



Separation of isomeric xylenes by permeation through modified plastic films
by John George Sikonia

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

The modification of polymer membranes by including various compounds in these films was investigated in order to develop a liquid permeation system which would be selective for one xylene isomer.

These studies were completed using cylindrically-shaped stainless steel permeation cells with an exposed membrane diameter of 7.3 cm and a feed liquid capacity of 400 ml. The upstream pressure was atmospheric while the pressure on the product side of the membrane was maintained at less than 1mm Hg. Feed temperatures ranged from 23 to 130° C.

The liquid permeation membranes were constructed by first combining a solution containing a solvent and either polyvinyl chloride or polyvinylidene fluoride with the additive material, then spreading this casting solution on a glass plate, and finally heating the plate in an oven to evaporate the solvent. The additive materials included complexes of the Werner type, xylene clathrates of these complexes, and various other materials including extractive distillation agents and a plasticizer.

Using membranes of vinylidene fluoride which when unmodified were found very impermeable to the xylenes rather than those of polyvinyl chloride which were found naturally selective, it was concluded that a selectivity for the para-xylene isomer resulted only from the addition of certain materials to the otherwise impermeable films.

The two basic additives investigated were $\text{Ni}(\text{SCN})_2(4\text{-methylpyridine})_4$.p -xylene and $\text{Ni}(\text{SCN})_2(\text{a-methylbenzylamine})_4$. o-xylene. It was found that both of these clathrates made the vinylidene fluoride film selective, but the second compound produced the larger para-xylene separations. The best para-xylene product-feed composition differences obtained were in the range of 8 percent beginning with a feed containing an equimolar mixture of the three xylene isomers. The total product flow rates obtained were about 1ml/(hr ft²) at the best separations, but ranged up to over 100 ml/(hr ft²).

Studies involving all the components of the clathrates, other types of additives, different feed compositions, and varied treatment conditions revealed that although the selectivity-producing mechanism was not due strictly to the clathration process, some elements of this process appeared responsible for the observed results.

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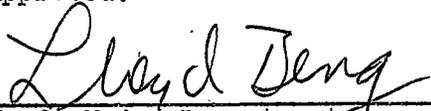
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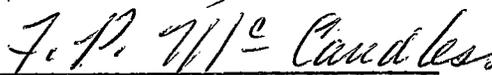
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ABSTRACT

The modification of polymer membranes by including various compounds in these films was investigated in order to develop a liquid permeation system which would be selective for one xylene isomer. These studies were completed using cylindrically-shaped stainless steel permeation cells with an exposed membrane diameter of 7.3 cm and a feed liquid capacity of 400 ml. The upstream pressure was atmospheric while the pressure on the product side of the membrane was maintained at less than 1 mm Hg. Feed temperatures ranged from 23 to 130° C.

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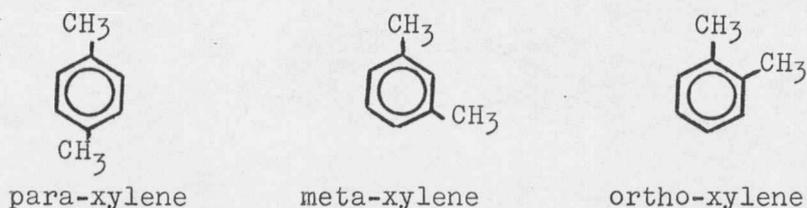
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The two basic additives investigated were $\text{Ni}(\text{SCN})_2 \cdot (4\text{-methylpyridine})_4 \cdot \text{p-xylene}$ and $\text{Ni}(\text{SCN})_2 \cdot (\alpha\text{-methylbenzylamine})_4 \cdot \text{o-xylene}$. It was found that both of these clathrates made the vinylidene fluoride film selective, but the second compound produced the larger para-xylene separations. The best para-xylene product-feed composition differences obtained were in the range of 8 percent beginning with a feed containing an equimolar mixture of the three xylene isomers. The total product flow rates obtained were about 1 ml/(hr ft²) at the best separations, but ranged up to over 100 ml/(hr ft²).

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INTRODUCTION

Among the higher homologs of benzene are the dimethylbenzenes, which are called xylenes. These three compounds have the chemical formula $C_6H_4(CH_3)_2$ and the following structures:



Some selected physical properties of these compounds are given in Table 1.

Table 1. Properties of the Xylene Isomers (1)

	Melting Point °C	Boiling Point °C	Density g/ml
para-xylene	13.26	138.35	0.8611
meta-xylene	-47.87	139.1	0.8642
ortho-xylene	-25.18	144.4	0.8802

Xylenes are recovered as a by-product of coke-oven operations and from petroleum sources, with the later accounting for over 99 per cent of the estimated 439.8 million gallons produced in the United States during 1971 (2). Commercially available xylene has a composition which is dependent on its source. Presently more than 95

percent of the petroleum xylenes are obtained by solvent extraction of reformat. A typical analysis of this product as well as those others encountered is shown in Table 2.

Table 2. Typical C₈ Aromatics Compositions from Various Sources (2)

Isomer	Catalytic Reformat	Steam Cracking	Disproportionation	Coke Oven
Ethylbenzene	17-20%	53%	Nil%	15-23%
Para-xylene	16-20	10	26	15-17
Meta-xylene	35-40	25	50	42-44
Ortho-xylene	19-26	12	24	14-20

In the growing petrochemical industry, xylenes find many uses. As of 1970, approximately 28 percent of the total production was used in solvents, mainly in paint, varnish and lacquers, and pesticides. Some mixed xylenes were blended into motor gasoline for octane control. The major outlets for the xylenes were as separate isomers used as chemical intermediates (2).

Ethylbenzene is converted into styrene and finds its end uses in such things as SBR rubber, polystyrene, plastics, and several other polyesters and plastics.

Para-xylene is in strong demand in world markets as a major raw material for the production of dimethyl terephthalate and terephthalate acid, intermediates used in the production of polyester

fiber and film. Dacron is an important example of a polyester and is polyethylene terephthalate, the condensation product of dimethyl terephthalate and ethylene glycol. Presently the manufacture of polyethylene terephthalate is the major outlet for para-xylene. The world polyester fiber production has grown from 1007 million pounds in 1965, to 3622 million pounds in 1970, a 27.7 percent yearly growth (4).

Meta-xylene, the most abundant xylene isomer contained in the mixed xylenes, has the smallest demand as a separate isomer. Most of the meta-xylene is left in the xylene stream where it is either isomerized, used as a solvent, or used in gasoline blending. The separated meta-xylene is mainly used to produce isophthalic acid which is used to make unsaturated polyesters, alkyd resins, plasticizers, and other esters. The U.S. isophthalic acid production capacity is 135-145 million pounds per year (5).

Ortho-xylene enjoys world-wide demand essentially as a raw material for phthalic anhydride production. Of the 850 million pounds of ortho-xylene produced in the U.S. during 1971, 46 percent was used to manufacture phthalic anhydride and 51 percent was exported (6).

The xylene isomers must be separated in order to be used in their many applications as chemical intermediates. This use demands a commercial para-xylene purity of 99.2 percent, meta-xylene purity

of 98.6 percent, and ortho-xylene purity of 95.3 percent (4,5,6). Some of these separations are conventional but difficult, while others may involve novel and fairly complex processes.

As indicated in Table 1, these isomers are quite identical as far as boiling points are concerned. However, there is enough spread in boiling point, heat of vaporization, and vapor pressure for ethylbenzene and ortho-xylene to be economically fractionated from each other and the xylene stream. Typical ethylbenzene towers are 300 to 400 actual trays with about a 25-50 to 1 reflux to feed ratio. Ortho-xylene fractionators are usually 100 to 150 trays with about a 5-8 reflux to feed ratio. Fairly recent technical developments in the recovery of these two components have been in the design of distillation trays able to operate at high capacity with a relatively low pressure drop (7).

The separation of para-xylene from meta-xylene is the most difficult. Because of the very small difference in boiling points, these two isomers cannot be economically separated by fractionation. However, as a result of the relatively large difference in melting points between para-xylene and the other isomers, low temperature crystallization is the major route in use. Currently there are about a dozen crystallization routes available which differ as follows: direct or indirect cooling; scraped-surface chillers, with separate or built-in crystallizer; pulse purification or conventional second-

stage crystallizer; separation by filtration or use of centrifuge (4). Another unusual crystallization process involves using an "inert" liquid to improve both the purity and recovery of para-xylene (8). In the Japan Gas-Chemical Corporation's process, the classic crystallization process is modified to include selective extraction and isomerization of meta-xylene using HF/BF_3 (9).

A recently developed adsorption process is Universal Oil Products' Parex process. Here para-xylene is recovered from an adsorbent by displacing it with another liquid of different boiling point. The UOP process is so designed to permit efficient use of the adsorbent and desorbent (10). At least four Parex units have been licensed (4). This process and another by Toray Co. (Japan) are thought to rely on potassium- and barium-substituted Type X and Type Y molecular sieves. However, none of these recently patented processes use the "sieve" action, but depend instead on selective adsorption due to preferential attraction (11).

A separation process known as clathration has been of interest for more than ten years. Here para-xylene is separated by a difference in shape from meta-xylene. This process has been developed by the Union Oil Company, but has not been of interest recently (12).

Relatively new works using a variety of plastic membrane systems indicate that significant xylene isomer separation may be obtained by liquid permeation through these films.

Therefore because no one separation process at the present is clearly accepted as the best method of separating para- and meta-xylene and because the demand for high purity para-xylene will increase in the future, more research into this area is certainly appropriate. The object of this particular investigation will be to construct membranes of a plastic or resin material which will also incorporate a xylene-selective clathrate or other suitable compounds and to evaluate their ability to separate the xylene isomers using a liquid permeation process.

TECHNICAL CONSIDERATIONS OF PREVIOUS RELATED WORK

Before dealing with the particular technical background of the problem at hand, it may be constructive to investigate and evaluate membrane separation processes and clathration as they are separately explained in the literature.

MEMBRANE SEPARATION

A membrane is a thin barrier separating two fluids. This barrier prevents all hydrodynamic flow so that transport through the membrane is by a diffusion-like mechanism generally referred to as permeation. The property of the membrane describing its rate of transport is its permeability. A semipermeable membrane is one which transports different molecular species at different rates. This phenomenon is the reason for interest in this process.

Of the permeation processes where the driving force for transport is pressure, this discussion will be limited to those processes in which a liquid feed material permeates through the membrane and leaves as a vapor. First to report that this process had good commercial separation potential, Binning, Lee, Jennings, and Martin called this process liquid permeation (13). Other prominent workers in this field have termed this process "pervaporization" (14). In this report both terms will be used interchangeably. This discussion will be limited to the pertinent material dealing with membranes composed of polymeric

