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Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations

Tina M. Nenoff, Mutlu Ulutagay-Kartin, Ron Bennett, Kaylynn Johnson, Gary Gray, Thomas Anderson, Manuel Arruebo, Richard Noble, John Falconer, Xuehong Gu, and Junhang Dong

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ABSTRACT

We present synthesis, characterization and testing results of our applied research project, which focuses on the effects of surface and skeletal modification of zeolites for significant enhancements in current hydrocarbon (HC) separations. Zeolites are commonly used by the chemical and petroleum industries as catalysts and ion-exchangers. They have high potential for separations owing to their unique pore structures and adsorption properties and their thermal, mechanical and chemical properties. Because of zeolites separation properties, low cost, and robustness in industrial process, they are natural choice for use as industrial adsorbents. This is a multidisciplinary effort to research, design, develop, engineer, and test new and improved materials for the separation of branched *vs.* linear organic molecules found in commercially important HC streams *via* adsorption based separations. The focus of this project was the surface and framework modification of the commercially available zeolites , while tuning the adsorption properties and the selectivities of the bulk and membrane separations. In particular, we are interested with our partners at Goodyear Chemical, on how to apply the modified zeolites to feedstock isoprene purification. For the characterization and the property measurements of the new and improved materials powder X-ray diffraction (PXRD), Residual Gas Analyzer-Mass Spectroscopy (RGA-MS), Electron Microscopy (SEM/EDAX), temperature programmed desorption (TPD) and surface area techniques were utilized. In-situ carbonization of MFI zeolite membranes allowed for the maximum separation of isoprene from n-pentane, with a 4.1% enrichment of the binary stream with n-pentane. In four component streams, a modified MFI membrane had high selectivities for n-pentane and 1-3-pentadiene over isoprene but virtually no separation for the 2-methyl-2-butene/isoprene pair.

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I. INTRODUCTION

1. Project Objective:

This project focused on developing a new family of inorganic crystalline porous materials under DOE/ITP that will lead to the improvement of energy efficiency and productivity *via* enhanced separations. Initially this project focused on materials for the separation of linear from branched hydrocarbons, in particular isoprene from C5 streams. However, it is anticipated that the results will provide the basis of knowledge to enable this technology to be applied toward additional hydrocarbon and chemical separations. Industrial involvement from Goodyear and Burns & McDonnell provided the needed direction for solving real industrial problems, which will find application throughout the US chemical and petroleum industries.

2. Background:

A strong team has been assembled to attack the aforementioned technical barriers. The intended pathway Sandia National Laboratories (SNL) for strong zeolite bulk and membrane growth and surface modification, University of Colorado (UC) for zeolite membrane growth, membrane growth and bench scale testing at NM Tech University (NMT; later moved to University of Cincinnati), and pilot-scale testing at facilities developed at Goodyear Chemical in Akron, OH. Through an iterative fashion, the generated data will be forwarded to Burns & McDonnell for economic process modeling. In addition, a well-known support tube manufacturer (Pall Corporation) has been consulted for commercialization.

This applied research program focuses on the effects of surface modification of zeolites for significant enhancements in current HC separations. This is a multidisciplinary effort to research, design, develop, engineer, and test new and improved materials for the separation of isoprene, and other similar olefins from HC streams *via* adsorption-based separations.

Previous commercial separations of similar HC molecules have used either cryogenic distillation or sieving by simple size exclusion. Cryogenic distillation is very energy intensive and pollution producing. Furthermore, it is a non-regenerative process. These energy intensive separations have motivated the petrochemical industry to explore alternative separation technologies, which is demarcated by the number of patents issued in the last ten years (USA 54; Japan 49; Europe 37). However, all these patented technologies represent incremental improvements in these energy intensive distillations. Separation processes using bulk or membrane zeolites have primarily relied on only size exclusion to achieve physical separation of molecules. Size exclusion alone is inadequate for separations of many commercially important HCs of similar boiling point and similar sized molecules in commercial mixtures. Thus, there is a need to further enhance the selectivity of zeolites by modifying their adsorptive property in order to change the interaction of the diffusing molecules with the internal surfaces of the zeolite structure. Due to the high acidity and chemical reactivity, many zeolites are not suitable for HC separations. Rather, their acidic properties and shape selectivity make zeolites more useful as catalysts for HC cracking and isomerization in many refining and petrochemical processes. However, coking from the cracked HCs is known to deactivate acid sites, resulting in loss of catalytic activity and fouling. Therefore, coke generally comprises a mixture of partially decomposed HC molecules.[1-5] Various post-synthetic coking treatments have been used to "caulk" the microdefects of zeolites with carbonaceous deposits for separations.[6] The coking process uses a large aromatic HC to fill the micro defects and thereby enhance selectivity, however, at the expense of reduced permeability. Although selectivity was restored, large reductions in permeability have been observed with these "caulked" membranes. It is unlikely that the HC molecules enter the zeolite nanopores during the caulking treatment. Therefore, the resulting enhanced selectivity is likely due to size exclusion, rather than selective adsorption. Therefore, a need remains for the controlled modification of sorptive capacity and pore size of zeolites used for separations. As with catalysts, the controlled carbonization of zeolites may provide a means to deactivate the acid sites that cause HC cracking, yet retain weak bonding sites required for selective adsorption. Therefore, the adsorptive properties and selectivity of zeolites can be modified with depositing coke into the void volume of the zeolite structure.

The motivation of this research is to create materials that can be used to enable breakthrough separation technology that will change the landscape of tomorrow's manufacturing. These materials will advance current separation technology towards greater energy efficient and waste reducing processes that will increase productivity, product quality, and global competitiveness. Implementation of this technology as compared to existing separation technology is schematically represented in Figure 1.

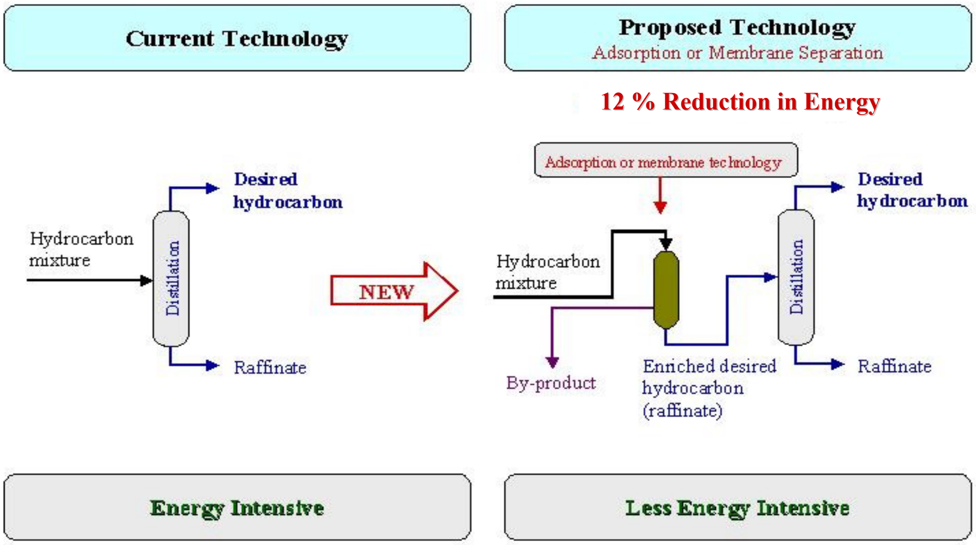


Figure 1. Current versus proposed technology for the adsorption or membrane based separation.

If this technology were employed in HC separations of C2-C5, it is anticipated to result in the following benefits:

- 12% Reduction in Energy for U.S. HC Separations

- Energy Savings of 39 trillion BTU's/yr
- Increase in domestic zeolite revenue
- Significant Technological Advancement for the Chemical and Petroleum Industry
- Increased Economic Competitiveness for the Chemical and Petroleum Industry

Our overall focus for this CRADA was to develop novel modified zeolites for energy-efficient HC separations. Controlled surface and framework modification of zeolites is the focus of this research project. Our three major goals were: 1) to develop new separation-based adsorbents or membrane materials *via* modification of commercially-available zeolites; 2) to establish zeolite structure-property models for this technology and others; 3) to decrease the energy consumption in the chemical and petroleum manufacturing industries by employing these new and improved materials. Our success has resulted in an enabling technology for future adsorbents, materials for membranes, and the potential development of shape selective catalysts.

II. EXPERIMENTAL

1. Materials and System Design

Detailed experimental procedure is reported previously.[7] Our general experimental approach is as follows:

• **Activating Zeolite and HC Adsorption/Desorption Experiment:** The commercially available zeolites are regenerated by exposure to a flowing inert gas at elevated temperatures to remove ancillary pore-blocking molecules, such as water. The activated zeolites are exposed to HC mixture at 50 ºC for 30-60 minutes. Then the adsorption/desorption properties are determined by increasing the furnace temperature up to >650 ºC, and recording desorption of the organics as a function of temperature. Desorbed species are identified *via* RGA/MS, see Figure 2 for the system design.

• **Bulk Carbonization:** The regenerated zeolites are carbonized by exposure to an inert carrier gas stream containing controlled amounts of the HC mixture (50/50 isoprene/n-pentane) at elevated temperatures, see Figure 2. The HC type, concentration, helium flow rate, exposure time, and temperature can be modified to control the properties of the carbon deposited. The kinetic diameter of the HC molecule should be smaller than the pore size of the zeolite to achieve interior carbon deposition.

• **Temperature Programmed Desorption (TPD) Experiments:** A Micromeritics® Autochem II Chemisorption Analyzer is used to perform TPD analysis of carbonized samples. Analysis uses He as the carrier gas and NH_3 as the dosing gas. Samples are placed within the furnace portion of the unit, allowing the temperature to be increased and decreased via the computer interface. Measurements are recorded using a thermal conductivity detector (TCD) for a total of three pulse dose periods of NH_3 followed by three desorption periods having different temperature ramp rates. The temperature ramp rates used for desorption were varied from 5 °/min to 30 °/min, by 5 °C/min increments.

• **Bulk Material Separation Experiments:** The carbonized zeolites are used for separation of a HC from a HC mixture using the unit reported previously.[8]

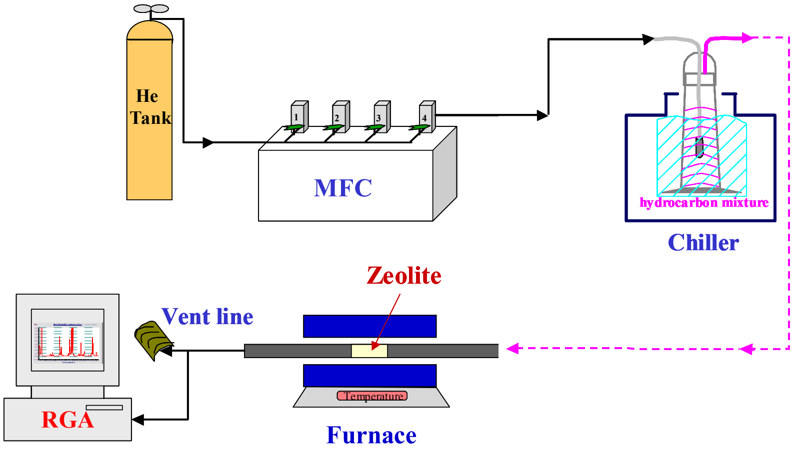


Figure 2. Adsorption/desorption and bulk/membrane carbonization unit at SNL.

- **Zeolite Membrane – Synthesis and Modification.** Zeolite membranes (pre-and post-modification) are synthesized for permeation testing with pure and mixed light gas mixtures. The membranes are hydrothermally grown on inorganic microporous supports, including commercially available Inoceramic alumina disks and TRUMEM disks (stainless steel with a coating of TiO_2), and in-house fabricated α-Al_2O_3 disks and Inoceramic tubes (from the University of Colorado).

- **Pilot Scale Testing at Goodyear Chemical (Akron, OH)**

The permeation testing was performed by passing a gaseous feed stream of helium containing approximately 2 mole % hydrocarbon through the Zeolite tubular membrane. The hydrocarbon was a 50/50 mixture of n-pentane and isoprene. The membrane was encased in an apparatus which allowed the feed stream to pass through the inside of the tube (retentate) and a 2nd helium stream to pass around the outside of the tube (permeate). The helium flows were measured by mass flow meters and controlled by a Foxboro system and the hydrocarbon mixture was measured and controlled with a syringe pump. An on-line GC was used to analyze both the permeate and retentate streams every ten minutes. The experiments were run at elevated temperatures by wrapping the apparatus with heating tape and insulation. Each test was continued until the system was at steady-state for at least 4 – 5 hours.

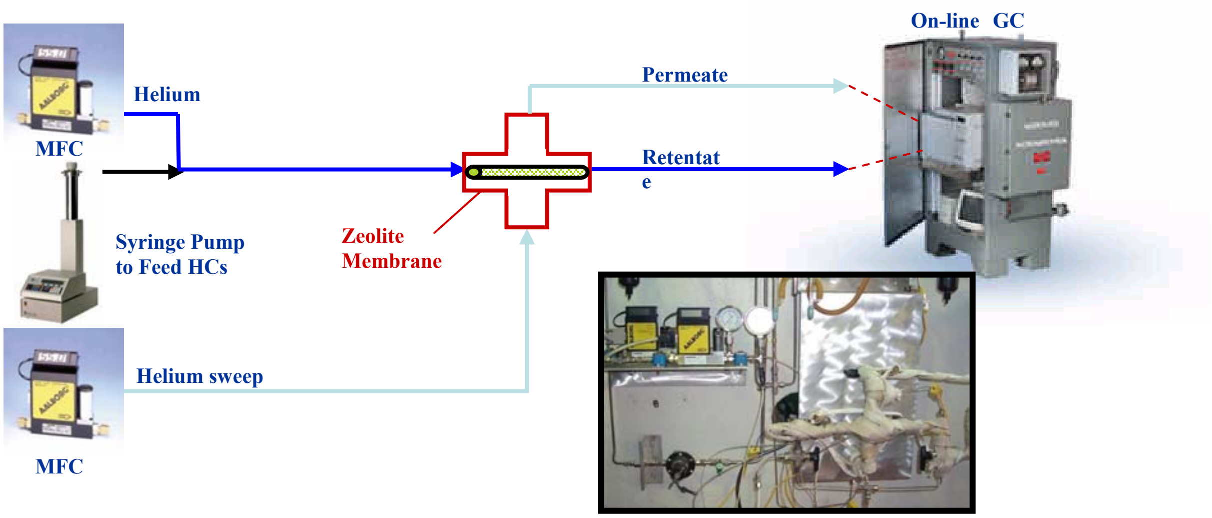


Figure 3: Goodyear Chemical on-line pilot bench-scale testing unit

2. Results and Discussions

It has been shown that the nature of the zeolite effects the nature and disposition of the carbon deposition. It is known that the carbonization is effected by zeolite structure, type of acid site and strength of the acid side. Therefore we have selected various zeolite types to conduct a matrix of experiments to understand the carbon deposition in different zeolites and in different conditions. The zeolites used in this study and some of their properties are listed in Table 1. Ion-exchanged forms of the different type of zeolites are prepared using the procedure reported in the literature.[9] Table 2 lists the selected zeolite types, their various ion-exchanged forms and different SiO_2:Al_2O_3 ratios of the zeolites used in this study.

Table 1. Framework properties of the zeolites studied in this project

Zeolite Type	Relative acidity	Pore diameter (Å)	Structure
Zeolite-β	High	6.6 × .7, 5.6	12 MR, 3-D, straight pores
FAU	Medium-high	7.4	12 MR, 3-D (cages), intersecting straight pores
Zeolite L	Low	7.1	12 MR, 1-D, straight pores
MFI	High	5.1 × 5.5	10 MR, 3-D, straight/sinusoidal pores

Table 2. Zeolite types, SiO_2:Al_2O_3 ratios and ion-exchanged forms of the zeolites used in adsorption/desorption experiments.

Zeolite Type	**Cation Type**	**SiO_2:Al_2O_3 Ratio**
FAU	H	(4:1) (30:1) (60:1)
	Na	(60:1)(4:1)
	NH_4	(4:1)
	Cs	(60:1)
Zeolite L	K	(3:1)
MFI	H	(50:1) (280:1)
	Na	(50:1) (400:1)
	NH_4	(50:1)

Figure 4 shows the desorption behavior of linear and branched HC, respectively, for zeolites containing different ions and having different silica to alumina ratios.

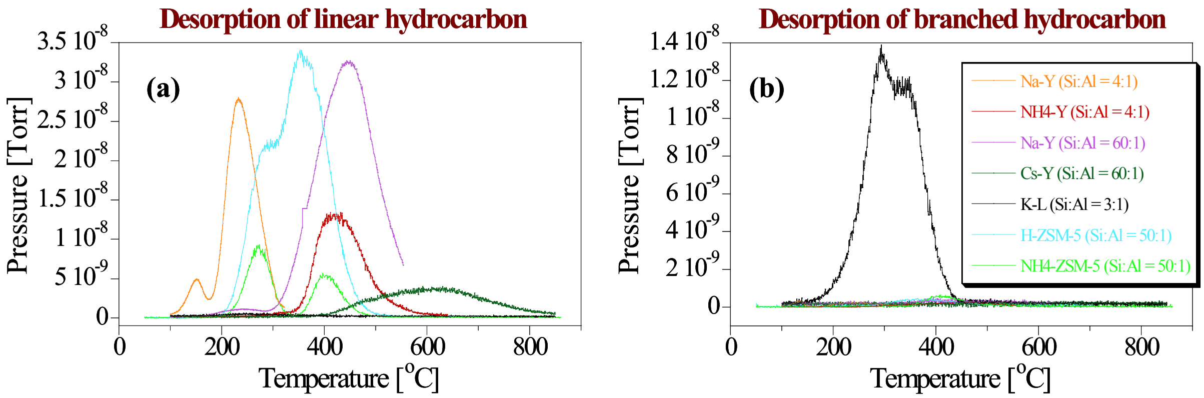


Figure 4. Adsorption and desorption behavior of (a) linear n-pentane and (b) branched isoprene on various zeolites.

The data demonstrates the ability of the desorption experiments to assess the relative effects of different exchanged ions, silica to alumina ratio, and zeolite type on the adsorption behavior of linear n-pentane and branched isoprene. The data shows that isoprene is preferentially adsorbed by zeolite L and the n-pentane is preferentially adsorbed FAU and MFI.

Temperature Programmed Desorption (TPD) data allows for the study of internal pore acidity strength in zeolites. Our intent was to use this method to study the acidity of each zeolite type prior to modification and also decreased acidity post modification procedure. TPD experiments were performed on our Micromeritics® Autochem II Chemisorption Analyzer, as described above in the experimental section.

See figure 5 for NH_3-TPD results on bulk FAU zeolite. Figure 5 (a) shows the graph of the pulse dosing of NH_3 as a function of time and Figure 5 (b) shows the graph of the desorption of the pulse dosed NH_3 as a function of temperature. The reported three graphs, in blue, red and green are of the same type of zeolite having different carbon modification conditions. Graph plotted in blue corresponds to unmodified (as prepared) sample, graph plotted in red corresponds to the sample, which was carbonized at 450 ºC and graph plotted in green corresponds to the sample, which was carbonized at 700 ºC.

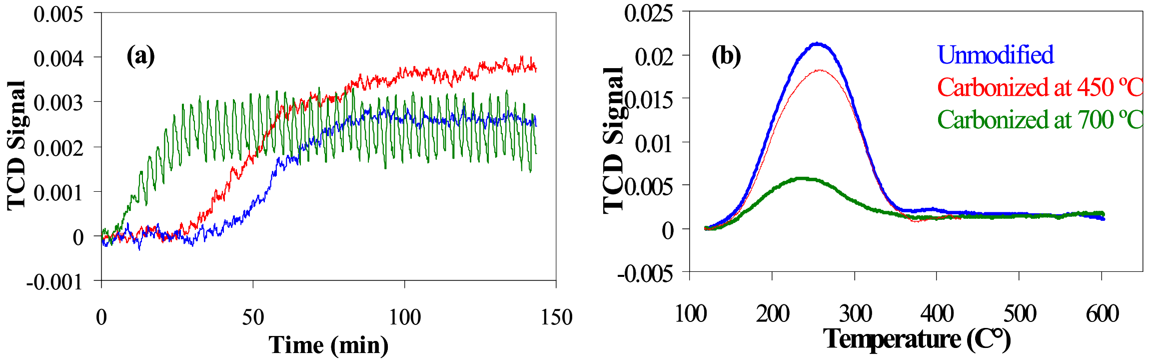


Figure 5. NH_3-TPD results FAU Zeolite, where three samples were prepared at different carbon modification conditions, see text for each sample condition. Graph (a) represents the pulse NH_3 dosing as a function of time; graph (b) represents desorption of the pulse dosed NH_3 as a function of temperature.

The NH_3-TPD experiments show that the carbon-modified samples do not adsorb as much NH_3 as of the unmodified sample. We used the bulk carbonization in our study to passivate the zeolite activity toward organic adsorption/decomposition. To confirm the acid site deactivation of the modified zeolites we employed the NH_3-TPD experiments. We prepared more carbon-modified samples of different zeolite types and studied the NH_3-TPD properties of them. Various carbonized samples are sent to our partner Goodyear Chemical to perform separation experiments. Branched *vs.* linear HC separation experiments using modified zeolites were performed at Goodyear Chemical on their in-house separation unit.

BET experiments. Microporous surface area measurements were performed on our Micromeritics ASAP 2010 BET instrument. Prior to analysis, the samples were degassed to 0.5 Torr at 200 °C. The surface areas were calculated by the Brunauer-Emmet-Teller (BET) method, assuming a cross-sectional area of 0.162 nm^2 for the N_2 molecule. The pore volume was assessed by the Barrett-Joyner-Halenda (BJH) technique, which is assumed to cover the cumulative adsorption volume of pores with a maximum diameter 1.7 - 300 nm.

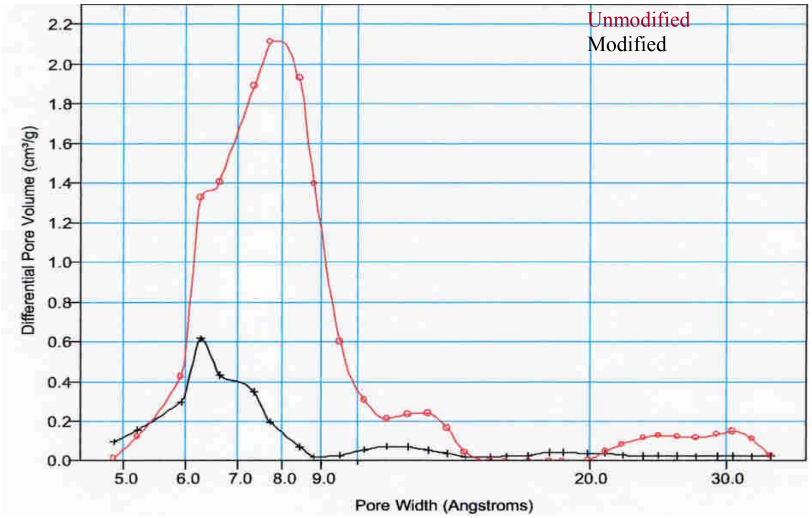


Figure 6: BET plot of bulk FAU zeolite membrane before and after surface modification. Both the pore volume and pore width were significantly decreased due to modification by carbon.

BET surface area and micropore measurements helped to confirm that the internal pores of the zeolite (in this case FAU zeolite) were being altered by the modification process. We believe that the homogenous coating of carbaceous species resulted in a decreased pore volume and width in the zeolite structure. See figure 6.

On-line testing of Bulk Separation Materials (pre & post modification)

Bulk carbonization of zeolite powders were preformed in the reactor in figure 1. The zeolite powder was loaded into a quartz tube and exposed to a cold stream of 50/50 isoprene/n-pentane (chilled prior to 0°C) and carried by a flow of He carrier gas. The gas stream and zeolite were heated to 550°C for 4 hours with a slow ramp and cooling rate. During the coking cycle helium, hydrogen, isoprene and *n*-pentane peaks were monitored on the P *vs.* T graphs on RGA unit. All samples turned black in color after carbonization, indicating surface modification (BET data confirms internal pore modification).

On-line testing of Membranes (pre & post modification). A variety of zeolite-type membranes were synthesized on either, or both, disk and tube supports. The methods used for membrane synthesis are all reported in the literature. Detailed descriptions of each membrane synthesis methods are referenced: ZSM-5 membrane method was developed at Sandia[10], Silicalite developed at NM Tech University[11], FAU (zeolite Y) membranes used two different recipes by Kita[12] and Dong[13], and metal doped ZSM-5 tube membranes at the University of Colorado[14].

The modification procedure for the membranes was preformed on-line in the modification unit and is derived from the procedure for the bulk zeolite modification[7]. The membrane is calcined in air at 550°C for 4 hours with a slow ramp and cooling rate. It is then placed in the quartz tube at the center of the modification reactor, and a 50/50 mixture of isoprene/n-pentane is flowed through it at 450°C for 30 to 90 minutes.

Framework Type: Based on bulk zeolite adsorption/desorption testing (see above) and unmodified Silicalite membrane permeation data from Noble's group at the University of Colorado[14], we determined that the optimized zeolite type for the isoprene/n-pentane separations should be the protonated MFI zeolite structure type. (see figure 7) Both all silica (Silicalite) and Al-doped MFI type zeolites were studied. Both have the same structure framework configuration; however, MFI has acidic sites due to the Al-doping.

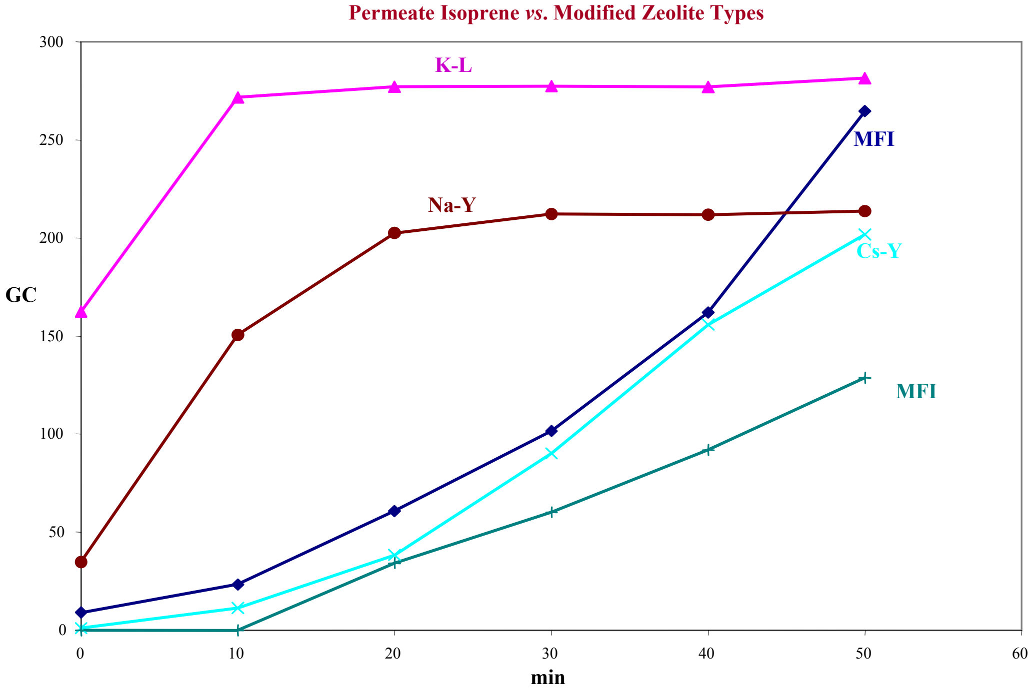


Figure 7: Pilot Scale Testing of Various Bulk Modified Zeolites

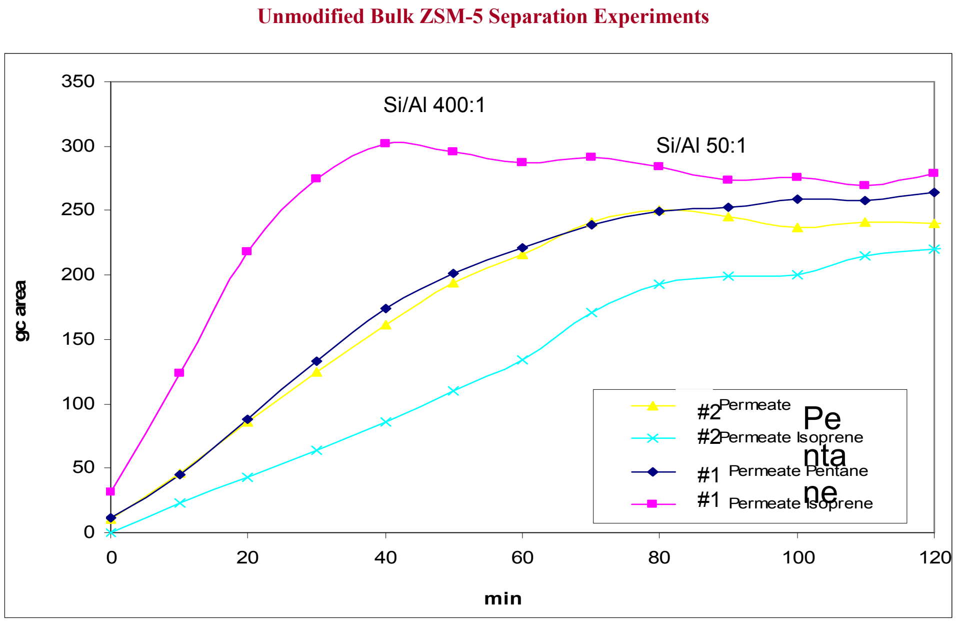


Figure 8 : Pilot Scale Testing of Unmodified MFI with Different Si/Al Ratios

Acidity: Testing of various acidities of ZSM-5 type zeolites show the results plotted in Figure 8. The low acidity sample Si/Al-400:1 showed quick saturation of isoprene, while the higher acidity version showed a much slower on-line saturation. For that reason, we determined the Si/Al 50:1 to be the optimized stoichiometry.

Pilot Scale Testing at Goodyear: Using bulk modified, protonated MFI, Goodyear Chemical ran on-line adsorption tests, both at room temperature and at 100°C, see figures 9-11. Improved separation data was collected at the higher temperature runs. Figure 9 shows the results of a binary mixture adsorption studies. Between 60-120 minutes on stream, we see our maximum separation between isoprene and n-pentane, with selectivity towards the isoprene. For comparison, studies were run on the bulk modified, protonated FAU zeolite powder. Essentially, no selectivity at equilibrium was detected. See figure 10. The MFI framework remained the best bulk modified zeolite for isoprene separation.

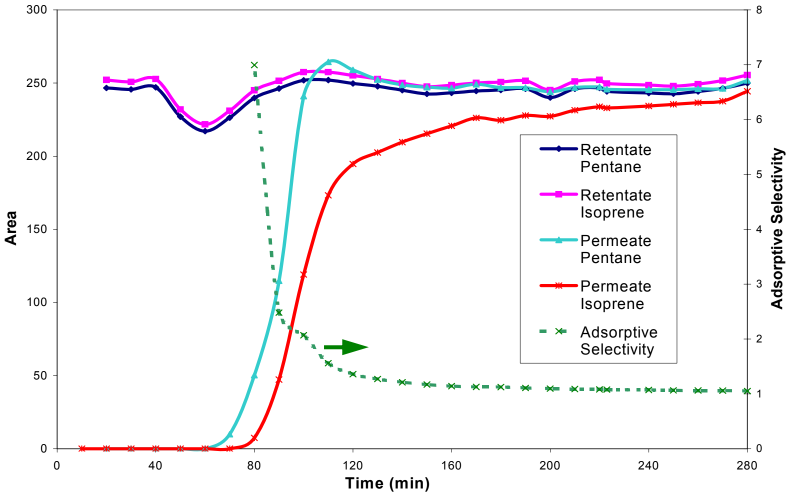


Figure 9: Pilot Scale Adsorption Selectivity Testing of Modified ZSM-5; Demonstrated isoprene/pentane separation using modified zeolite in dilute concentrations

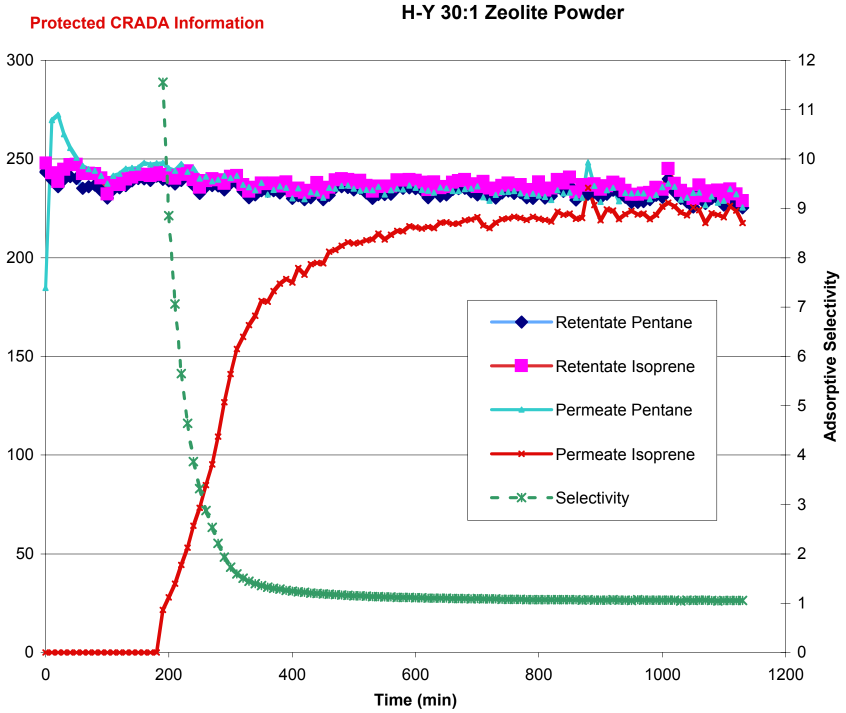


Figure 10: Pilot Scale Testing of Modified Protonated FAU (Zeolite Y); H-Y 30:1 Powder @100C, 50/50 n-pentane/isoprene.

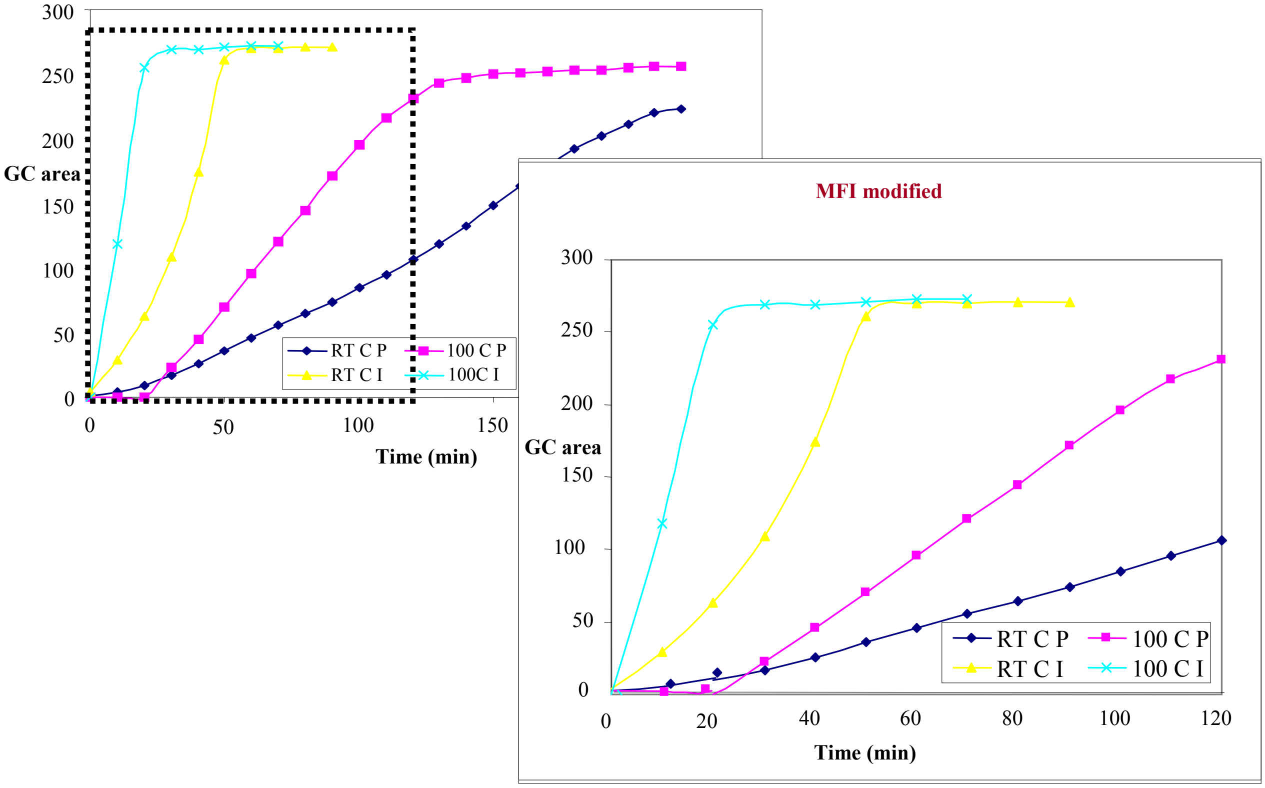


Figure 11: On-line testing of binary mixture of isoprene/n-pentane over modified, bulk H-MFI at room temperature and at 100°C. (left) full plot , (right) enlargement of first 120 minutes

Optimized Separations: Due to earlier described results, Goodyear ran protonated and modified MFI bulk samples in their reactor, and monitored the separation via adsorption at both room temperature and 100°C. See figure 11. We observe maximum separation of isoprene (I) versus n-pentane (P) over the first 120 minutes of operation. This is further confirmation that we have isolated the correct zeolite framework, charge balancing cation, modification procedure and operation temperature. With this baseline on bulk adsorption materials, we proceeded in making membranes with the same characteristics for only separations testing.

Membranes: Initial on-line testing of unmodified MFI membranes (synthesized by the UC group) were tested on pure isoprene and n-pentane gases at Goodyear Chemical, with a maximum separation value at 60°C of 29.[14] Calculations from Gary Gray of Goodyear Chemical approximate 3% enrichment of n-pentane. See Figure 12 for results.

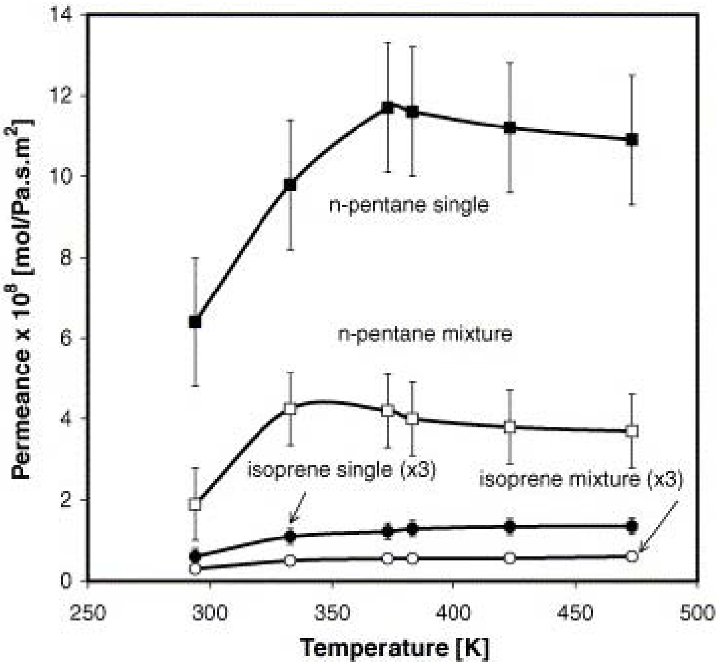


Figure 12: Tubular Membrane Testing at Various Temperatures[14]; Single gas and mixture permeances for n-pentane and isoprene using MFI tubular membranes. (Open symbols: binary mixture; closed symbols: single component.)

Modified Membranes: The MFI membranes synthesized at Sandia and UC were all modified and sent to Goodyear Chemical for testing in their pilot scale unit. Through processing and transport, a number of the membranes were damaged or deemed "defect-filled" (possibly due to cracking during the modification process or transport). Of those tested, the best results on binary isoprene/n-pentane came from the Sandia-modified UC samples of acidic Al-doped MFI tube membranes. (see results and experiment parameters in figure 13) As predicted by the bulk experiments, the modified protonated and acidic Al-ZSM-5 (MK-7-39) run at 60°C had enhanced separation abilities versus those run at RT. The enrichment value of this sample was the highest recorded for this program, 4.1%. However, contrary to the bulk samples, enrichment was of n-pentane rather than isoprene.

Permeance
(mol/Pa-s-m2)

Temperature	MK-7-37	MK-7-39
25	#N/A	3.00E-08
23.5	3.50E-08	#N/A
60	5.30E-08	#N/A

Process Info	
Retentate & Sweep Rates =	50 ml/min
Organic Rate =	0.25 ml/hr
Total Organic Composition in Feed ~	2.1 mole %
Isoprene/Pentane (by volume):	50/50

Membranes	
MK-7-37	Modified B-ZSM-5 Tube
MK-7-39	Modified Al-ZSM-5 Tube

(from 10/15/2004 batch from Mutlu)

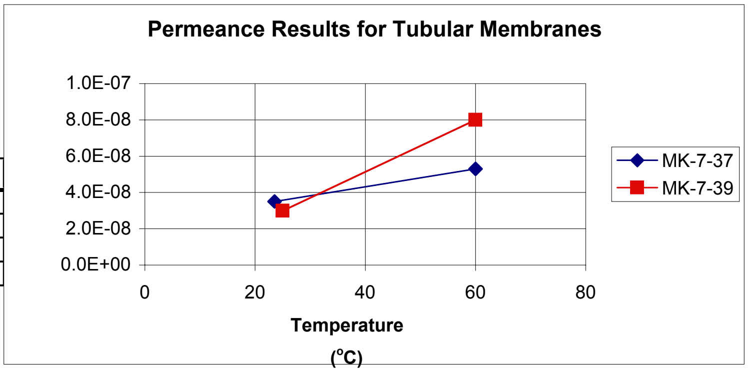


Figure 13: Pilot-Scale Modified Zeolites on Tubular Membrane; Similar pentane permeance values as previously reported but with zero isoprene permeance. Results: 4.1% enrichment of n-pentane.

3. Economic Analysis of Goodyear Facilities by Burns & McDonnell:

The success of this project will be based upon the economic process modeling performed by Tom Anderson of Burns & McDonnell. The criterion for success has already been established by performing a series of ideal separation simulations necessary to obtain the desired energy savings via membrane augmentation. Membrane performance, throughput, lifetime and cost have been factored into the overall project success/failure criteria.

Metrics used in analysis by Burns & McDonnell:
- Baseline isoprene plant separation performance (lbs. steam/ lb. isoprene recovered) has been calculated using conventional distillation.
- A reduction in metric #1 *via* tubular membranes such that it generates a substantial energy savings.
- Membrane throughput, lifetime and cost (initial and annual).

These were targets for implementation of the zeolite membranes into the Beaumont, TX Goodyear Chemical plant. However, they were also guidelines for our research to see if our results were good preliminary results that might be further developed and optimized by continuation funding.

Reported in December 2004, Tom Anderson analyzed the 29 component stream typical of those at the Beaumont, TX plant for isoprene feedstock, with focus on percentage loss to raffinate, permeate and stream composition pre & post membrane. The analysis ranged from best results to-date to a worst-case scenario. Note, isoprene distillation recovery was adjusted to compensate for the 1% membrane loss; steam savings is less than 1% compared to the base case issued in 2001.

Table 3: Economic Analysis energy savings for implementation of membranes to plant

					D-101	**D-100**
	Sep Factor	% pentane & i-pentane in permeate as % of total feed	% isoprene loss to permeate	% others loss to permeate	% isop enrich	% isop enrich
Bad	20	17	1.0	1.0	1.05	1.08
Best to date	75	43	1.0	1.0	3.04	3.1
Goal	396	80	1.0	1.0	6.7	6.8

We were able to use this analysis (see Table 3) as a guideline for isoprene enrichment percentage targets for our pilot-scale studies. For our binary studies of 50/50 n-pentane/isoprene, we were able to enrich our stream with n-pentane through the modified membranes, carbonized Al-ZSM-5 tube (synthesized at UC, modified at SNL: MK-7-39), by 4.1%, with this maximum enrichment achieved at 60°C operation temperature.

Though this was not isoprene enrichment, and we were below the target of 6.8% established by Burns & McDonnell, we have shown significant improvement over any other type of membrane separation attempted on isoprene feedstocks.

III. CONCLUSION for CRADA Years 1-3

We have used a combination of membrane synthesis and modification, characterization and separation properties to develop a new energy efficient method of separating isoprene feedstock from its delivery components. For zeolite carbonization optimization, we analyzed commercially available zeolites of zeolite-Beta, FAU framework, zeolite L and the MFI frameworks. We first performed the HC adsorption/desorption experiments on as purchased bulk zeolites. The results showed that the isoprene is preferentially adsorbed by zeolite-L and the n-pentane is preferentially adsorbed by FAU and MFI frameworks. Due to these results, we focused on developing and optimizing modified FAU and MFI membranes for lab and pilot-scale permeation testing. In these experiments, we used the bulk carbonization to passivate the zeolite activity toward organic adsorption/decomposition. The acid site deactivation of zeolites was confirmed by NH_3-TPD experiments. Gas and organic vapor permeation units are designed and set up at Sandia and Goodyear. Using these units, and utilizing the “best” separation framework and modification techniques, we demonstrated the 4.1% enrichment of n-pentane over isoprene in a binary mixture using a modified protonated/acidified Al-MFI membrane on stream at Goodyear Chemical test facilities.

These results were promising and encouraging enough so as to garner support for continued funding from DOE/ITP for more industrially relevant separation studies. To that end, DOE/ITP generously funded us for one extension year, CRADA year 4 ending 10/23/06, to study modified MFI framework membranes at elevated temperatures in binary and 4-component streams. See section 4 below.

IV. CRADA extension, Year 4

Due to the substantial separation values achieved during the 3 year duration of the CRADA, an additional and final year of funding was provided by DOE/ITP to attempt separations to the 6.8% level. Our milestones for that year were focused on optimization of internal and external surface modifications for the zeolite membrane. Furthermore, we were focused on determining if any other modification processes were able to separate the relevant C5 components from an industrially relevant simulant stream (composition to be provided by Goodyear Chemical). Sandia (Tina Nenoff), in partnership with Dr. Junhang Dong's research group at the University of Cincinnati (formerly NM Tech University), leveraged skills, techniques and equipment past programs in which para-xylene (PX)[15] hydrocarbon was separated from its isomers and a multicomponent industrial-simulant stream. Ron Bennett and Kaylynn Johnson of Goodyear Chemical remained as partners (Goodyear Chemical remained on the CRADA), and acted in a guidance capacity for this forth and final year of the CRADA.

To this end, the following is the task schedule set for the final CRADA extension year (YR 4).

Tasks/schedule for Sandia (Tina Nenoff) and NMT/Univ. Cincinnati (Junhang Dong, Xuehong Gu):
(1) Synthesis and characterization of MFI membranes with Al/Si ratios of 0 and 1/100, respectively;
(2) Membrane modification by online coking of organic compounds;
(3) Silicalite membranes modification by depositions of ionic oligomers to improve the membrane modification by the in-situ coking method;
(4) Separation of Pentane/Isoprene binary mixtures;
(5) Separation of the four-component mixtures containing Isoprene/Pentane/1-3 Pentadiene/2-methyl-2-butene separation.

Results:

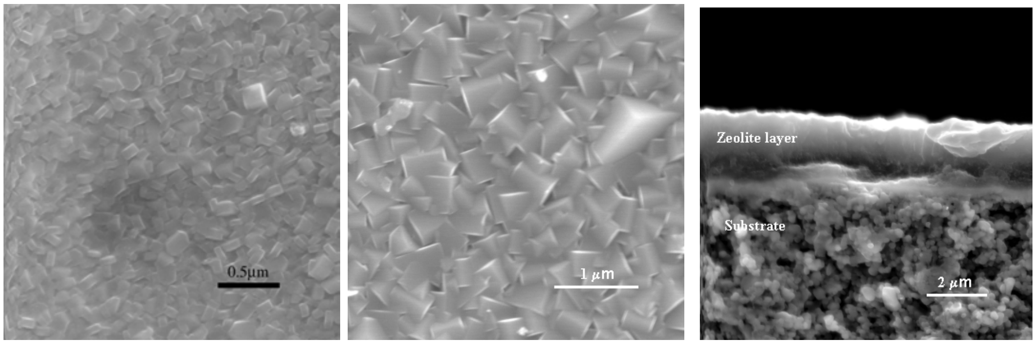
Tubular silicalite membranes synthesized by in situ crystallization method were used for testing isoprene separation from n-pentane. The MFI membrane was selective toward n-pentane. The temperature and feed pressure dependencies of the n-pentane flux and selectivity suggest that the permeation is controlled by an adsorption-diffusion mechanism. For the equimolar n-pentane/isoprene mixture, at 50^{o}C and feed pressure of 32 kPa, the n-pentane separation factor over isoprene is ~25.

Membrane modification by on-line carbonization of 1,3,5-triisopropylbenzene (TIPB)[15] were found to moderately improve the separation performance. The limited improvement was due primarily to the block of large intercrystal pore but not the modification of zeolitic pores. The separation of a four-component mixture containing isoprene, n-pentane, 1-3-pentadiene, and 2-methyl-2-butene was also tested on the modified membrane.[16] The membrane had high selectivities for n-pentane and 1-3-pentadiene over isoprene but virtually no separation for the 2-methyl-2-butene/isoprene pair.[16]

1. Membrane Preparation

Membrane Synthesis

MFI-type zeolite membranes were synthesized by two methods: seeded secondary growth[11] and in situ crystallization[15]. The secondary growth synthesis was conducted on disc-shaped α-Al_2O_3 substrates (pore size 0.15μm and porosity of 0.35) using template-free precursors with Al/Si ratio varied from 0 to 1/50. Nano-sized MFI particles (~60 nm) were used as seeds. In situ crystallization synthesis was performed on the practical tubular substrates from Pall Corp. (pore size 0.2μm). Good quality MFI zeolite membranes were obtained by both methods. Figure 14 shows the SEM images of MFI membranes synthesized by secondary growth method. The in situ synthesized silicalite membrane appeared to be the best membrane as indicated by very high p-/o-xylene separation factor ($\alpha = \sim 47.9$ at 250 °C)[15]. Thus the tubular silicalite membranes were used for isoprene separation tests.



(a) (b) (c)

Figure 14: SEM images of zeolite membranes obtained by second growth method: (a) Al/Si = 0, (b) (Al/Si=55) membrane surfaces and (c) cross-section

2. Separation of n-Pentane/Isoprene Binary

Permeation Stability

Separation of n-pentane/isoprene was studied as a function of time-on-stream for a 50/50 binary vapor mixture at 50 °C under a feed partial pressure of 14.7 kPa. The n-pentane/isoprene separation factor increased with time (see Figure 15). The separation tended to stabilize after ten hours of operation. The stabilized separation factor of n-pentane over isoprene was ~25.

Separation factor of component *i* is defined by $S_i = \dfrac{y_i/(1-y_i)}{x_i/(1-x_i)}$, where y_i and x_i are the mole fractions in permeate and feed streams, respectively

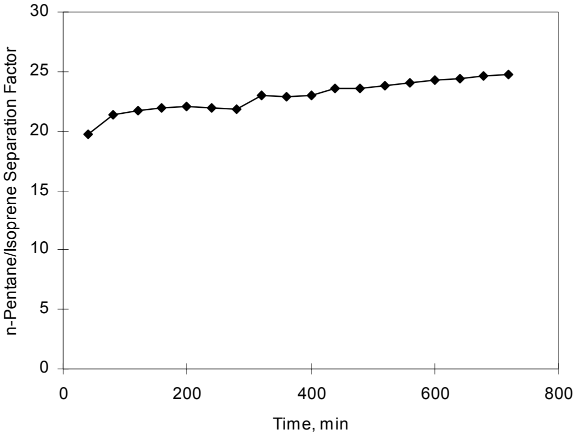


Figure 15: Separation of 50/50 n-pentane/isoprene vapor mixture as a function of time at 50^{o}C.

Effects of temperature and feed pressure

The effects of temperature and feed pressure on n-pentane/isoprene separation were investigated. Figure 16 shows the separation results for the 50/50 n-pentane/isoprene vapor mixture (feed pressure = 14.7 kPa) as a function of temperature (from 23 to 180 °C). The separation factor for n-pentane over isoprene decreased continuously with an increase in temperature. The highest separation factor was observed at 23 °C, which was about 27. The n-pentane/isoprene separation factor was ~17.5.

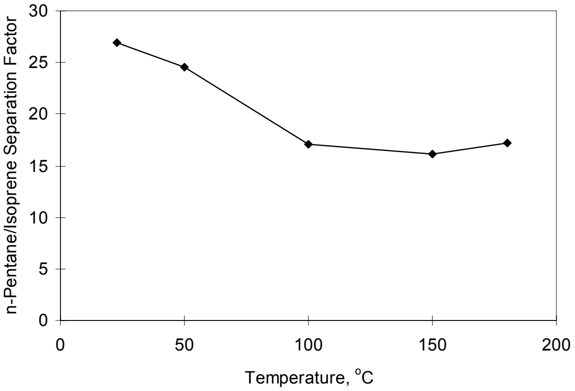


Figure 16: Effect of temperature on separation of n-pentane/isoprene (feed 14.7 kPa).

Separation was performed for the 50/50 n-pentane/isoprene vapor mixture at 50°C with feed partial pressure varied from 7.4 to 32 kPa. The results are shown in Figure 17. The n-Pentane separation selectivity was found to increase with increasing the feed partial pressure. At a feed pressure of 32 kPa, the n-pentane separation factor over isoprene was ~25.

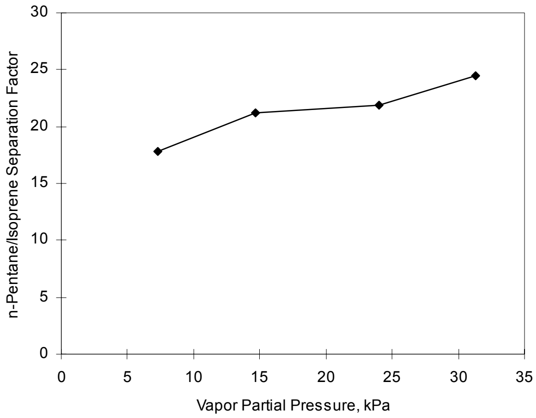


Figure 17: Effect of partial pressure on separation of n-pentane/isoprene (50°C).

The above temperature and feed-pressure dependencies of the separation performance suggest that an adsorption-diffusion mechanism dominated the separation process. The experimental results indicated that, for practical applications, operation at relatively high temperature with high feed pressures might be necessary.

3. Membrane Modification

MFI membranes modified by on-line carbonization of 1,3,5- triisopropylbenzene (TIPB) vapor exhibited moderate improvement in n-pentane/isoprene separation factor in relatively high temperature range (>50°C). As shown in Figure 18, the n-pentane and isoprene separation factor increased at >50°C. This observation indicates that some large inter-crystal pores are blocked by carbon deposition but the zeolitic pores are not changed because the TIBP molecules (dynamic size 0.84nm) too large to enter the zeolite channels (dia. 0.55nm).

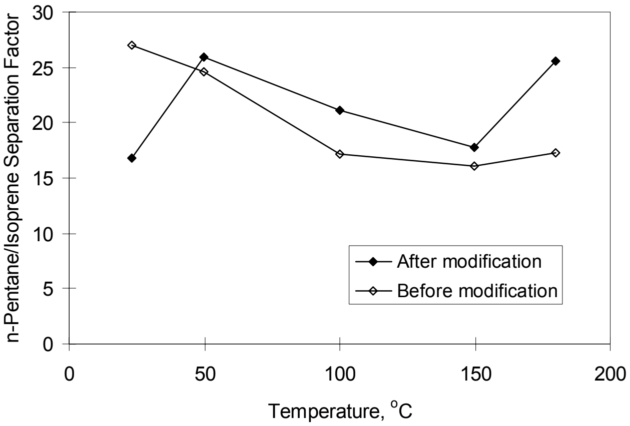


Figure 18: Comparison of n-Pentane/isoprene separation on the MFI membrane before and after modification.

4. Separation of multicomponent vapor mixture

The modified membrane was used to test separation of a quaternary mixture (composition provided by Goodyear Chemical) containing isoprene (IP), n-pentane (NP),1-3-pentadiene (PD), 2-methyl-2-butene (MB) mixture with IP/NP/PD/MB molar ratio of 40/40/2.15/17.85. The total feed partial pressure was 14.7 kPa. Figure 19 shows the separation results obtained in a temperature range of 23 – 180°C. The membrane exhibited high selectivity for n-pentane and 1,3-pentadiene. The highest n-pentane/isoprene selectivity was ~14, which was observed at 50°C. The 1,3-pentadiene/isoprene selectivity increased continuously with temperature and reached a very high value of ~50 at 180°C. However, there was almost no separation achieved on the MFI membrane for 2-methyl-2-butene/isoprene.

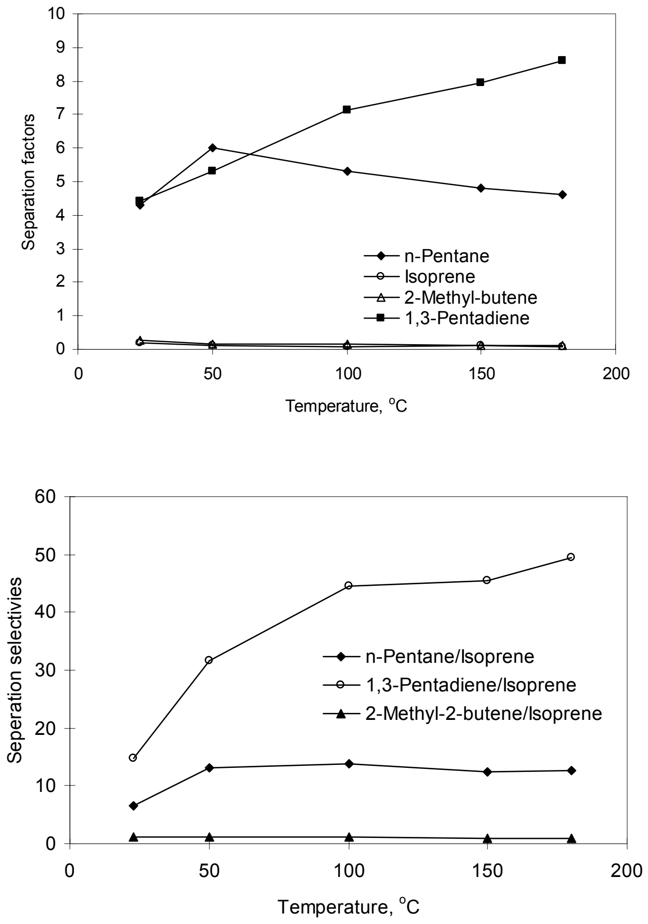


Figure 19: Results of separation for the quaternary mixture.

5. Conclusions for YR 4

High-quality MFI zeolite membranes were synthesized on tubular substrates by in-situ crystallization method. The membranes were demonstrated to be technically feasible for isoprene separation from mixtures containing n-Pentane (NP),1-3-Pentadiene (PD), 2-methyl-2-butene (MB) by vapor permeation.[16] During the separation, isoprene is concentrated in the retained stream as NP and PD can preferentially permeate through the membrane. The separation process appeared to be controlled by an adsorption-diffusion mechanism and the selectivity might be enhanced by operating at relatively high pressures and temperatures. The MFI membranes, unless further modified, is not suitable for separating IP from MB.

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