with acid resins (especially beyond 130°C) there is a relevant formation of by-products i.e. alkenes: after 6 hours we loose about 10% of the alcohol. This reaction is proportional to the amount of resin employed.

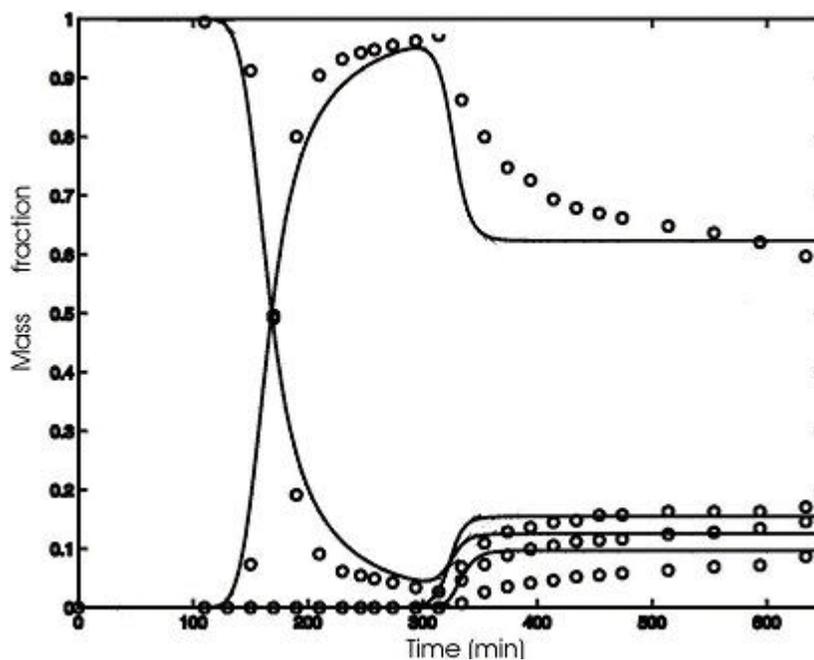
After these preliminary tests for the esterification towards butyl acetate and triacetin we decided, in consideration of the good results, to continue the experiments in a chromatographic reactor with Amberlyst 15. With more precision, some tests in fixed bed reactor have been developed for the reaction to butyl acetate, taking care particularly of the choice of the desorbent.

For the reaction to diethylphthalate (DEP) and to dioctylphthalate (DOP) we decided to use new catalyst / sorbent materials. The aim is to modify the distribution of the sulfonic groups in

the particle and microparticle of the copolymer (styrene/DVB), in order to avoid the formation of ethers (DEP and DOP) and alkenes (DOP).

### Butyl acetate

For this reason we realized some experiments in a chromatographic reactor using acetic acid as desorbent agent. In **Figure 3a** the progress of all products in the reaction phase, feeding acetic acid/butanol mixture and in **Figure 3b** the progress of all products in the desorption phase have been reported.



**Figure 3a.** Reaction phase

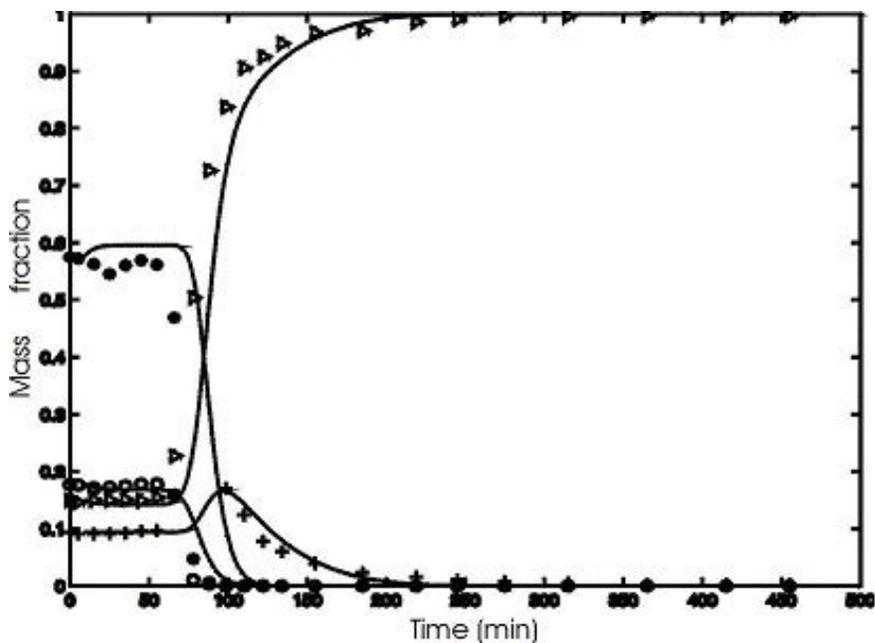


Figure 3b. Desorption phase

As we can see, starting from acetic acid in the column, the reaction phase doesn't change and we obtain a good separation between butyl acetate and water. About the desorption phase, a lower amount of desorption agent (acetic acid) is needed to completely regenerate the column, compared to butyl alcohol.

### Triacetin

We worked at different residence time, acetic acid/glycerol ratio and amount of initial water. From the obtained results, it is clear the essential requirement of completely drying of the bed to improve the separation between triacetin and diacetin. In fact very small amounts of the initial water compromise the chromatographic separation, as we can see in **Figure 4a** and **Figure 4b**, respectively with 0.68% and 0.06% of initial water. The following figure compares the model calculations with the experimental results for the esterification reaction from glycerol and acetic acid to triacetin. The behavior of the chromatographic reactor has been described by a non-equilibrium dispersive mathematical model, accounting for mass-transport resistances, axial dispersion and changes of the swelling ratio of the resin caused by composition variations. The homogeneous reaction rate has been neglected; temperature and fluid flow rate are assumed to be constant and uniform. The points are the experimental results and the curves are the results of the mathematical model.

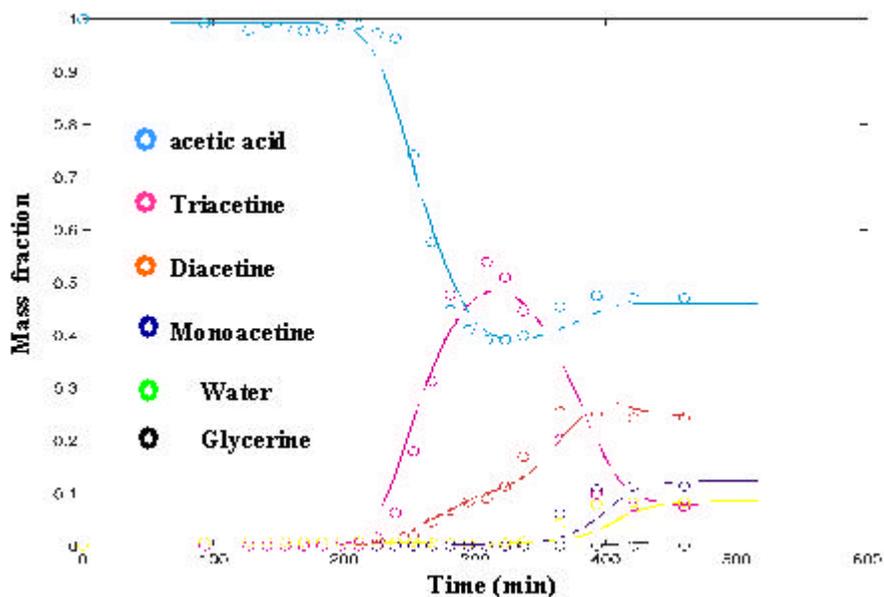


Figure 4a

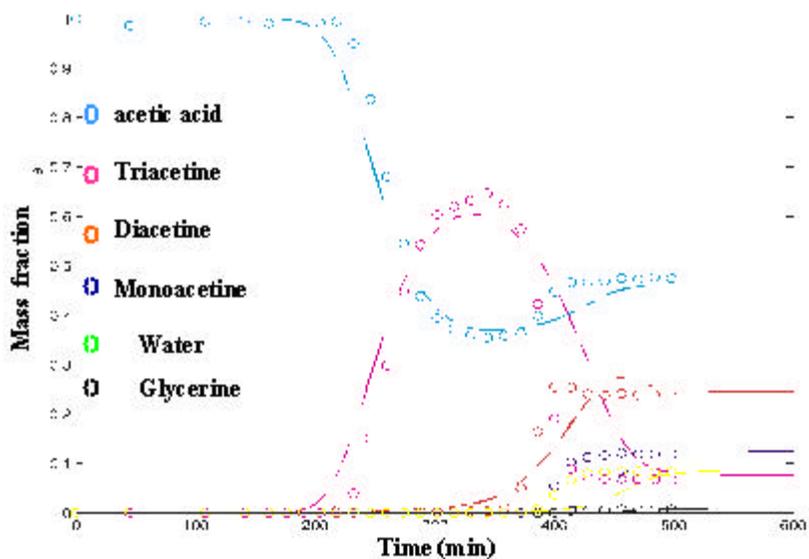
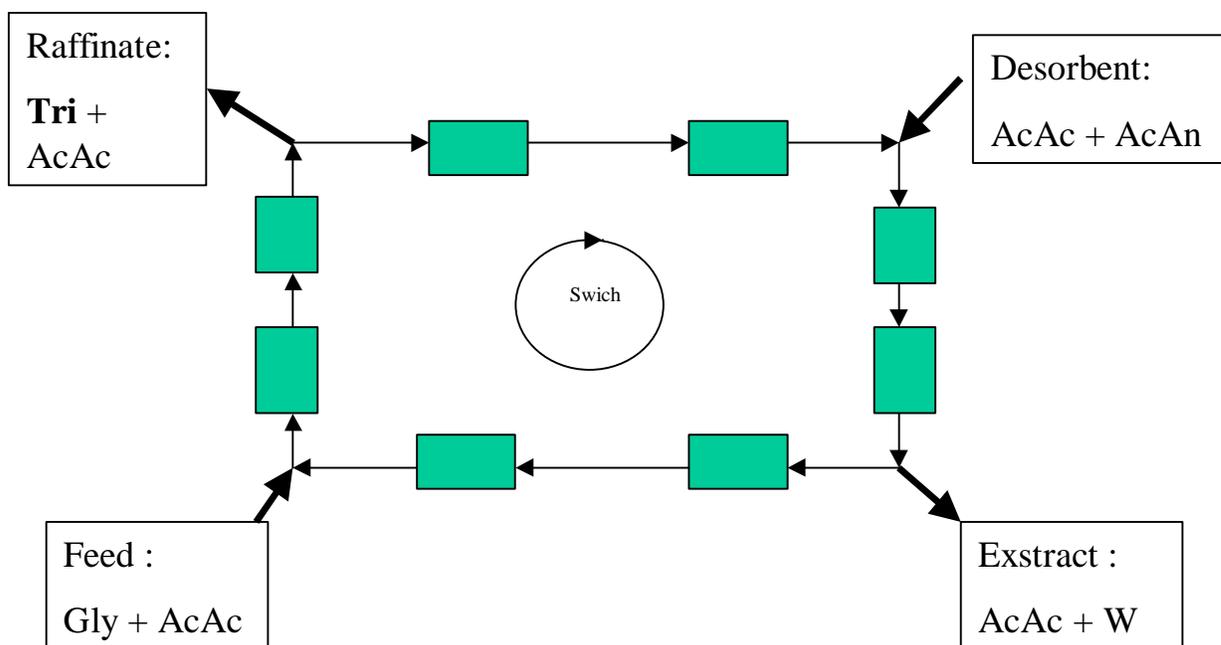


Figure 4b

Starting from good results obtained in the fixed bed configuration and from modeling results on a SMBR (Simulated Moving Bed Reactor) applied to the triacetin synthesis, the SMB reactor performances are further investigated with a modeling approach in order to identify the optimal operating conditions.

Eight columns constitute the SMB reactor, the columns are distributed in the four sections of the reactor (Figure 5).



**Figure 5.** Reactive SMB- -8 columns in configuration 2-2-2-2

The influence of several parameters on the reactor performance was investigated, in particular:

- The configuration of the columns, i.e. how the columns are distributed in the four sections of the SMB reactor.
- The feed composition.
- The desorbent composition.
- The flow ratios  $m_i$  between the liquid flow and the apparent solid flow in each section of the SMB reactor.

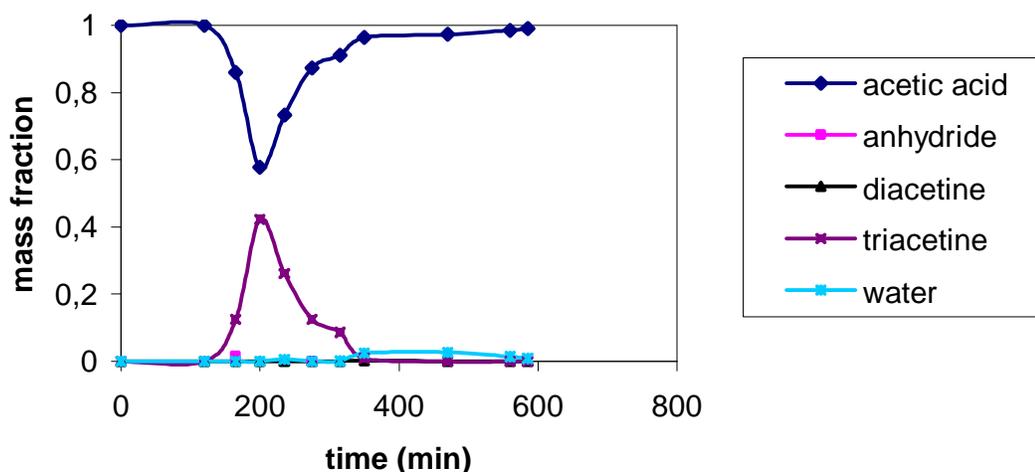
Changing the  $m_i$  parameters it was possible to obtain the 99% of water purity in the extract also with a configuration 2-2-3-1 which permits a higher length in the third section and thus a higher contact time between the reagents (acetic acid and glycerin).

Effectively, if only pure glycerin is fed into the reactor, a triacetin content of 36.14 % is obtained with a purity in the raffinate of about 99% and a purity of water in the extract equal to 99.2%.

SISAS has performed several cycles of reaction and desorption on a pilot reactor, in order to acquire the necessary information to perform an industrial evaluation of the process.

The pilot plant consists of two fixed bed reactors (with a overall volume of about 1000 ml for each one); each reactor was filled with 430 g of macroreticular cation exchange resin.

In order to test the performances of the pilot scale fixed bed reactor under industrial operating conditions, some runs with pulse feeding of reactants have been performed. The main objective is to obtain pure (> 99%) food grade triacetin followed only by a water peak. The results of these runs were then compared with numerical simulations in order to verify the reliability and in order to estimate better some chemical-physical parameters.



**Figure 6.** Weight fraction distribution with a pulse feed.

In this case (**Figure 6**) the separation between triacetin and water is good and pure triacetin is obtained, thus practically no diacetin was detected in the outflow of the reactor. Triacetin obtained was analyzed in SISAS laboratory and it appeared to be food grade.

With these operating conditions the productivity increases up to 480 kg of triacetin per kg of resin, per year.

For the esterification to DEP and DOP, we have defined a different strategy of work, because in these reactions Amberlyst 15 presents a very low activity and high formation of by-products compared to sulfuric acid. We have focused our attention on the reaction to DEP. The possibility of improving catalyst performance through an appropriate non-uniform distribution of the sulfonic groups has been investigated.

All the new modified resins have been tested using esterification to DEP in batch reaction. The reaction has been carried out at 130°C to emphasize the formation of ethers and with the same amount of acid sites to make a fair comparison between different resins.

In **Figure 7a** and **Figure 7b** are shown respectively the monoester conversion values as a function of time and the ethyl ether production as a function of the monoester conversion for all different catalyst systems. This allows seeing the ether production directly as a function of the ester production.

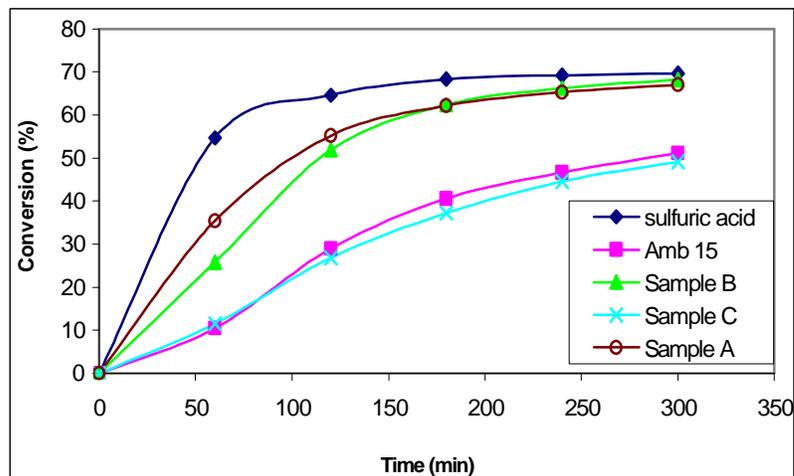


Figure 7a

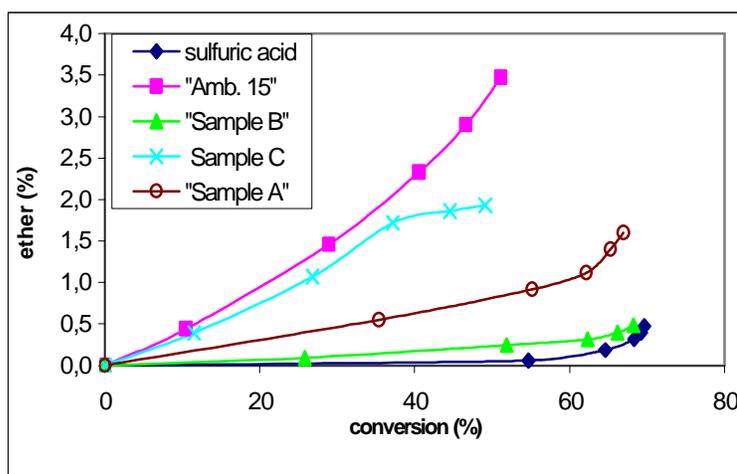


Figure 7b

As we can see, sulfuric acid always shows the highest reaction rate, but that obtained with sample A and sample B are very similar. Significant differences arise in terms of selectivity. In particular, in case of homogeneous catalysis and with desulfonated resin, a very small amount of by-products is formed. Also using surface sulfonated resin the etherification reaction is reduced, in fact the values of ethyl ether conversion as a function of monoester conversion are intermediate between these of sulfuric acid and Amberlyst 15.

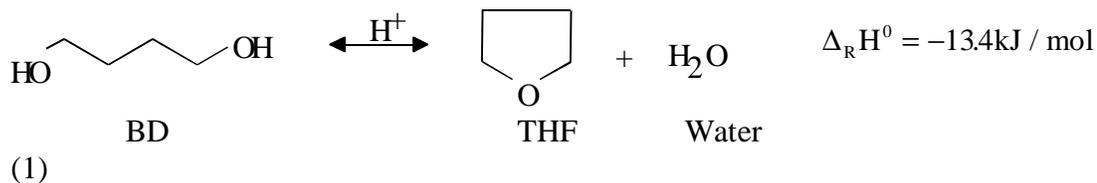
In case of sample C, the conversion rate and the by-products production are comparable to that obtained with Amberlyst 15.

## 6.2 Preparation of a mega-porous carrier material and monolithic column system for use in reaction/chromatographic separation process (TUCL)

In many technical processes conversion is limited by equilibrium, by-product formation and/or catalyst inhibition. Examples are esterification, etherification and cyclization reactions in which water appears as a by-product that needs to be separated. From a technical point of view it is beneficial to integrate the chemical synthesis reaction with a separation step. Membrane and chromatographic reactors are suitable concepts for this purpose. To improve the performance of these reactors a new approach was investigated. Catalytic polymer/carrier composites with outstanding properties were developed and evaluated by experimental and theoretical studies. The synthesis of tetrahydrofuran (THF) was chosen as model reaction to test and evaluate a chromatographic reactor. The reactor design requires kinetic data, which were measured in a batch reactor. Based on the results of the kinetic studies, the requirements for the composite catalyst were determined. A new preparation procedure for ion exchange catalysts inside megaporous carriers was developed, as well as a fiber reinforced casing. Monolithic chromatographic reactors were prepared and tested successfully.

As mentioned above the 1,4-butanediol cyclization was chosen as a model reaction for the investigations of new developed polymer/carrier catalysts in a multifunctional chromatographic reactor. The choice of this model reaction is reasonable because of the great economic importance of the THF synthesis.

The combination of reaction and separation for this synthesis seems to be attractive, because the reaction products form a minimum boiling azeotrope and the reaction product water inhibits the catalyst as described below.



The aim of our investigations was the determination of a rate equation that describes the intrinsic kinetics of the butanediol cyclization on ion exchange resins. An important requirement for rate equations is their validity in the whole concentration range and their independence from the used solvent. Therefore the rate equation should be given in terms of activities.

A further important aspect is the determination of the inhibition effect of water on ion exchange resins. For this reason the butanediol cyclisation is a useful model reaction for studying resin catalyst deactivation by water because the reaction can be regarded as irreversible and highly selective. The main characteristic of this reaction is the inhibition of the catalyst by the side-product water that is expressed in the developed rate equation:

$$r = \frac{k}{1 + K_{\text{H}_2\text{O}} \sqrt{a_{\text{H}_2\text{O}}}} \frac{K_{\text{BD}} a_{\text{BD}}}{1 + K_{\text{BD}} a_{\text{BD}}}$$

In many processes convective mass transport improves the productivity of the reactor. But it is not possible to prepare pure polymer based ion exchange resins in the shape of membranes or chromatographic materials with high mechanical stability as required for this purpose. To achieve high flow rates in chromatographic and membrane processes large pores should be present inside the final catalyst. Therefore the first step for the development of new composite catalysts was the choice of an appropriate carrier material. The carrier should be inert and stable under the process conditions of chromatographic and membrane reactors. Acid polymer particles have to be included inside the carrier. The polymer particles are large compared to the pore diameters in commonly used catalyst supports. Standard carrier materials with nanometer pores will not satisfy the requirements for the new composite catalysts. A solution is to use megaporous carriers with pores in the micrometer range.

To incorporate a polymer inside the carrier material a polymerization process was developed. The requirements for this process are:

- High polymer load (to reach a high concentration of active sites per volume)
- Cross-linked interconnected polymer phase (polymer should not be removed from the carrier under catalytic process conditions)
- Large pores (enhanced mass transfer in the catalyst)
- Small polymer particles (short diffusion path length)

Several polymerization methods were evaluated and finally precipitation polymerization was chosen as the method for the preparation of polymer carrier catalysts for chromatographic and membrane reactors. After the polymerization step, the copolymer particles were activated by sulfonation with chlorosulfonic acid. The result is a polymer/carrier composite with strong acid properties, suitable as a catalytic component in chemical reactions. The activity per volume can be adjusted by changing the monomer concentration during the polymerization step. The polymer load in the carrier material is a parameter to influence active site accessibility.

The distribution of the active sites inside the polymer particles can be adjusted by the parameters of the sulfonation procedure. Complete sulfonation results in a resin with a resin based exchange capacity of about 4.5 meq/g. The load of the carrier materials can be adjusted between 5 – 20 % (by weight).

Modeling of polymer particle growth during precipitation polymerization allowed to calculate cross-linker concentration profiles across single polymer particles. The core of the particles is highly cross-linked whereas the shell is much less cross-linked, resulting in a material with a gradual change of the cross-linker concentration exhibiting high resistance against swelling forces.

During precipitation polymerization inside the pore volume of megaporous carriers, small interconnected spherical polymer particles are formed (**Figure 8**).

Based on the prepared composite catalytic materials a monolithic reactor was developed. A scheme and a photo can be seen in **Figure 9**. The porous glass carrier is a rod of 110 mm length with a diameter of 5.3 mm. This rod is PTFE-lined and encapsulated in a fibre reinforced epoxy resin casing. This allows operating pressures up to 100 bar. Easy connection is achieved by integrated standard HPLC-fittings. The total ion exchange capacity of the described reactor is

about 1 meq<sub>H+</sub>. Larger reactors with higher capacity are also possible (length 200 mm, diameter 12 mm).

This chromatographic reactor was used for the THF-synthesis. Experiments revealed that this reactor allows conversion of 1,4-butanediol to THF and water and simultaneously separates the products. This can be seen in **Figure 10**, where the response to a step function of the reactant is depicted. The breakthrough curves indicate that THF leaves the column first followed by water and non-converted butanediol. In addition to the measured points simulated curves are presented. The simulation calculation bases on an extended tank in series model including the determined kinetic equation and also sorption data for the involved components.

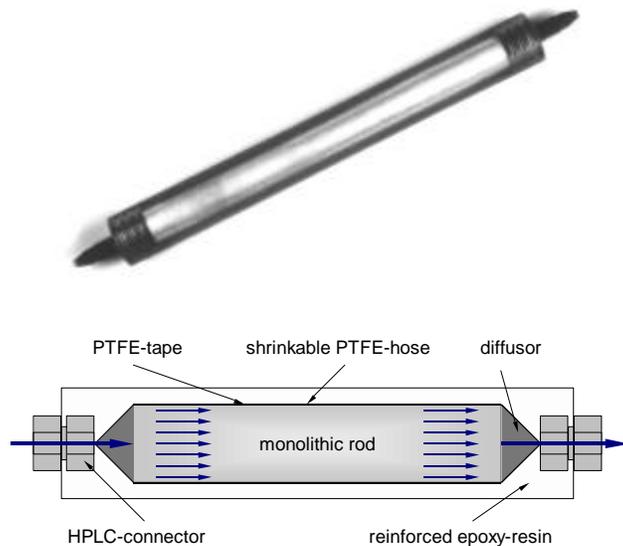
Based on the outstanding properties of the new developed components

- composite material with functional groups
- short diffusion path length inside small polymer particles
- high accessibility of active sites by convective flow
- shape of a monolithic column
- compatible with existing flow-through-systems by standard HPLC-fittings
- low cost fiber reinforced epoxy resin casing

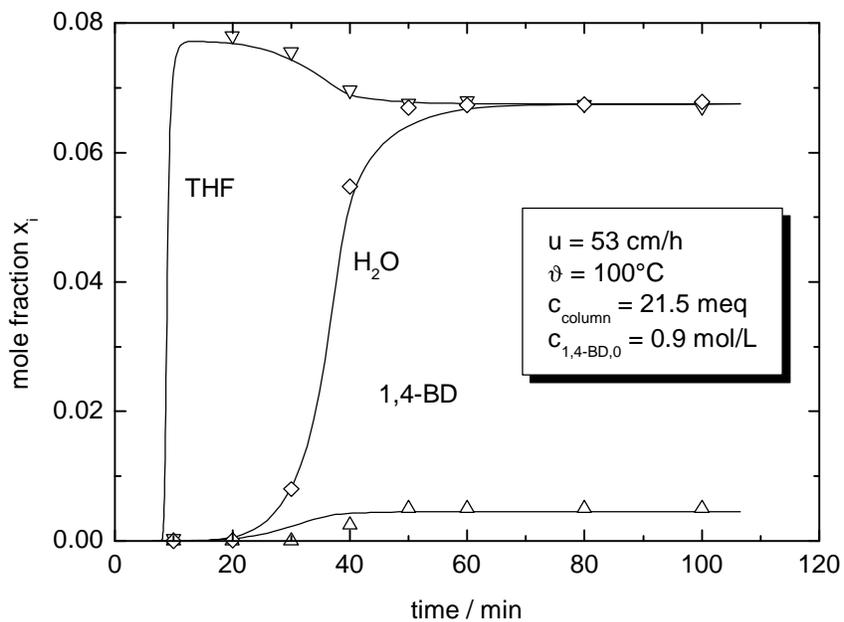
a wide variety of further applications seems promising. Some possibilities are presented in **Figure 11**. As a further example reversed phase chromatography was successfully investigated using a non-sulfonated poly(styrene-co-divinylbenzene) polymer phase. Times for analysis were cut dramatically in comparison to a commercial chromatographic column.



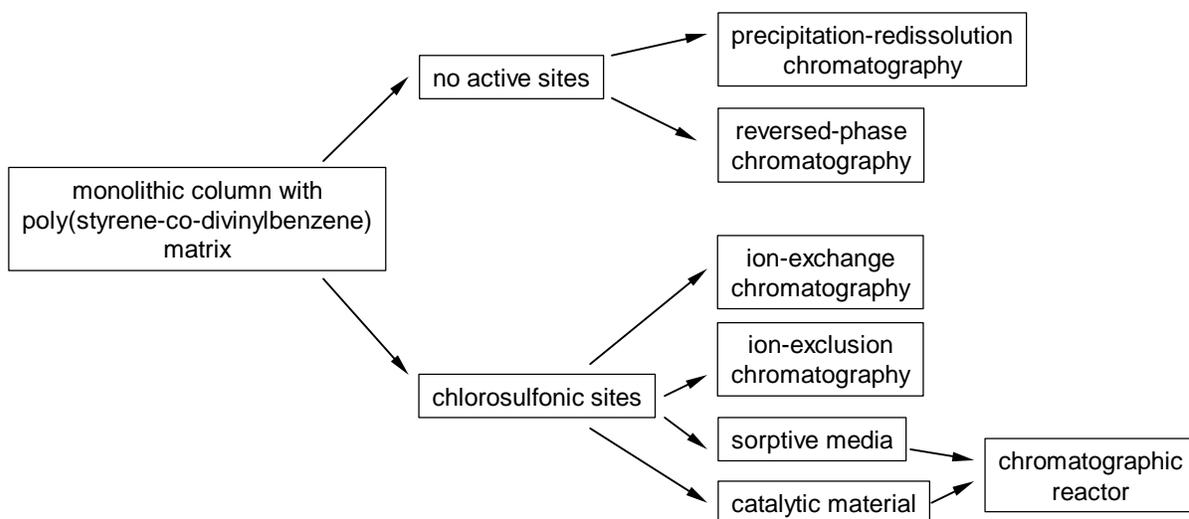
**Figure 8.** Scanning Electron Micrograph of a monolithic rod with an incorporated sulfonated poly(styrene-co-divinylbenzene) phase.



**Figure 9.** Photo and scheme of the developed monolithic chromatographic reactor.



**Figure 10.** Measured and calculated breakthrough curves as a response to a stepwise 1,4-butanediol pulse on a catalytic monolithic column.



**Figure 11.** Potential applications of the developed monolithic components.

### 6.3 Development of a membrane reactor system (VUB)

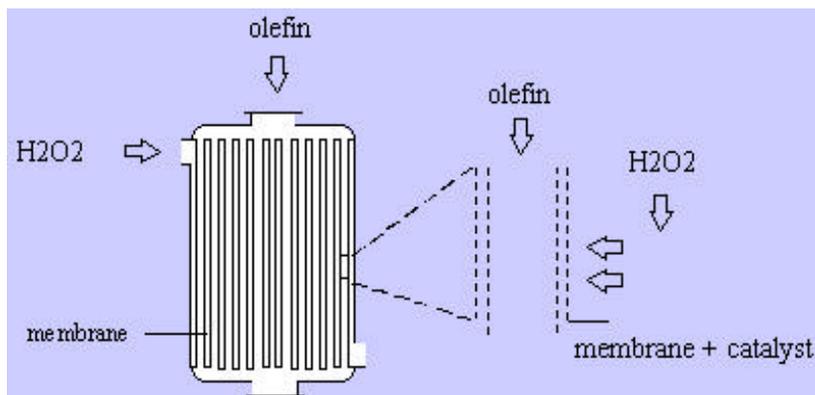
Partial oxidation of hydrocarbons to produce oxidized products (alcohols, ketones, epoxides) is another important family of reactions in the liquid phase. It was first attempted to perform the oxidation of cyclohexane with a ship-in-a-bottle complex immobilized in a membrane: Fe-phthalocyanine in Y zeolite in a PDMS membrane. The catalyst still deactivated by irreversible adsorption of the products and the run length of this system was only a few hours at best. The selectivity of this system was also not as previously reported in literature. Hence it was abandoned.

The selected reaction was then the epoxidation of 1-alkenes with hydrogen peroxide towards 1,2-epoxyalkanes and water catalyzed by Titanium-silicalite-1 (TS-1). TS-1 transforms the rather inert  $H_2O_2$  into a potent reagent for the selective epoxidation of most alkenes. According to literature no deactivation of the catalyst seems to occur. Epoxidation of olefins are among the most important reactions in organic synthesis, because epoxy compounds are widely used as intermediates in the laboratory and for chemical manufacturing. The product value is very high and hence this is a good candidate for process innovation. The epoxidation of terminal olefins is the most important epoxidation but also the most difficult one. An important advantage of TS-1 is that it can be applied to many other olefins and that is more stable than other catalysts such as VAPO-5.

By using membrane reactors it is possible to embed the catalyst into a membrane so heterogeneous catalysis can be applied. Another advantage is that the membrane itself acts as a “solid solvent”. Because epoxidation of olefins involves working with two immiscible phases, use of phase transfer agents or solvents can be avoided when the membrane acts as solvent by bringing the reactants together on the active sites of the membrane. By applying membranes the concentration of the reactants near the active sites of the catalyst can be controlled by tuning their respective sorption. This results in an enhanced substrate/oxidant ratio for reaction and in an increased peroxide efficiency. PDMS (polydimethylsiloxane) membranes are used because they concentrate the non-polar hydrocarbon around the catalyst particles, because it has good

physical properties (heat stability, resistance to peroxide...) and because it is cheap and easy to prepare and work with.

Reaction setups with flat membranes did show promising results but the conversion was believed to be low because of the low surface area of the membranes. So a switch was made towards hollow fiber modules whereby the surface area was doubled compared to flat membranes. The reaction setup for epoxidations with hollow fibers is given in **Figure 12**.



**Figure 12.** Design and experimental set-up of membrane reactor.

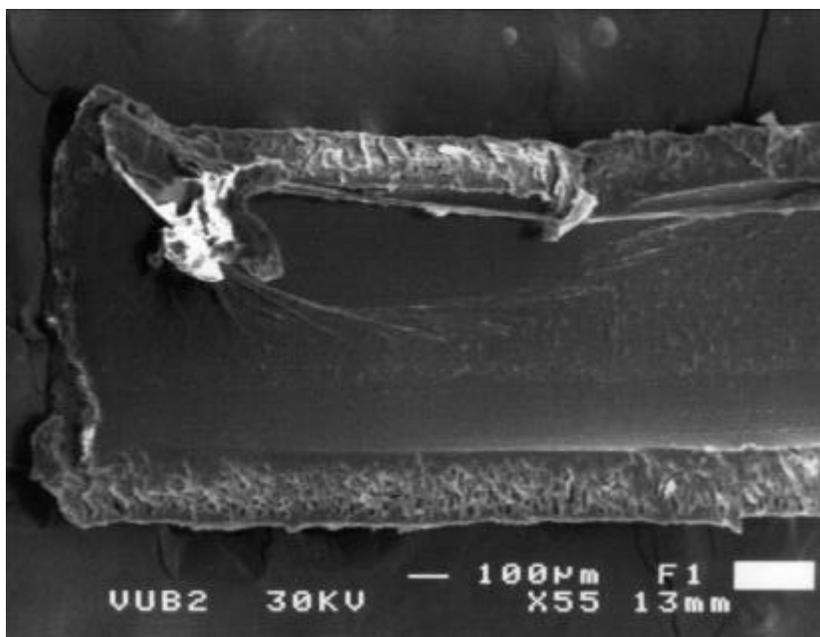
A preliminary version of the hollow fiber membrane reactor was delivered by GKSS (Hamburg, Germany) with membranes containing TS-1 catalyst.

Even when using an HPLC pump to control and handle smaller flow rates, no conversion was achieved.

Calculations were made to estimate the amount of TS-1 catalyst embedded in the PDMS layer of the membranes, giving rather low amounts. However batch experiments with these low amounts resulted in immediate reaction and low but measurable conversion, so the problem was due to other effects, since previous experiments with flat membranes with similar loading also worked. Obviously there was something wrong with the preparation method of the hollow fiber modules. Preparation of flat membranes involves adding the catalyst after the prepolymer is crosslinked. For the preparation of the hollow fiber membranes TS-1 catalyst is added to a partially crosslinked solution that is crosslinked afterwards by adding more crosslinker solution. By using this method side-chains of the PDMS structure most probably could enter the pores of the zeolite catalyst and thus prevent the substrate from entering the active sites of the catalyst. This problem was approached by changing the preparation method for the hollow fibers. The same coating solution was used as for preparing the flat membranes, and the catalyst was added after crosslinking the prepolymer. Only the solvent was changed from chloroform to octane because chloroform dissolves the hollow fiber material. The coating procedure remained the same.

Part of the coating solution was used to prepare a flat membrane used in a small batch test with solvent to check the activity of the membrane. No difference could be observed between flat catalytic membranes prepared with chloroform as solvent and this one.

**Figure 13** shows a tangential section through a hollow fiber. The PEI support and the PDMS layer containing catalyst particles can be seen; the surface of the PDMS layer is damaged by cutting the fiber.



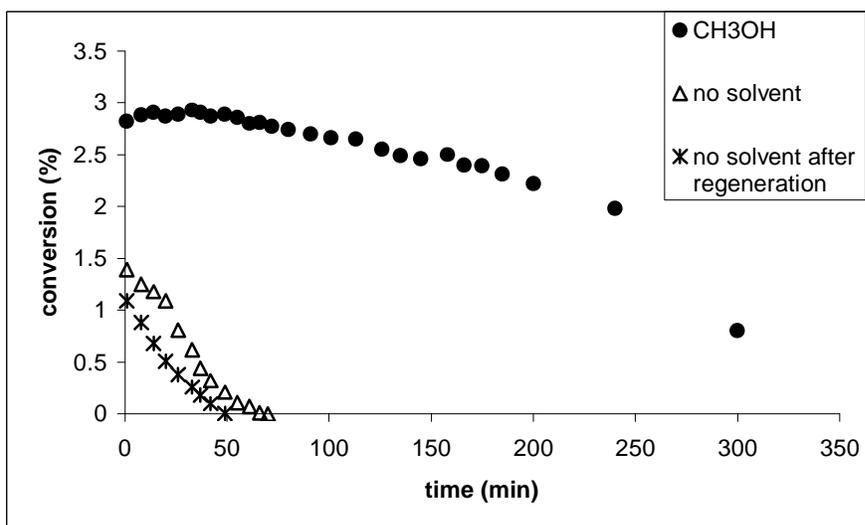
**Figure 13.** Tangential section through hollow fiber showing PEI support and PDMS layer

The amount of catalyst inside the hollow fiber modules was estimated, resulting in about 11 mg TS-1 per module (8 fibers per module, total surface area per module 35cm<sup>2</sup>).

The same reaction setup was used as before. To check whether the catalyst was active or not, a first experiment with use of solvent was performed.

In this first experiment a mixture of 13.6 ml 1-hexene (substrate), 97.68 ml methanol (solvent) and 2.32 ml hydrogen peroxide 35 % (oxidant) was pumped through the inside of the fibers. The flow rate applied was 0.05 ml/min.

A maximum conversion of 2.9 % is achieved but the conversion decreases slowly within some hours. This graph showed good similarity with previous continuous experiments in a packed bed reactor with solvent.



**Figure 14.** Comparison of membrane experiments with and without solvents

A stainless steel column filled with TS-1 was fed a mixture of substrate, solvent and oxidant and at the outlet the conversion is measured. This reaction is characterized by a “jump start” followed by a rather rapid deactivation which is faster in methanol than in acetone. This can be explained by the less strong retention of products (epoxide) in acetone than in methanol.

This experiment proved that the membrane system itself had catalytic activity in presence of solvents.

New experiments without solvent were performed with the same reaction setup as before. Flow rate is 0.01 ml/min, the membrane module is heated at 80°C in an oven, H<sub>2</sub>O<sub>2</sub> is circulated on the outside of the membrane and the substrate 1-hexene is pumped through the fibers. Results are given in **Figure 14**. It shows the conversion of 1-hexene towards the corresponding epoxide in reaction experiments with and without solvent. A maximum conversion of 1.4 % is reported in absence of solvent but as shown, the conversion decreases extremely fast (within hardly one hour) to zero. An attempt was made to regenerate the membrane module by rinsing the system with acetone at 80°C and drying overnight. A second experiment with this regenerated module shows a lower conversion and a faster deactivation, probably due to residue of product or heavier side products. However no side products were found in these reactions.

When the numerical values of membrane experiments with and without solvents are compared (**Figure 14**) it is clear that the use of solvents results in higher conversion and slower deactivation.

This proves that solvents are needed in these reactions for two purposes. Solvents do help to facilitate the transport of the substrate and the oxidant towards the active sites of the catalyst resulting in a higher conversion. Clearly, solvents are also needed to help the products on their way out of the pores of the catalyst and thus slowing down the deactivation process that results from pore blocking by excess product formation inside the catalyst. The newly prepared hollow fiber membranes also prove our theory that previous membrane modules did not work because of side chains of the PDMS precursor entering the pores of the catalyst. Unfortunately however, just as in the FePcY system described before, strong adsorption of products also deactivates this catalyst.

The active sites of the catalyst are known to be the Ti-sites. Activity of the catalyst can be expressed as the turnover number (TON), this is the amount of epoxide molecules formed per active site, or as the turnover frequency (TOF), the amount of epoxide molecules formed per active site and per second.

The results are given in the following table:

Reactor type	Solvent	Approx TON for 1 Ti-site	Approx TOF for 1 Ti-site
Hollow fiber	-	40	0.021
Hollow fiber	methanol	240	0.126
Batch stirred	methanol	370	0.094
Continuous	methanol	-	0.060

TON = turnover number

TOF = turnover frequency, s<sup>-1</sup>

This calculation proves that a reasonable TON can be achieved for solvent-free epoxidations, compared to reactions with solvent. It also proves that quite a large amount of epoxide can be accumulated in the catalyst thus blocking the active sites and preventing the hydrogen peroxide and the 1-hexene from entering the pores of the catalyst (the epoxide adsorbs more strongly than the polar peroxide). This happens in all cases, but clearly less in batch with methanol solvent and most in solvent free operation in the membrane system. The presence of methanol solvent reduces the concentration of epoxide and facilitates H<sub>2</sub>O<sub>2</sub> entering, hence giving higher rates and slower deactivation.

Summarizing, one can state that we have been able to obtain reasonable TON for conversion of 1-hexene on a TS-1 catalyst embedded in PDMS in a hollow fiber membrane reactor without solvent. This is a major achievement, but unfortunately this system has itself a poor performance in normal conditions and always deactivates by adsorption of the products. This deactivation will always be stronger in the membrane and hence this more expensive system can never be economical.

## 7. Results and conclusions

Esterification reactions (alcohol+acid=ester+water) are traditionally carried out in the presence of a strong acid as homogeneous catalyst, require large energy consumption to separate reactants and products and generate vast amounts of waste products (environmental problems). For the POLIMI/SISAS-groups, the main objective of this project was the identification of novel materials as catalyst/sorbent for esterification reactions in heterogeneous catalysis. Four esterification reactions (Buthylacetate, Triacetin, Diethylphthalate (DEP), Doctylphthalate (DOP)) have been chosen both for their industrial relevance and for the difficulty that arises if we want to obtain total conversion and to minimize the formation of by-products. Cationic exchange resins (macroreticular Sty/DVB copolymers functionalised with sulfonic groups) seem to satisfy the necessary requirements (catalytic properties and selective adsorption).

After first experiments, two different strategies for the considered reactions were defined. In particular, for the reaction to buthylacetate and triacetin, it was decided to continue the experimentation in a chromatographic reactor with Amberlyst 15, while for the reaction to DEP and DOP we investigated the possibility of improving catalyst performance through an appropriate non uniform distribution of the sulfonic groups.

For the first two reactions (triacetin and buthylacetate) several experiments on lab and pilot scale chromatographic reactor have been realized. Especially for the reaction to triacetin, it is essential to completely dry the bed to improve the separation between diacetin/triacetin. In fact very small amounts of the initial water compromise the chromatographic separation.

The behavior of the chromatographic reactor was described by a non-equilibrium dispersive mathematical model and the profiles obtained confirm the experimental results. Then a new mathematical model for SMBR (Simulated Moving Bed Reactor) unit for this reaction was developed and the influence of several parameters on the reactor performances was investigated. The productivity of the SMBR unit was calculated to be equal to about 1200 Kg triacetin/Kg resin/year, while the productivity of the lab and pilot scale chromatographic reactor was about 450-500 Kg triacetin/kg resin/year.

A careful economic evaluation has been carried out to compare the traditionally industrial process, a continuous chromatographic reactor and a SMBR unit. The continuous chromatographic reactor (compared to Sisas process) brings savings of about 4% (30% excluding raw materials) and the SMBR unit brings savings to about 8% (56% excluding raw materials).

For the other two reactions (DEP and DOP) the POLIMI/SISAS group studied new modified resins. These modified resins seem to increase the performance of the cationic commercial resins both for the reaction rate and the formation of by-products. For these reasons they can be used as heterogeneous catalyst in connection with a separation process (distillation, chromatography or others).

The TUCL-group has developed the preparation and characterization of polymer/carrier composite components for catalytic applications. Monolithic rods for chromatography with simultaneous reaction as well as membrane shaped components were prepared by a precipitation polymerization process and have been investigated. The distribution of the cross-linker concentration across the particle radius has been calculated based on copolymerization parameters and has been discussed. The active sites are sulfonic acid groups. The distribution of the active sites was measured by electron probe microanalysis (EPMA). For the cyclization reaction of 1,4-butanediol to tetrahydrofuran and water the application of monolithic rods as a chemical reactor was demonstrated.

By their work, the TUCL group succeeded for the first time to express the intrinsic kinetics of the BD cyclisation on ion exchange resins in one rate equation that is valid in aqueous and in non aqueous phase, covering the whole concentration range. To achieve this, it was necessary to express the non-idealities of the liquid phase in terms of activities. Moreover the presented rate expression is independent from the solvents used. The influence of inhibiting water was quantitatively described. An important aspect is, that the inhibition effects cannot be described by a Langmuir-Hinshelwood mechanism, but by the presented inhibition factor. This procedure could be a guideline to other comparable liquid phase reactions. Based on a precipitation polymerization process inside the pore volume of megaporous carrier materials polymer/carrier components are available. The stability against swelling forces of the polymer particles is high because the precipitation polymerization leads to particles with a gradual change of the crosslinker concentration across the particle diameter. This is supported by model calculations. The accessibility of the active sites is high due to the small particle size of the polymer phase. The pressure drop is lower than for commercial resins due to large pores between the interconnected polymer particles. This material in the shape of the newly developed monolithic column has a high commercial potential for a lot of applications. Provided by the opportunity of tailor-made polymeric resins, the enhanced mass transfer, short and uniform diffusion path length inside the polymer particles and a low pressure drop this leads to monolithic columns for processes where these criteria are essential for a high and selective conversion, e.g. in reaction systems, in separation techniques or in a combination of both.

The new monolithic catalytic column was used for the conversion of 1,4-butanediol to tetrahydrofuran and water. These investigations reveal, that the monolithic column can be used as a chemical reactor and simultaneously as a chromatographic device. Additional investigations at POLIMI for their esterification reaction confirm these results. It was even shown that our monolithic column is superior to conventional ion exchange resins. The chromatographic

column with simultaneous chemical reaction can be described by an extended tank-in-series-model including the kinetic data of the butanediol cyclization. This offers the possibility to calculate chromatographic reactors for many reactions, if kinetic data and sorption data are available.

The properties of a prepared and tested prototype are listed in the following:

Properties:

Length:	180 mm
Diameter:	12 mm
Polymer particle size:	1-2 $\mu\text{m}$
Weight of prepared porous carrier:	20.88 g
Total exchange capacity:	21.5 meq
Back pressure at $F = 1.0 \text{ mL/min}$ (1,4-dioxane):	20 bar

Preparation:

14.0 % wt. PS-DVB-polymer loading  
7.5 % wt. DVB cross-linker  
cleaned with THF for 5 hours at  $F = 1.0 \text{ mL/min}$  before first usage

The work done in the VUB group on partial oxidations has thrown a completely new light on the possibilities of heterogeneous catalysis in this field. Clearly much better catalysts are needed before more advanced reactor concepts such as designed here can be economically used in industrial practice. However, it was shown that partial oxidation of hydrocarbons can be performed in solvent free continuous operation in hollow fiber catalytic membranes, which could be used in industrial scale reactors, but only with low conversion. Reactors and membranes can be designed to withstand the harsh conditions of the oxidation. Catalyst loadings are low on a volume basis. Separation costs would not be lower than in conventional stirred tank reactors.

The reasons for the conversion limitation have been identified and are intrinsic to this type of reactions: products accumulate and deactivate the catalyst. This is worse in the membrane based catalyst due to diffusion limitations. Productivity is low in comparison to batch stirred tank reactors directly using the catalyst in a solvent. Increasing the catalyst loading would probably not help due to diffusion limitations in the catalyst layer.

Although other systems may exist which have less intrinsic limitations, we have not found them in the family of liquid phase oxidations which was a good candidate for improvement by membrane reactor operation, based on all literature and our own preliminary experimental results.

Clearly, although the system may be used to produce chemicals where catalyst immobilisation and recovery are important, the intrinsic problems associated to solvent free operation in membranes will always lead to inferior performance versus batch operation with solvents.

Given the fact that performance is less good than in conventional systems an estimate of improvement cannot be given. The operation with membranes is similar to conventional operations, requires similar amounts of energy and has similar environmental impact. The use of

TS-1/H<sub>2</sub>O<sub>2</sub> versus other oxidation routes yields however environmental benefits: no side products, no toxic waste formed.

All tasks in the project have been accomplished and yield a coherent picture of the potential of membrane reactors in oxidation reactions. This was the primary goal of the part on membrane reactors. Our understanding has now considerably increased and has pointed out many misconceptions and errors in literature and claims by other groups. We consider it a major feat to have conceived and operated a hollow fiber catalytic membrane reactor for partial oxidation in solvent free conditions, which had never been reported before. Our failure to improve over existing technology is entirely due to factors intrinsic to the available catalysts for such reactions. Our results clearly point out what is needed in liquid phase catalytic membrane systems to succeed. Whether systems exist that satisfy the requirements, and hence would yield the corresponding energy savings, needs to be seen in the future.

## **8. Exploitation plans and anticipated benefits**

### ***8.1 Exploitation plans POLIMI/SISAS***

A fixed bed reactor in the transient pulse mode has been realized both at the laboratory and pilot scale. This constitutes the basic unit for a SMBR unit operated continuously. This operation has been investigated by simulation models validated with the fixed bed units.

The advantage of this technology is to couple reaction with a low temperature separation. This involves significant energy savings; in fact considering the high energy consumption of the conventional production process, even modest performance of the novel reactor/separation unit should yield a significant reduction of energy consumption (a factor of 2 to 5 reduction if the expected performance from present knowledge can be obtained).

The strongly positive economic impact from the drastically reduced energy consumption is augmented by additional benefit such as: better use of raw materials and smaller compact equipment, environmental benefits (reduction of side products formation, waste streams and the possibility to avoid strong acid and toxic salt solutions). No unusual social or employment impacts are expected that are specific to these process.

The realization of 6/8 beds and their dynamic operation required by the SMBR process need the collaboration of engineering companies which were not included in the project.

Potential other applications are reactions with two products which can be separated by adsorption. In particular we refer to acid-catalyzed processes which both have equilibrium reaction and quite different polarity of the reaction products. These include several reaction families: esterifications, transesterifications, etherifications, acetylations, dehydration

The technology can also be successful when reactive distillation is not viable. This is the case for thermo-sensitive products (fine chemicals, food, pharmaceuticals) or when the required reaction temperature has to be lower than the distillation temperature due to selectivity or equilibrium limitations.

Different processes of acid functionalization of styrene-DVB resins have been widely investigated in order to obtain products with a better catalytic activity and lower by-products formation. At present it is necessary to use lab-chromatographic reactors to check the

applicability of these resins for suitable esterification reactions which show by-products and low reaction rate.

Polimi has developed the know-how to design and realize an optimized resin (in term of sulfonation degree and intraparticle profile) for specific reactions.

Partners are sought in the direction of chemical producers willing to change their current technology based on homogeneous sulphuric acid or partners invested in the marketing of tailor mode catalytic resins.

Potential application of these resins is the change of the current technology based on the homogeneous catalysis (with sulfuric acid or other soluble acids).

It is convenient to get tailor mode resins in the case where the desired reaction exhibits selectivity problems. Another feature of these resins is the possibility of being easily regenerated after water adsorption.

### ***8.2 Exploitation plans TUCL***

The Institute for chemical process engineering of the TUCL-group will contribute with the know-how of the preparation and operation of the monolithic columns. Introducing the described technology on the market offers the opportunity of a new product with advantages not reached by commercially available products of the state of art so far. The exploitation potential of the monolithic column can be concluded as follows:

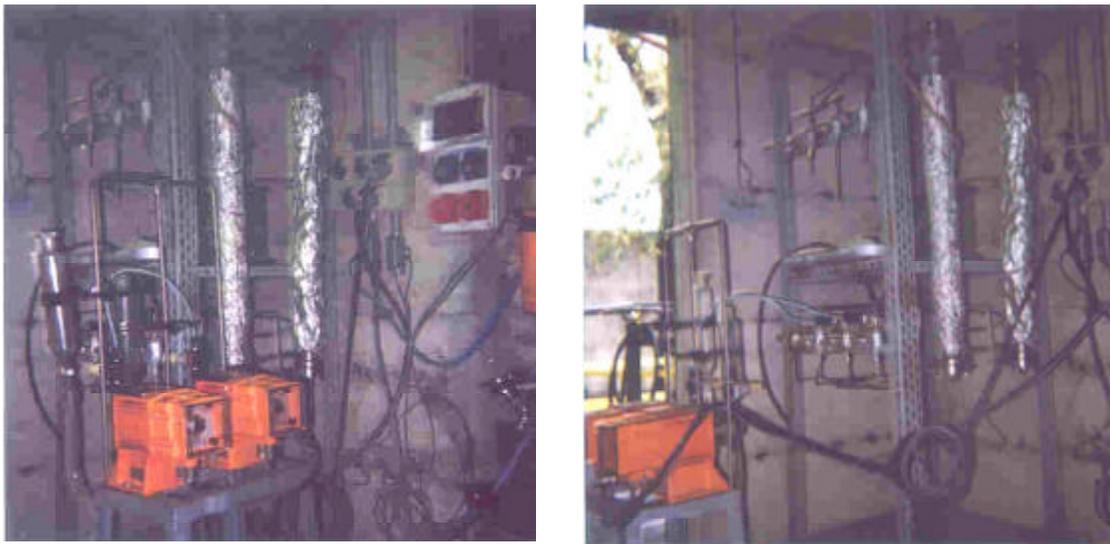
- application in high pressure/performance liquid chromatography
- application in the analytical and chemical industry
- low pressure drop, high throughput, short analysing times
- short diffusion path length because of small polymer particles and enhanced mass transfer
- integration of reaction and separation possible
- so far no potential barriers are known

Basic information of the new product was made accessible to a potential manufacturer who is the manufacturer of the raw material (carrier material). Interest was produced, but no decisions were made so far. Further partners for the commercial production and marketing are actively looked for.

### ***8.3. Exploitation plans VUB / DUPONT***

As unfortunately the system developed does not have the required performance, no direct exploitation is possible. We will continue the work on analysing this solution and look out for more favourable systems, even out of the oxidation area. There might be applications for the type of membrane developed in other fields. The results will be written up in papers and published as was already done with intermediate results. This might give contacts for further work.

## 9. Photographs



**Continuous pilot scale chromatographic reactor**



**Monolithic column for combined reaction/chromatographic separation**



**Catalytic membrane module for epoxidation of alfa alkenes with hydrogen peroxide**