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Branched *vs.* Linear Hydrocarbon Separations with Novel Modified Zeolites

Tina M. Nenoff, Mutlu Ulutagay-Kartın, Kaylynn Johnston, Gary R. Gray, Manuel Arruebo, Richard D. Noble, Thomas M. Anderson

Sandia National Laboratories, Albuquerque, NM 87185
Goodyear Chemical, Akron, OH 44316
University of Colorado, Boulder, CO 80309
Burns & McDonnell, Kansas City, MO 64114

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DOE/Industrial Technologies Program (ITP)
Annual Review Meeting

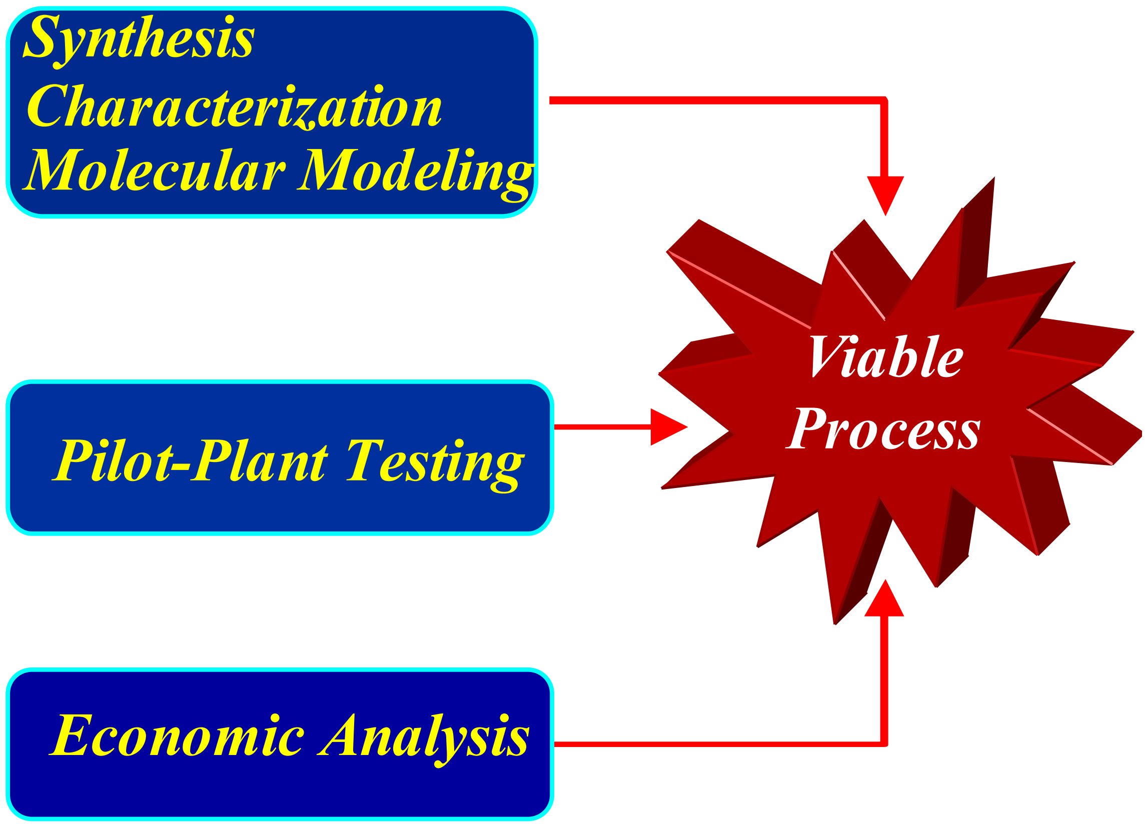
Research Team

Sandia National Laboratories
Tina M. Nenoff
Mutlu Ulutagay-Kartin
Marcus G. Martin

University of Colorado
Richard D. Noble
Manuel Arruebo

Goodyear Chemical
Gary Gray
Kaylynn Johnston

Burns & McDonnell
Tom Anderson



Branched *vs.* Linear Hydrocarbon Separations With Novel Modified Zeolites CPS# 1779

Goal: develop modified zeolite adsorbents and membranes for energy efficient purification of isoprene

Challenge: modified membranes show promise for isoprene purification, but need enhanced selectivity and lifetime for industrial streams

Benefits: replacement of energy intensive distillation columns with energy-efficient, durable ambient separations materials

Schematic: Nonselective porous membrane support w/ selective molecular sieve top layer in green.

Actual Membrane Supports

- *Ceramic*
- *Stainless steel*
- *Hybrid materials*

Potential End-User Applications: Isoprene purification; C_2-C_5,C_7 separations (Energy savings)

FY06 Activities (continuation funds): Evaluate membranes and powders using multicomponent streams; lifetime studies; enrichment goals of 7% for binaries & 3% for quaternary streams

Participants: Sandia National Labs, Goodyear Chemicals Co., Univ. CO, Burns & McDonnell

Tina M. Nenoff; tmnenof@sandia.gov

Branched *vs.* Linear Hydrocarbon Separations With Novel Modified Zeolites CPS# 1779

Barrier-Pathway Approach

Barriers

- low energy-efficiency distillation separations of isoprene feedstock from refinery mixture
- lack of high selectivity, long life, robust separations materials

Pathways

- development of modified zeolite adsorbents & membranes
- pilot bench-scale testing of bulk and membranes at Goodyear facilities
- simultaneous economic analysis for implementation of technology

Critical Metrics

- Isoprene: 7% enrichment translates to 12% Energy savings; baseline for implementation
- translation of technology to C_2-C_5, C_7 stream purifications

GPRA FY2007 (est.)

Isoprene Benefits	2020/year
Energy Savings	5 trillion Btu
Cost Savings	$67 MM
Carbon Reduction	0.07 MM TCE

Tina M. Nenoff; tmnenof@sandia.gov

DOE/ITP Project Funding

"Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations"

Collaborative Research

238K/yr OIT/IMF "Direct to SNL"
188K/yr Goodyear "In-Kind"
120K/16 mo. Univ, of Colorado via SNL
10K/yr Burns & McDonnell "In-Kind"

$1.3M / 3yr program (FY02-04)
50% "in-kind" industry funding,
commenced 4/23/2002.

Tina M. Nenoff; tmnenof@sandia.gov

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Goodyear/Sandia/UC/B&M Project Milestones

Milestones (current project)

- ✓ Yr1: Zeolite Modification and testing; Go/No Go
  Initial Economic Analysis
- ✓ Yr2: Selection of "best" modified zeolite through
  characterization and testing; modification optimization
- ✓ Yr3: Pilot Plant testing, material modification;
  In-depth economic calculations; Engineering Analysis

Commercialization Plans, pathways, risks (ie., FY06-09):

target enrichments, figures of merit identified
lifetime studies of modified zeolites (bulk vs. membranes)
with binary and quaternary gas mixes
Go-No/Go decisions of membrane vs. adsorbents
Module design, building & testing
Partnerships: end users, module builders, economic analysis

Potential Energy Benefits to U.S. Chemical Industry

- Goodyear is the domestic leader in isoprene production (60%)
- Economic Modeling from Burns & McDonnell shows 22% reduction in Energy of Isoprene Process Using modified Zeolites (membranes)
- Reduced environmental emissions:

  steam generation; feedstock/raffinate transportation; VOC's, COx's, NOx's

- Extrapolation to C_2-C_5 industries predicts 64 Trillion BTU's savings (Burns & McDonnell):

		Btu/yr Trillion	2002 Billion lbs	Btu/lb.
Ethylene-	C2	214	53	4,058
Propylene-	C3	53	39	1,359
Butadiene-	C4	21	4	5,366
Isoprene-	C5	5	0.4	8,000+
Total		293		

22 % Reduction

64 Trillion Btu's

Source: CMAI - 2003
DOE/OIT Energy & Environ. Profile 2002

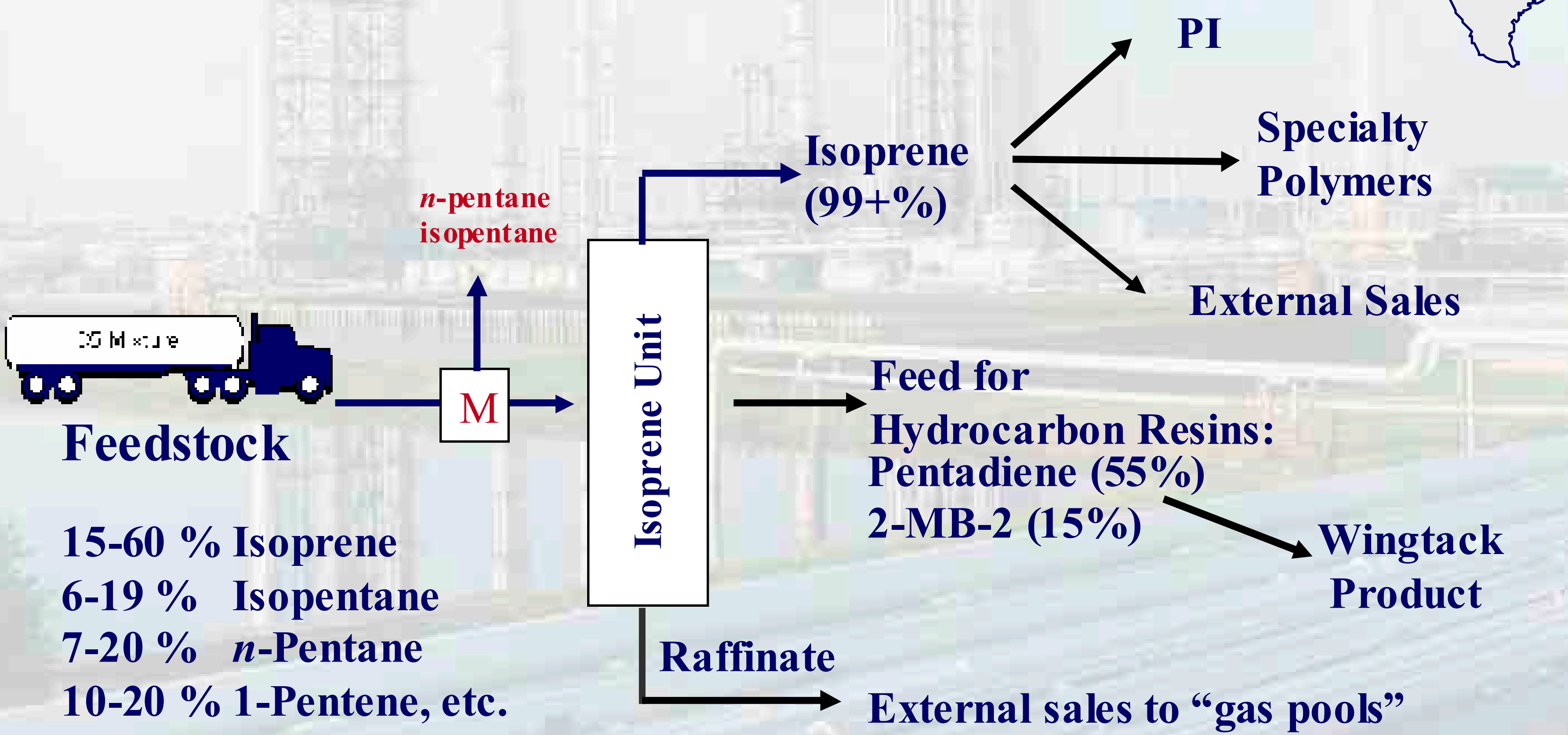
Tina M. Nenoff; tmnenof@sandia.gov

Current *vs.* Proposed Technology

Currently extractive and cryogenic distillations are the dominant separation technologies

Objective: Reduced Energy Consumption Using Membranes

Current Isoprene Monomer Technology
Proposed Isoprene Monomer Technology



M = Membrane Location

Goals

Overall goal: develop novel modified zeolites for energy efficient hydrocarbon (HC) separations

Focus:

surface control + framework modification =
selectivity (adsorption + molecular sieving)

Develop new separation-based adsorbents or membrane materials *via* "modification of commercially-available zeolites"

Establish zeolite structure-property models for this technology & others (C_2-C_5)

Decrease energy consumption in the chemical & petroleum industries by employing these new & improved materials

Tina M. Nenoff; tmnenof@sandia.gov

Experimental

- ***Preparation of Zeolites:*** Bulk zeolites variations of framework and cations. Membranes hydrothermally synthesized, seeded growth methods.
- ***Bulk Carbonization*:*** The regenerated zeolites are carbonized by exposure to an inert carrier gas stream containing binary mixture of hydrocarbon at elevated temperatures.
- ***Characterization:*** The effect of bulk carbonization on pore size and acid sites studied with BET and NH_3-TPD. Structures studied by XRD, ICP-MS & TGA.
- ***Separation Experiments:*** Pure and mixed gases at varying temperatures; bulk and membranes. RGA and GC used for permeation analyses.
- ***Economic Analysis:*** Economic calculations of energy and transportation savings for isoprene separation from a hydrocarbon stream are being evaluated by Burns and McDonnell.
- ***Modeling:*** Determination of Adsorption Isotherms underway.

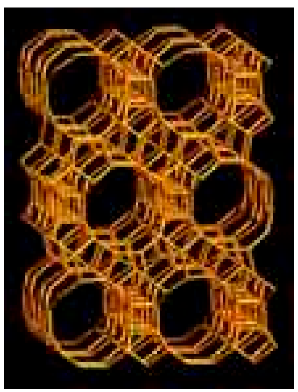
Tina M. Nenoff; tmnenof@sandia.gov

*** US Patent Pending: Nenoff, Thoma, Kartin; submitted 4/03**

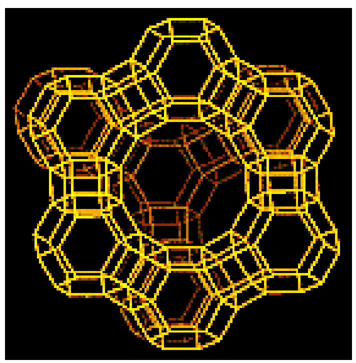
Results- Bulk Zeolites

Zeolite type	**Relative acidity**	**Pore diameter (Å)**
Zeolite-β (BEA)	high	6.6 x 7.7, 5.6
Zeolite-Y (FAU)	medium-high	7.4
Zeolite-L (LTL)	low	7.1
ZSM-5 (MFI)	high	5.1 x 5.5; 5.3 x 5.6

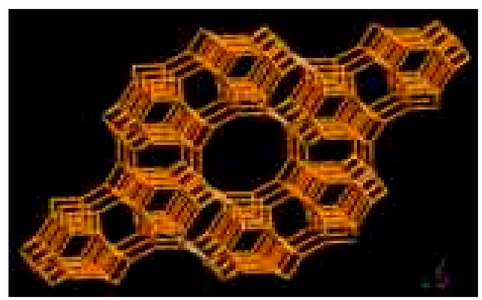
HC type	**Kinetic diameter (Å)**
n-pentane	5.1
isoprene	5.5



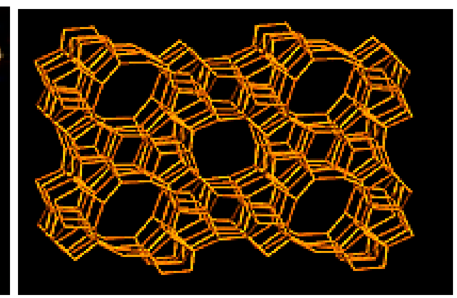
BEA
12 MR (3-D) straight pores



FAU
12 MR (3-D, cages) intersecting straight pores



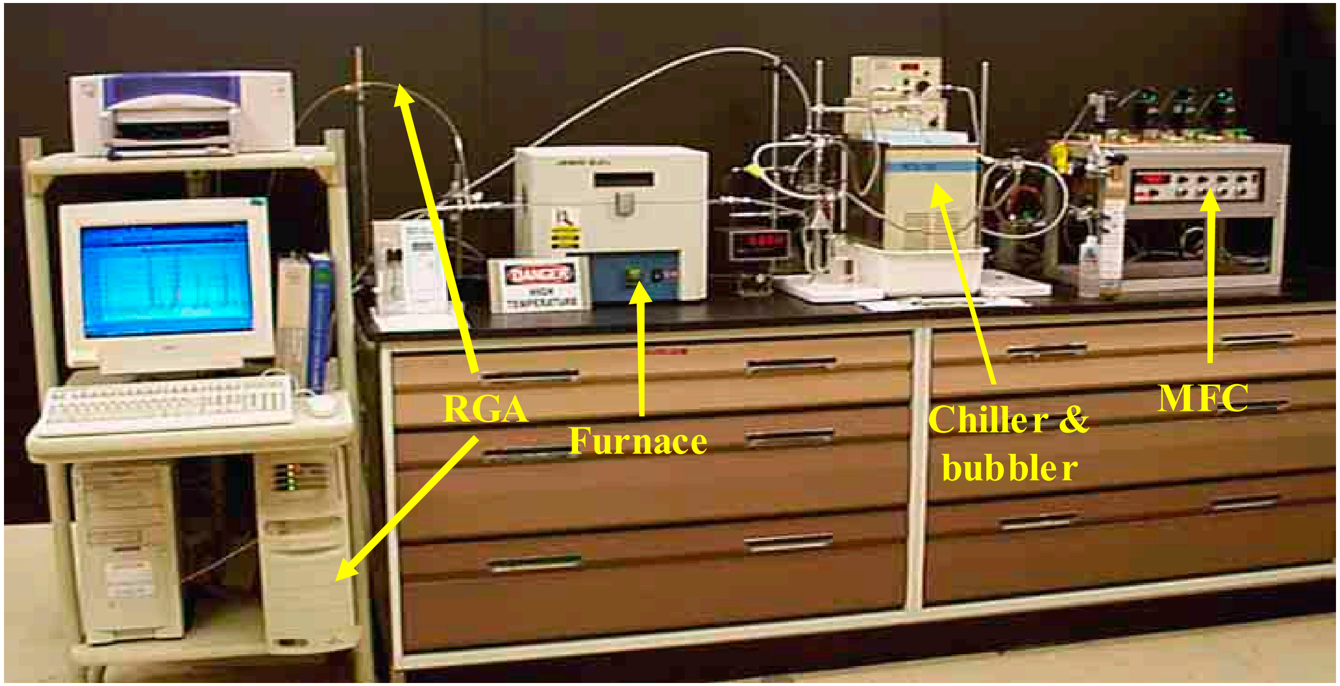
LTL
12 MR (1-D) straight pores



MFI
10 MR (3-D), Intersecting straight / sinusoidal pores

Tina M. Nenoff; tmnenof@sandia.gov

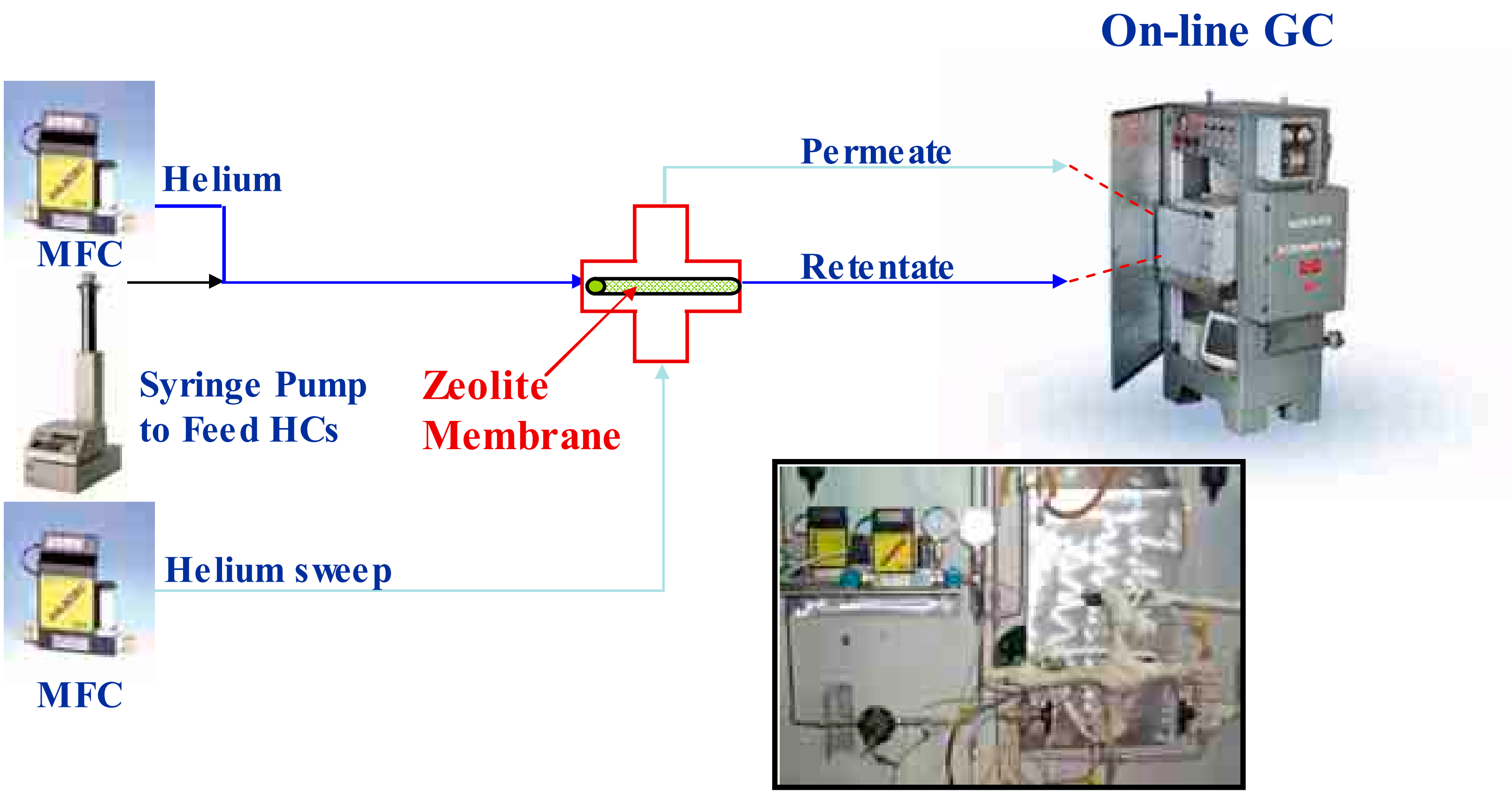
Bench Scale Reactor-Surface Modification



Sandia bulk modification unit

Tina M. Nenoff; tmnenof@sandia.gov

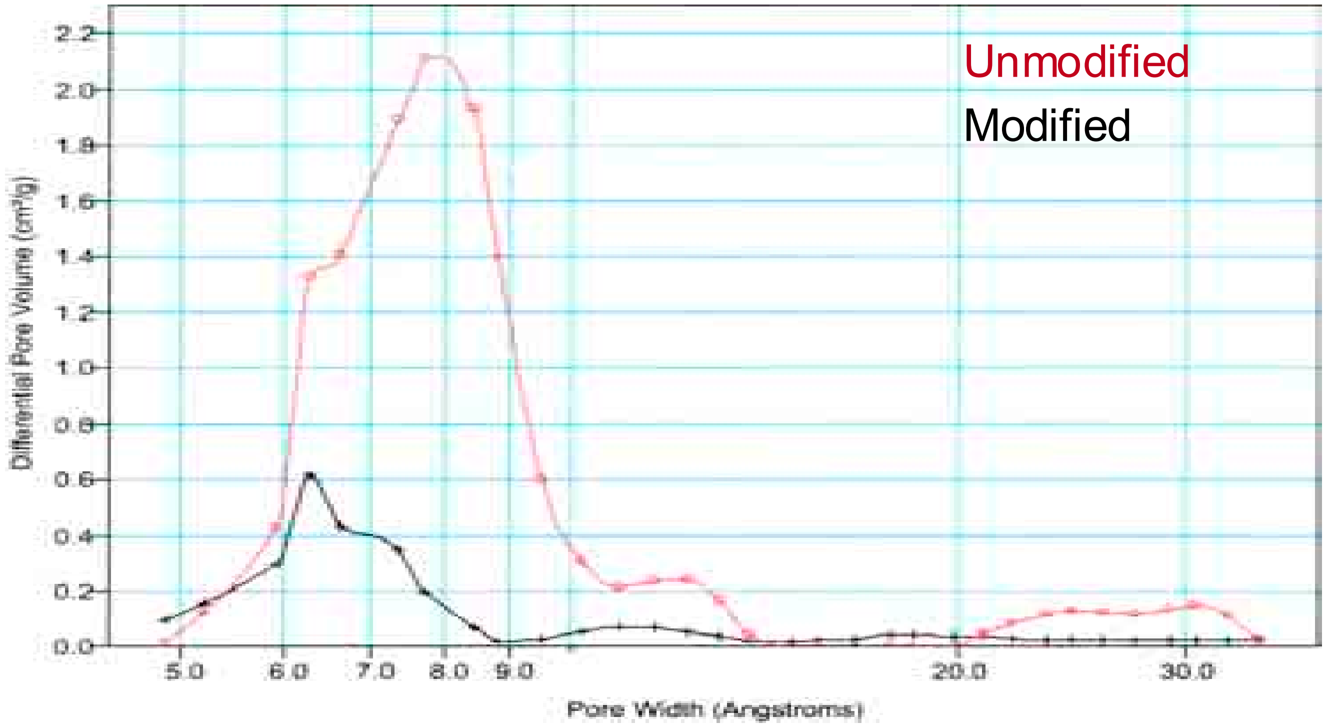
Pilot-Scale Industrial Reactor



Goodyear separation unit

Tina M. Nenoff; tmnenof@sandia.gov

Characterization of Bulk Modified and Unmodified Zeolites



Micropore area measurements of modified *vs.* unmodified Na-Y samples. Pore size and pore volume reduction are monitored by the adsorption of N_2 at 77 K

Tina M. Nenoff; tmnenof@sandia.gov

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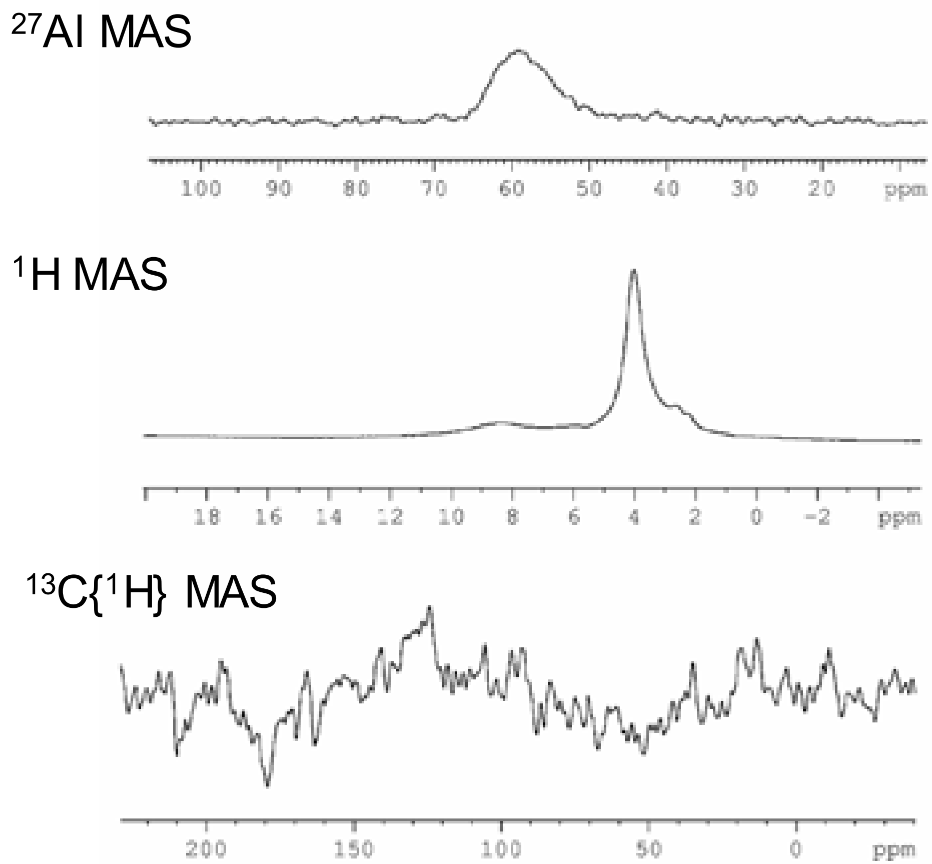
Characterization of Modified Zeolite Membranes (NMR*)

- ^{27}Al MAS NMR
  - Tetrahedral $AlO_{4/2}$
- ^{1}H MAS
  - H_2O, Si-OH sites
  - Minor, unknown organics
- $^{13}C\{^{1}H\}$ MAS
  - Broad resonance consistent with char

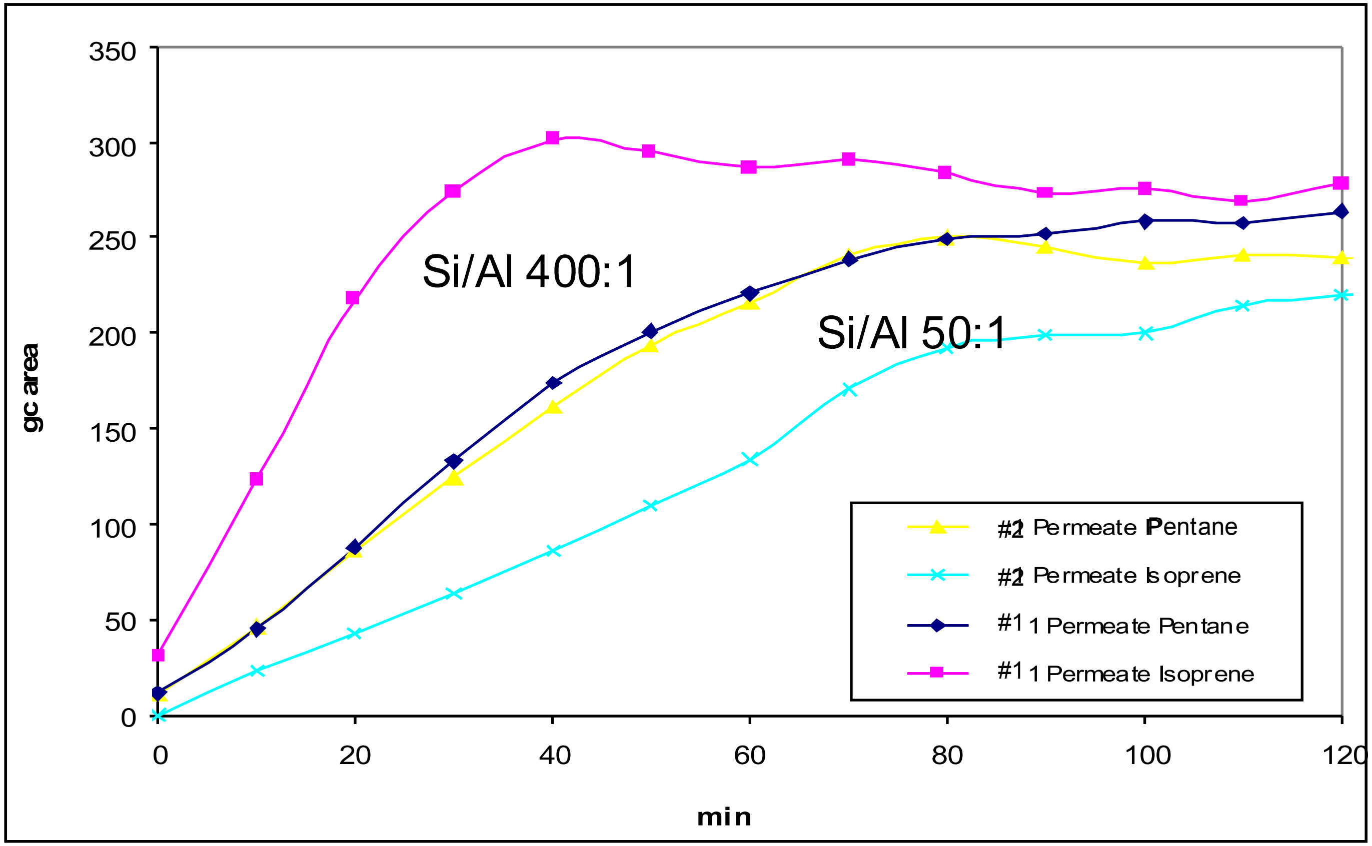


*Robert Maxwell, LLNL

Tina M. Nenoff; tmnenof@sandia.gov

Pilot Scale Testing of Unmodified ZSM-5 with Different Si/Al Ratios

Unmodified Bulk ZSM-5 Separation Experiments



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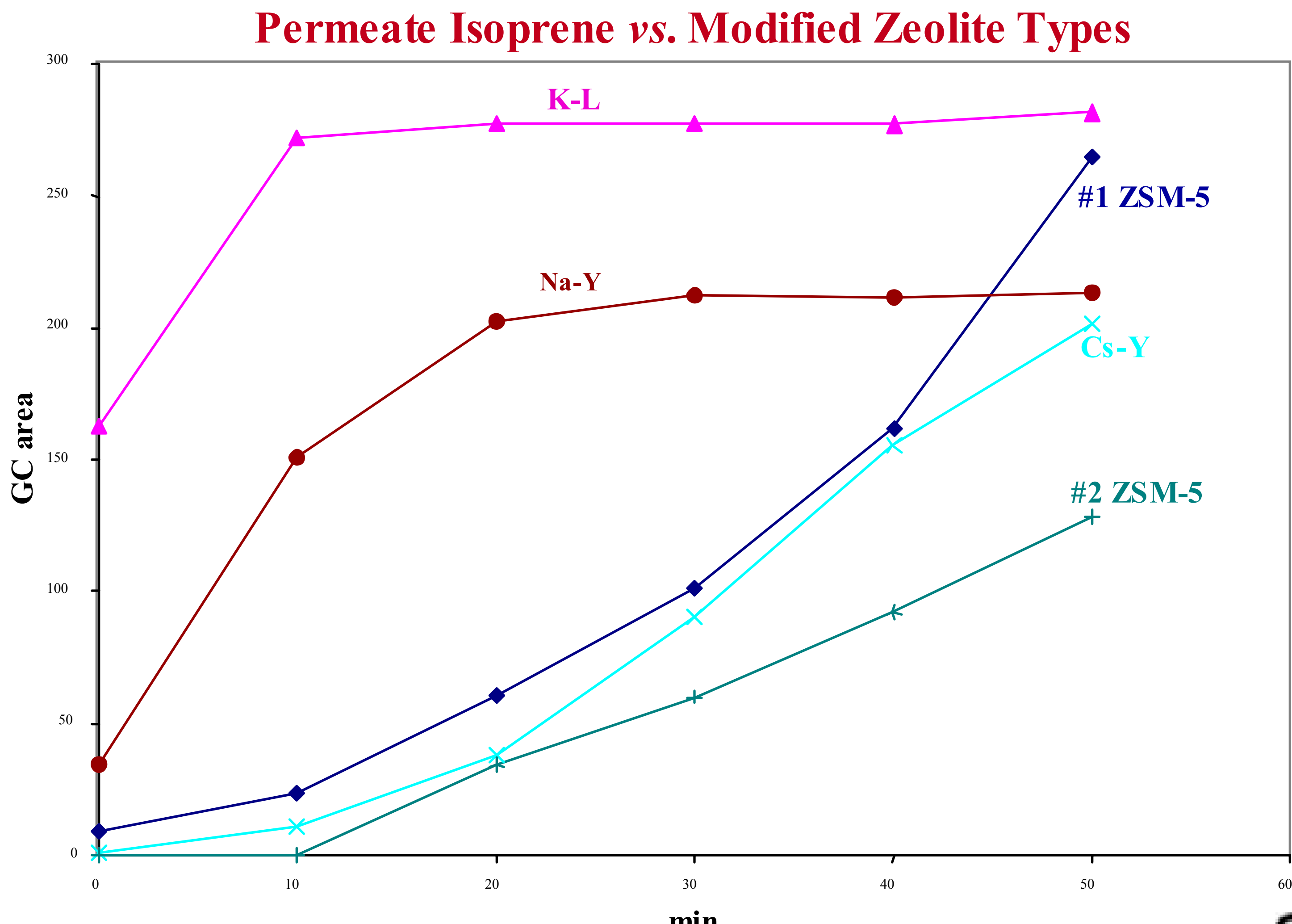
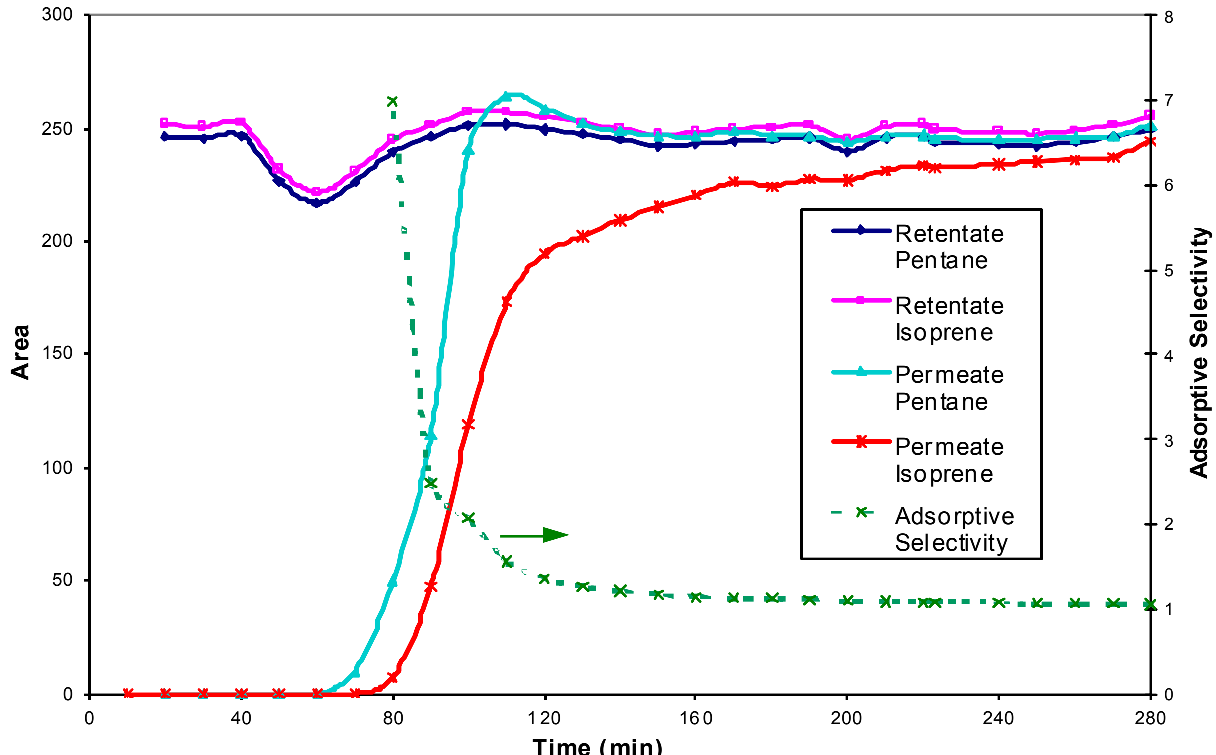
Pilot Scale Testing of Various Bulk Modified Zeolites



Tina M. Nenoff; tmnenof@sandia.gov

Longer time to desorb isoprene : 50:1 (#2 ZSM-5)

Pilot Scale Adsorption Selectivity Testing of Modified ZSM-5

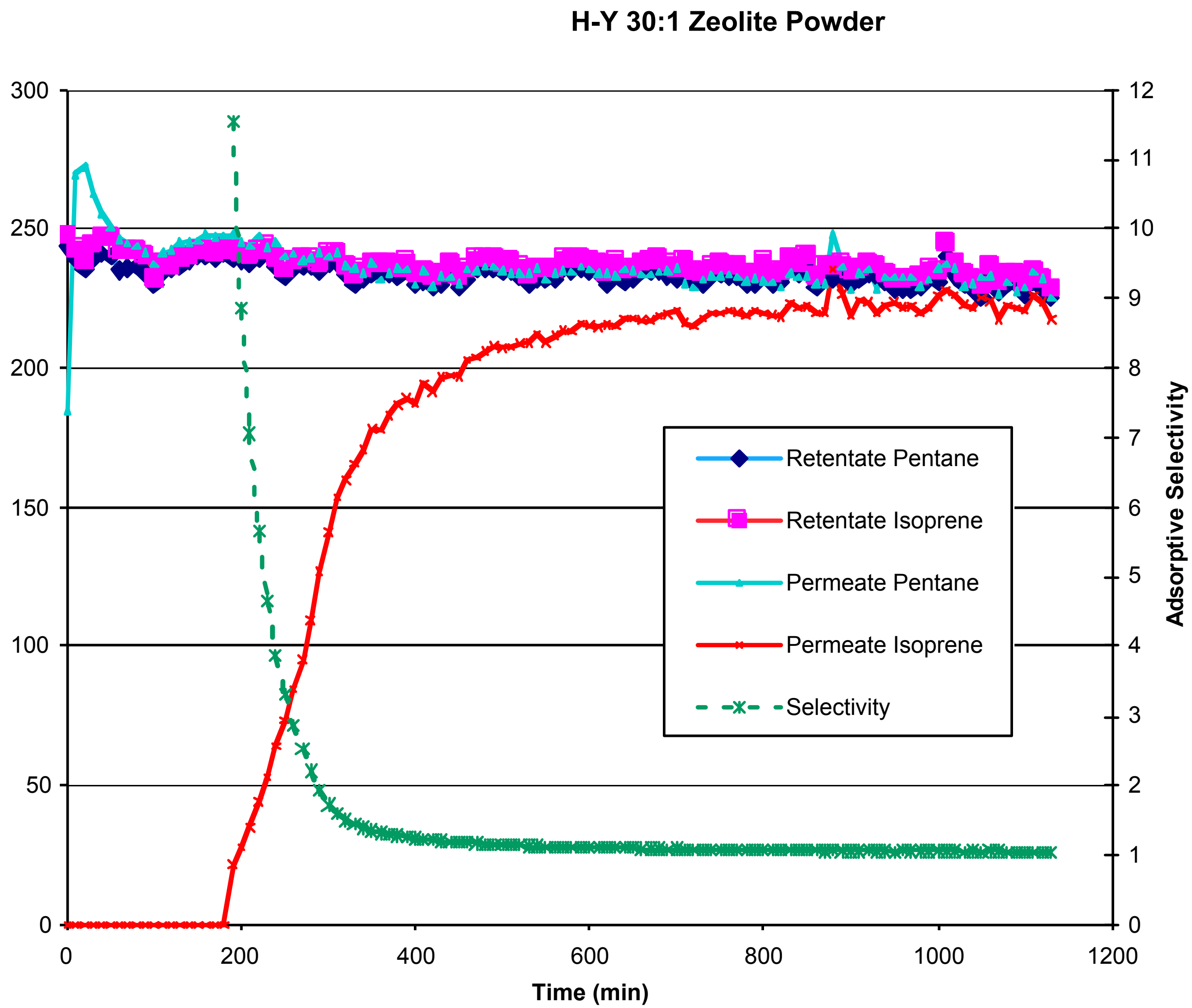


Demonstrated isoprene/pentane separation using modified zeolite in dilute concentrations

Initial experiments show selectivity towards isoprene separation

Tina M. Nenoff; tmnenof@sandia.gov

Pilot Scale Testing of Modified Protonated ZSM-5



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H-Y 30:1 Powder @100C, 50/50 n-pentane/isoprene

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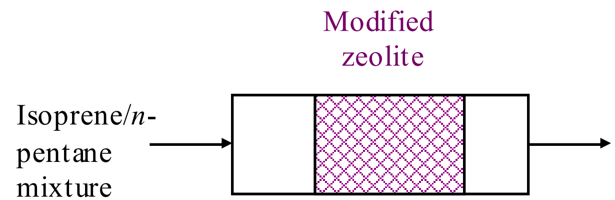
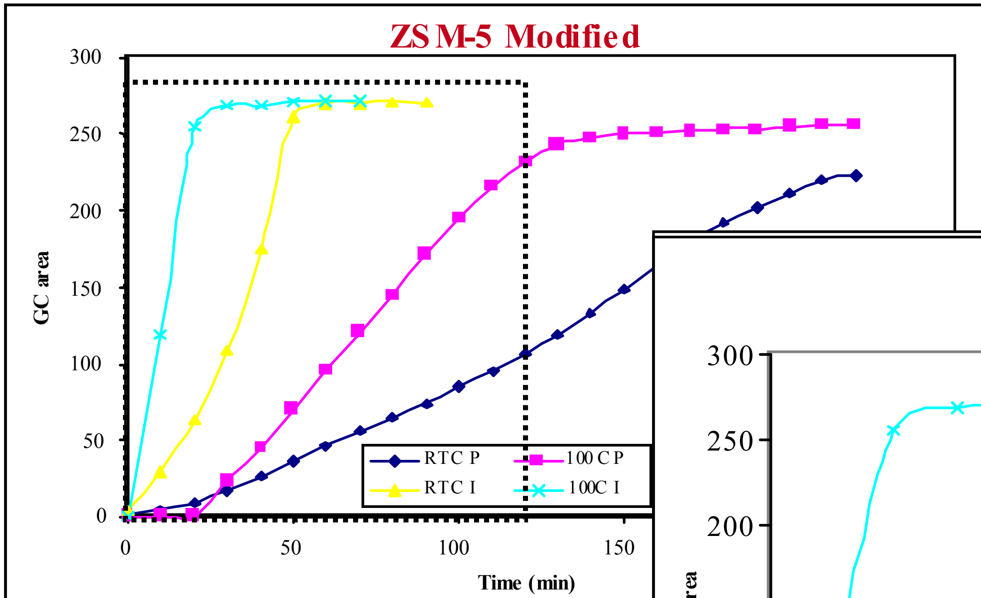
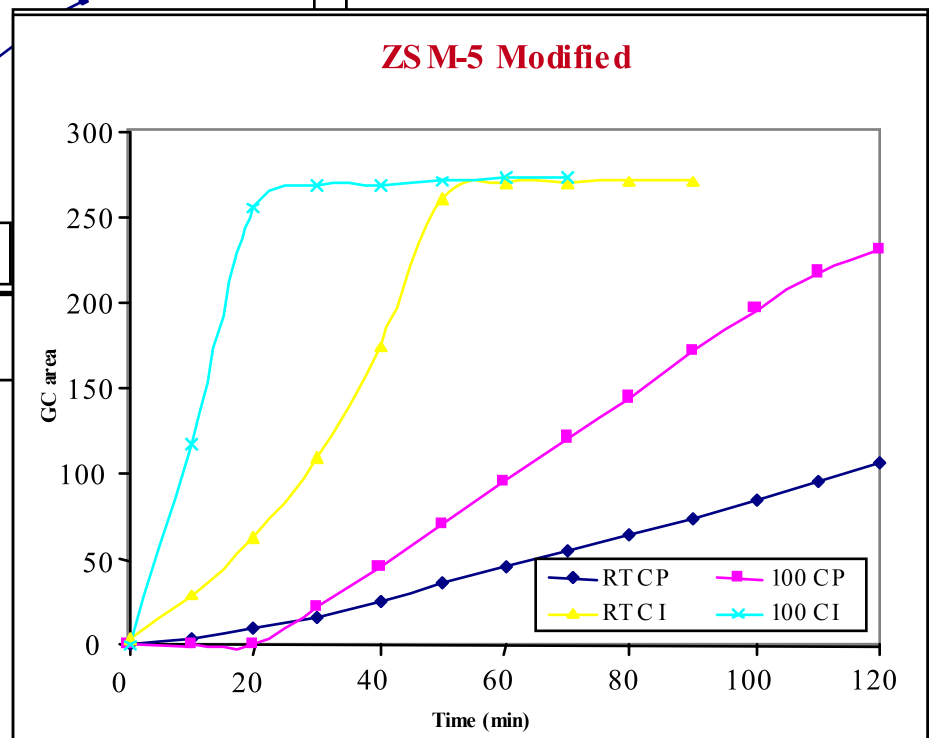
Pilot Scale Testing of Bulk Modified ZSM-5 *vs.* Temperature







Temperature optimization studies continue

Tina M. Nenoff; tmnenof@sandia.gov

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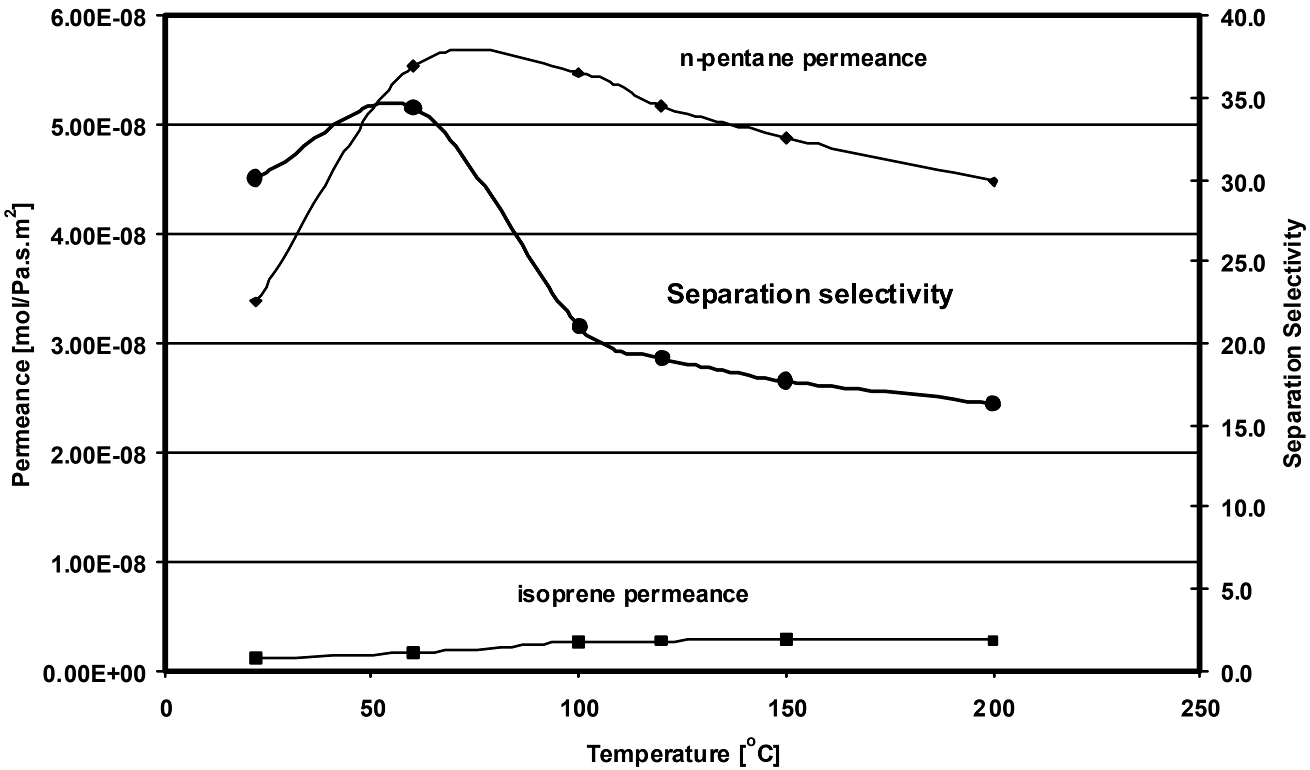
Pilot-Scale Tubular Membrane Testing on Various Temperatures



Initial separation experiments (≈3% enrichment) on tubular membranes demonstrate the possibility of isoprene/*n*-pentane separation

Pilot-Scale Modified Zeolites on Tubular Membrane

Temperature	MK-7-37 Permeance (mol/Pa-s-m2)	MK-7-39
25	#N/A	3.00E-08
23.5	3.50E-08	#N/A
60	5.30E-08	#N/A

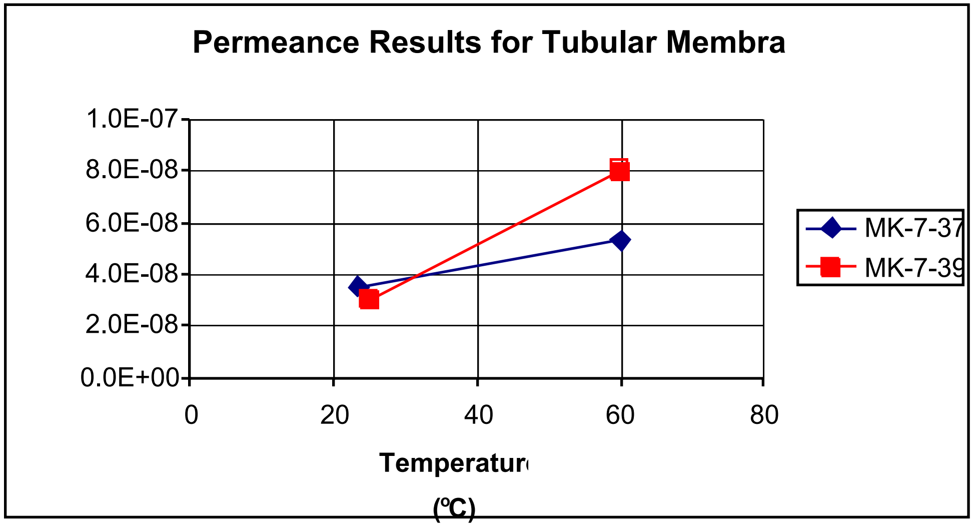
Process Info

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)



⇒ Similar pentane permeance values as previously reported but with zero isoprene permeance! Results: 4.1% enrichment

Tina M. Nenoff; tmnenof@sandia.gov

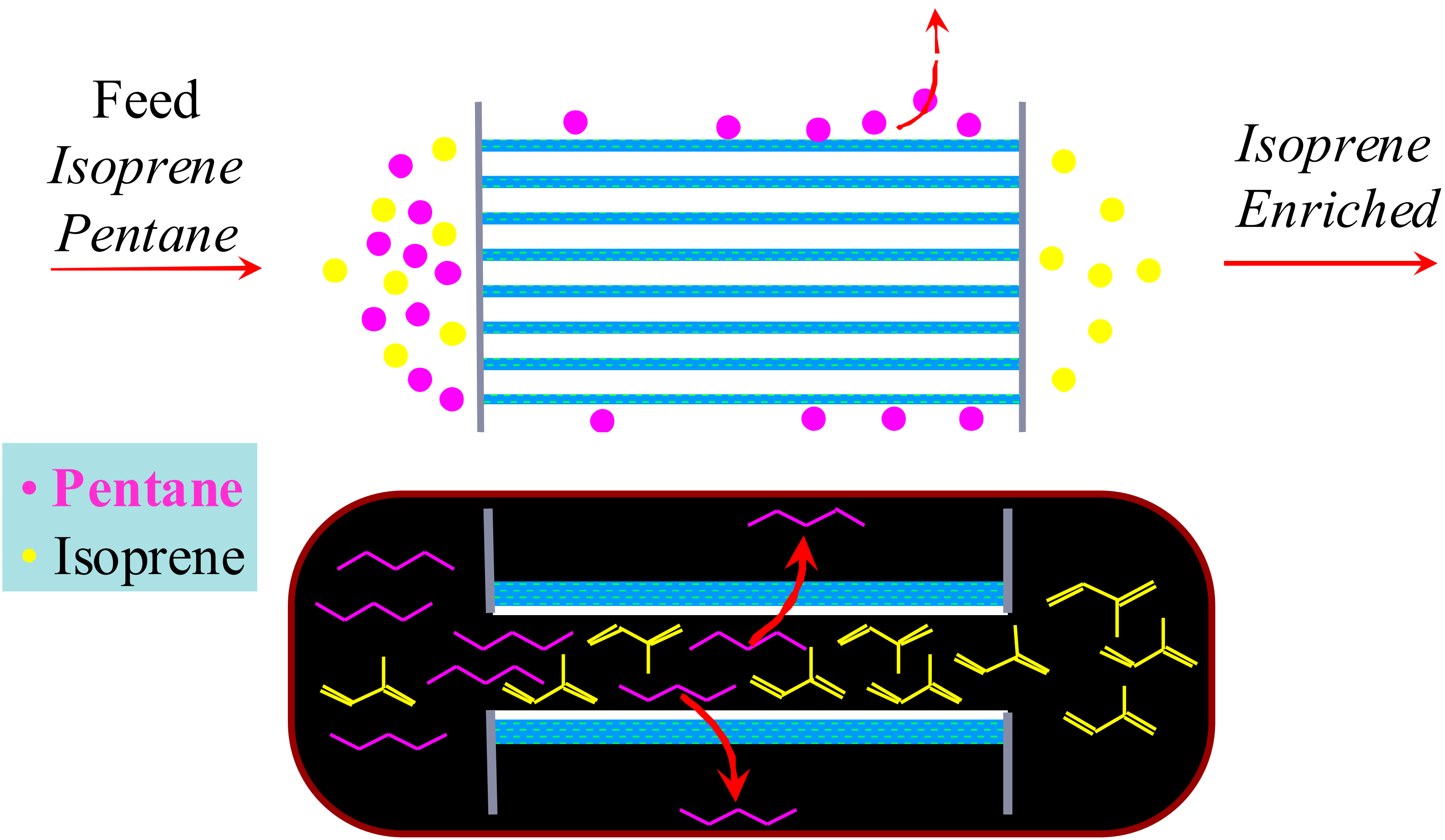
Economic Analysis Based on Membrane Separation Results

Separation Performance	% isoprene enrichment	% Energy Savings
Base	*0*	*0*
Demonstrated	3.0	6
Best case to date	4.1	7.8
Goal	6.7	12

Realistic and possible!

Possible Module Design

Enhanced Selectivity: Molecular Sieving + Adsorption



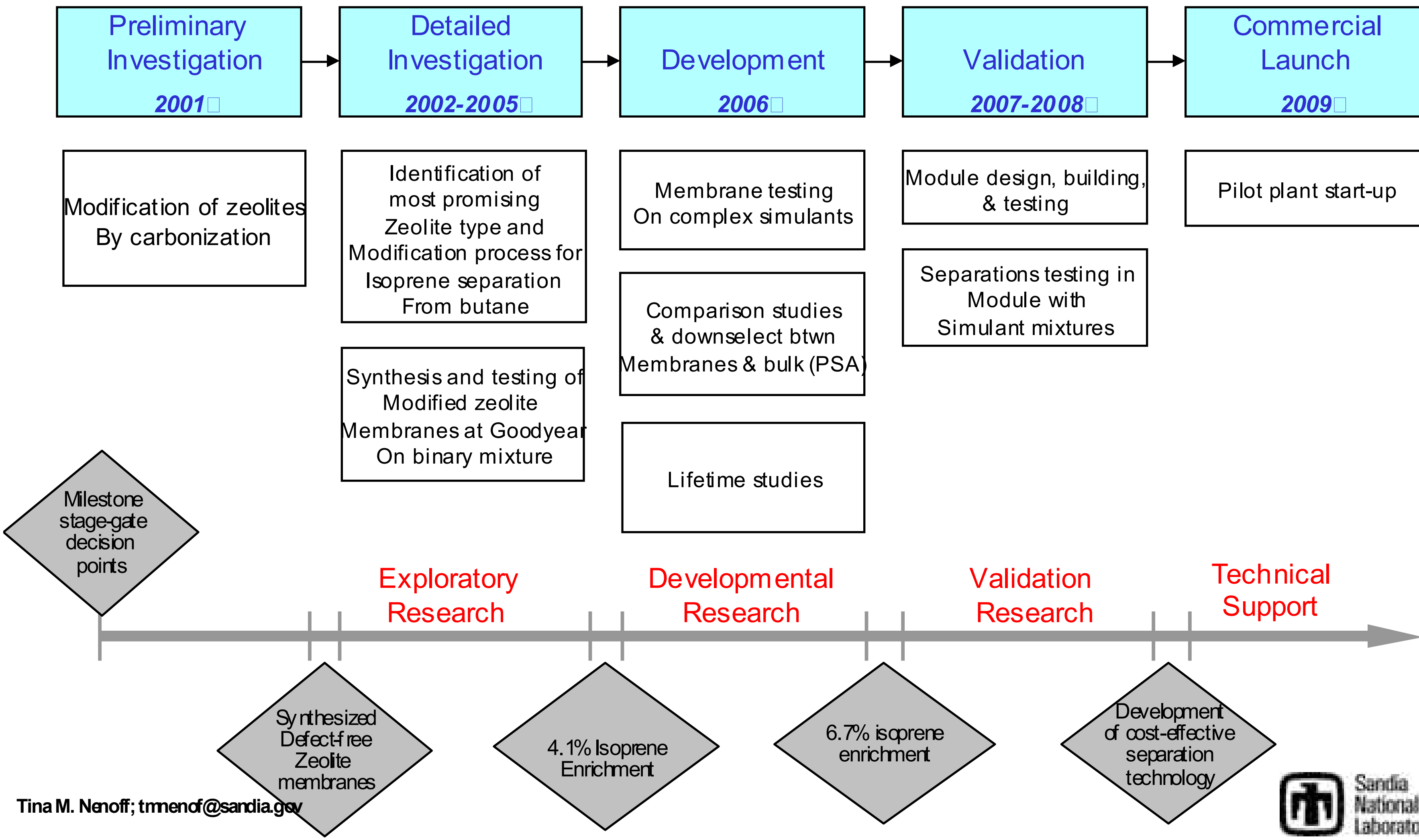
Tina M. Nenoff; tmnenof@sandia.gov

Conclusions

- Adsorption/desorption on bulk unmodified zeolites showed isoprene adsorbed by zeolite-L and n-pentane adsorbed by zeolite-Y and ZSM-5.
- Bulk carbonization is used to passivate zeolite activity toward organic adsorption/decomposition.
- Based on the bulk modified zeolite separation results, we have determined that the MFI type has the most potential for isoprene enrichment.
- Modified MFI type membranes are are jointly made by Sandia and the Univ. of Colorado. Separation experiments are performed by Goodyear Chemical.
- Isoprene/*n*-pentane separations have been demonstrated by using both zeolite membranes and modified bulk zeolites at various temperatures on the Goodyear Pilot-scale unit.
- Target zeolite membrane separations values of **6.7% isoprene enrichment** have been established by economic analysis calculations by Burns & McDonnell.

Tina M. Nenoff; tmnenof@sandia.gov

Project Timeline - Proposed



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- Modeling of Adsorption Isotherms: Dr. Marcus Martin, SNL
- MAS NMR : Dr. Robert Maxwell, LLNL

- For more info: www.sandia.gov/nenoff