PROCEEDINGS OF SECOND INTERNATIONAL CONFERENCE ON PERVAPORATION PROCESSES IN THE CHEMICAL INDUSTRY

Edited by
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PREFACE

This volume contains the papers presented at the Second International Conference on Pervaporation Processes in the Chemical Industry, held in March of 1987, in San Antonio, Texas. This event, as well as the first conference, was co-sponsored by Bakish Materials Corporation of Englewood, New Jersey, U.S.A., and GFT of Homburg/SAAR, G.F.R. R. Rautenbach and R. Bakish co-chaired the event.

The papers here are arranged essentially in the sequence presented at the conference. Except for the missing paper of H. Lonsdale for which only an extended abstract was available, this is the complete conference record. It is the hope of the organizers that this volume will contribute in a small way to the dissemination of material relevant to this young, but rapidly expanding technology. It is a technology which has made considerable strides in the last few years, and which is on the verge of making major contributions to the chemical industry.

With the publication of these proceedings the work on the second conference is complete. Work has began for the third conference and the sponsors look forward to greet you there. This event, scheduled for Nancy, France, September 19-21, 1988, will honor Professor Neel, one of the leading contributors to this technology.

R. Bakish,
Englewood, N.J.
June 29, 1987.

INTRODUCTORY REMARKS

Ladies and Gentlemen,

On behalf of Robert Rautenbach, the Conference Co-Chairman, and myself I wish to extend a most cordial invitation to you here in San Antonio on the occasion of the Second International Conference on Pervaporation Processes in the Chemical Industry. On this second gathering of the leaders in pervaporation technology the U.S. contingent of participants is joined by one from England, two from France, four from Japan, three from the Netherlands, one from Sweden and seven from West Germany.

It is my sincere hope that you, the participants will find the program content and all the arrangements which we have made to your satisfaction. Let us also hope that as this technology expands and begin to make truly consequential contributions to the chemical industry, we will reconvene this group, so that we may present to it the fruits of this progress. My introductory remarks will not be complete if I did not give credit to Gunter Tusel, the prime mover of this event.

Before I move to my second assignment of this morning, the kick off of talks for the morning session, I have two reminders. First, those of you who have not turned in their manuscripts, please make sure I have them before we part. Second, we are in the lovely city of San Antonio, do not leave it before you have seen and enjoyed its beauty of today and its landmarks of yesteryear.

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STATE OF THE ART OF PERVAPORATION

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Separation of liquid mixtures by permeation through polymer membranes is a process known at least since the beginning of our century. In 1917 Kober (1) described an observation that "a liquid in a collodian bag, which was suspended in the air, evaporated, although the bag was tightly closed". Kober called this phenomenon "pervaporation" and reported, too, that some less volatile components of the mixture permeated faster through the collodian wall than more volatile ones and concluded that this effect could be used for the separation of liquid mixtures, such as azeotropes. Around 1960 Binning and his co-workers (2) tried hard to introduce pervaporation as a commercial separation process in the chemical and petrochemical industry. Although they investigated and developed several membranes for a variety of separation problems, pervaporation did not find its breakthrough, but was rather forgotten for the next decade. Ten years later pervaporation slowly arose again the interest of scientists and engineers and names like Rautenbach (3), Neel (4), Cabasso (5) - now quite familiar to those working in this field - appeared in publications on pervaporation membranes and processes. In 1982, eventually, the first commercial pervaporation plant started its operation in a small alcohol distillery in Brazil (6).

Up to now only systems for dewatering of organic-aqueous mixtures have reached industry. These are systems for the dehydration of ethanol, isopropanol and other simple alcohols up to 12000 l/day. Worldwide a large number of diverse membranes have been tested for dehydration purposes, yet only a small number of these can meet the requirements necessary for industrial applications, i.e. high selectivity combined with high flux, as well as chemical and mechanical stability at high temperatures. Furthermore, these membranes must also be economical to produce. The membranes meeting these requirements are the ion-exchange membranes produced by DuPont and Asahi Glass, partially the CTA films produced by Kalle, the GFT composite membrane and last but not least some specially treated PE films.

These membranes show selectivities up to several thousands, which are sufficient, considering most of the known dehydration problems. They also have fluxes, which are high enough for economical process applications.

Today dehydration by pervaporation can replace azeotropic distillation at lower investment costs, lower operation costs and with drastically reduced environmental problems. Over and above the benefits of lower costs and reduced environmental problems, many of those active in the field of pervaporation processes, regard their simplicity as their principal advantage. The second area for the use of pervaporation is the removal of organics from aqueous streams. This process is referred to in the literature as "dealcoholization process". It is mainly used in bio-technology, as for example in fermentation processes, where volatile products such as ethanol, butanol and/or acetone must be continuously removed from the reactor, thus preventing inhibition of cell cultures. The so-called dealcoholization membrane has been successfully tested also for water purification, where volatile substances such as chlorinated hydrocarbons and high boiling compounds, like phenols, have been removed below the values specified in standards and codes.

Organic/organic separations have been tested on laboratory scale. Mixtures like hexane/benzene or xylene isomers have been separated but membranes for these purposes are not yet available on industrial scale.

Literature reports on removal of organic vapors from air streams by pervaporation processes. Yet the selectivities of the membranes used are by far too low for an effective cleaning of the air. Pervaporation can - in very special cases - be used to concentrate solutions where the solvent can either be water or an organic solvent and the dissolved materials can be salts, urea or valuable organic substances.

In order to give you a feel for what is happening here, I will take you on a quick trip round the world. I will begin in Japan and end up looking in our own backyard.

JAPAN

In membrane R&D, pervaporation occupies here one of the most important areas. To the best of my knowledge the following institutions (among others) are working in this field:

1) Tokyo University

Its group led by Prof. Kimura is trying to find industrial applications for dealcoholization and dehydration membranes. Beside work on ethanol dehydration, efforts are made to improve for example the ester reaction efficiency by continuously removing water out of the process or to improve the efficiency of non-water-reacting enzymatic processes by on-line dewatering.

Another field of investigation is the search for processes where molecular sieves can be replaced by pervaporation. The university itself has no membrane activities as such and it acquires membranes from other sources for testing.

2) University of Kyoto

Here Dr. Tanigaki's group is concentrating on alcohol separation.

3) Yokohama University

Its group led by Prof. Oya is involved in an R&D program to prepare for the next generation membranes. They are working on the basis of pervaporation processes, concentrating on dealcoholization. The main target of their initial activities are bio-reactors.

4) Meiji University

Prof. Nakagawa and his group have been working at membrane development for some time. They are looking mainly into the interaction of the polymer solvent and the permeate. Their membrane efforts are directed at methyl-l-glutamate, PVC and other related materials. In addition to membrane R&D, they are looking into the possibilities of industrialization of pervaporation in solvent recovery from waste waters and for medical purposes. Here the high selectivity of some membranes for specific toxic components at low pressure appears to be a simple way for blood cleaning.

5) Industrial Products Research Institute of MITI

Dr. Yamada is looking into the possibilities of utilization of pervaporation processes.

6) Fiber Research Institute of MITI

Dr. Mizoguchi and his team are working on the development of the next generation membranes, utilizing plasma polymerization and grafting. They have already produced some grafted cellulose membranes. Like other investigations in Japan, also membrane reserach is closely related to process development and both are proceeding in parallel.

7) Hiroshima University

Prof. Asaeda and his group are studying the economic possibilities of dehydration of ethanol and other solvents by pervaporation.

8) Daikin

Beside general activities in applications of pervaporation systems, one of the main areas of R&D here is the quest to develop a fluorine group based ion-exchange membranes modified with hydroxyl, sulphonic acid or other groups.

9) Yamagata University

Prof. Suzuki and his associates have been working on the basic understanding of the interaction of membrane polymers and permeate. They also make efforts to develop different pervaporation membranes using nitro-cellulose, polyacrylic acid/methyl compounds, cellulose acetate and poly- -methyl-glutamate. In parallel, considerations are also given to module configuration and process requirements.

10) Kogakuin University

Prof. Hirata and his team are trying to optimize ethanol dehydration by pervaporation and comparing it with other processes. They - like some other Japanese institutes - use membrane acquired from sources outside the university for their studies.

11) Research Association for Basic Polymer Technology

In a recent gathering here, Dr. T. Doi reported on MITI's R&D program for the next generation of membranes. He emphasized the remarkably good selectivities of newly developed membranes for the separation of EtOH/H_2O mixtures and acetic acid/water mixtures.

In addition to these academic activities, development of membranes and processes is in progress in most of the known companies in the field of membranes, as for example Toray , Mitsubishi Heavy Industries, Nippon Oil & Fat, Kurita, Nitto Denki, Daicel, Kuraray, Toyobo, Asahi Glass, Mitsui Engineering & Shipbuilding and others.

Out of all these, Mitsui Engineering & Shipbuilding is the only Japanese company with industrial pervaporation projects completed or in the process of completion.

For the time being it so appears that pervaporation in Europe is more advanced - both on industrial and university level - than either in Japan or North America. Whilst it is suspected that work at a number of countries in Eastern Europe is in progress, however, nothing specific can be said about the activities there.

In Poland work related to evaporation appears to be in progress at several universities. Ten years ago, J. Stellmaczek published some very interesting results on IPA and EtOH dehydration. Most of the information obtainable is related to process development and application consideration. Stellmaczek used cellulose acetate membranes for her tests. Little is known about R&D work on high selectivity/high flux membranes.

In Hungary I. Nagy has been working on pervaporation for many years. For his tests he used mainly commercially available films such as cellophane, PE sheets.

It is known that in Eastern Germany work on membrane processes as well as membrane development is conducted at several places. Some 20 years ago W.R.A. Vauck and H.A. Müller predicted in their book "Grundlagen Chemischer Verfahrenstechnik" that azeotropic distillation can economically be replaced by pervaporation. Basic work on pervaporation appears to be in progress in Yugoslavia, Rumania and Bulgaria. I failed to locate information on pervaporation work in the Soviet Union, but one will have to assume that such work is likely to be performed.

In Western Europe pervaporation work is done almost in all countries:

GERMANY

1) GKSS

For the last eight years a strong and relatively large group headed by Dr. C. Böddeker has been working on development of membranes, modules and processes. Some remarkable membranes have been developed as well as new module configuration (cushion module). Process work is done on dehydration of EtOH as well as on other solvents. Work on removal of solvents from waste water and on pervaporation-based bioreactors is also in progress.

2) University of Hannover

Professor Schluegerl has started to evaluate the use of pervaporation membranes in biotechnology and especially in bioreactors.

3) University of Cologne

Dr. Ellinghorst and his team have devoted their efforts to developing pore-free pervaporation membranes. They are utilizing either plasma polymerization or irradiation to modify the membranes. Their membranes and the membrane manufacturing procedures are so well advanced that they are likely to be on the market in less than 3 years. Ellinghorst's family of membranes are showing excellent selectivities combined with very good fluxes. The membranes can be used for dehydration of various solvents. Some of these membranes also offer excellent properties for solvent/solvent separation as for example hexane from benzene or vice versa.

4) University of Heidelberg

Professor Lichtenthaler and his co-workers are working on the basic understanding of pervaporation and are trying to develop theoretical models which allow not only the description of the transport phenomena in the membrane but also to predict separation behaviour for various feed streams in contact with the membrane polymer. Professor Lichtenthaler is partly continuing the work which professor Fischbeck began at Heidelberg some 30 years ago.

5) Technical University of Aachen

For the last 10 years Professor Rautenbach and his team have been working on all aspects of pervaporation except membrane development. Beside modelling of pervaporation membranes and modules, the main emphasis has been put on applications and engineering aspects. I believe that in this area Rautenbach's institute is one of the world's leading institutes on process technology.

Several other universities and institutes are entering the pervaporation field. Worthy of mentioning are the University of Oldenburg, Munich and the Max Planck Institute under Professor Pusch in Frankfurt.

In the industrial sector there are two companies. The first company in this sector is GFT and the second is Lurgi, which as a leading engineering company in the chemical industry is trying to introduce pervaporation to this industry. It has already built a 12000 l/day ethanol plant equipped with GFT membranes, which it has had in the field for almost 2 years. Lurgi's pervaporation process evaluation test facilities are probably the best equipped in the world.

As for GFT, it entered the pervaporation market several years ago with its dehydration membranes. It is now starting to produce pervaporation membranes for solvent removal for waste water streams and bioreactors. The membranes are sold in general in plate-and-frame configuration modules. About 20 plants of diverse types have been engineered and are either in operation or under construction. The plants are mainly for applications such as dehydrating of EtOH, IPA, MEOH or dehydrating of multi-component mixtures such as ethanol/toluene and/or MEOH with other organic solvents.

THE NETHERLANDS

At twente University and under the direction of Professor Smolders, membrane, module and process R&D is in progress. In almost a decade of work, Smolder's group has developed diverse dehydration and solvent removal membranes. Some work in hollow fiber module development has also been done here.

On the industrial side SETEC is manufacturing pervaporation plants. It utilizes either in-house engineering designs or others acquired from outside. SETEC is also a producer of plate-and-frame pervaporation modules. At TNO, by contrast, the emphasis is on pervaporation process R&D.

AUSTRIA

Vogelbusch, which is one of the leading biotechnology companies in Austria, is active and, I believe, successfully marketing pervaporation systems for EtOH dehydration. They are also active in bio-reactor and dealcoholization membrane and module R&D. This work is done in partial co-operation with the Technical University of Vienna.

FRANCE

At the University of Nancy, in France, Prof. Neel's laboratory has been active in the field for many years. Also activities in the University of Toulouse have been in progress under the guidance of Dr. Aptel, one of Neel's students.

THE UNITED STATES AND CANADA

And now to come to our backyard, the United States and Canada. Let us first look at the matter from an academic point of view.

At the University of Syracuse a group, under the leadership of Professors Stern and Cabasso, has been working for a number of years on several aspects of pervaporation.

Rensselaer Polytechnic Institute (Professor Belfort) started activities here in 1986.

At the University of Ottawa (Canada) Dr. Sourirajan has started a membrane research institute and pervaporation will be one of its missions.

At the University of Maine, Professor Thompson has been doing work on pervaporation for the last few years. Similarly Professor Gooding is developing pervaporation activities at Clemson University.

By contrast, Professor Huang at the University of Waterloo has been active in the field for several years and is also conducting - among others - pervaporation membrane research.

Going to industry one should mention Monsanto, Dow, Membrane Technology and Research, Inc., DuPont and Bend Research as companies which are likewise involved in the field and except for Membrane Technology and Dow, which have published some work here, there is no information on them.

According to Dr. Lonsdale no pervaporation work is in progress at Bend Research, but one never knows and things might change.

Thank you.

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AN APPROACH TO MEMBRANE SEPARATIONS BY PERVAPORATION

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ABSTRACT

The pervaporation process is regarded as a combination of reverse osmosis (RO) separation, followed by evaporation and gas/vapor transport through the capillary pores on the surface layer of a RO-membrane. It has already been established that RO separation and fluid permeation through the capillary pores on the membrane surface are adequately described by the preferential sorption-capillary flow (PSCF) mechanism and its quantitative expression given by the surface force-pore flow (SFPF) model. According to this approach to membrane separation, the effective size of the component molecules in the feed fluid, membrane material-component molecule interaction forces and the pore size and its distribution on the membrane surface together determine the separation of fluid components and the product permeation rate through the membrane. This approach to membrane separation is assumed valid for the pervaporation process also. Accordingly, a transport model for the pervaporation process is developed on the basis of the liquid flow in the pore as the rate determining step followed by evaporation at the pore outlet. The test of the above approach is currently being undertaken.

The preferential sorption-capillary flow (PSCF) mechanism (1), and the surface force-pore flow (SFPF) model (2,3) as a quantitative expression of PSCF mechanism, have proved to be an effective means for predicting the solute separation and the product rate data of reverse osmosis and ultrafiltration experiments on the basis of the effective size of solute molecules, the interaction force working in the solute-solvent-membrane material system and the pore size distribution on the membrane surface (1). It has been found later that the same approach is applicable for the prediction of the separation factor and the product permeation rate for the membrane