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Project Objective: The objective of this project is to explore the application of the company's proprietary mesoporous zeolite technology to large-scale, energy-intensive separations in the chemical industry, specifically propane and propylene separation. Rive Technology proposes to achieve these objectives by producing zeolitic materials with different degrees of mesoporosity and testing these materials in a bench-scale unit to generate kinetic and equilibrium separation data. Upon completion of the project, Rive will have demonstrated applicability of the technology in the process with sufficient experimental results and modeling data to interest partners in working with us to translate the technology into commercial use.

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Table of Contents

• Executive Summary	Page 6
• Introduction	Page 7
• Materials Preparation and Characterization	Page 11
• Pulse Test Unit and Adsorbent Testing	Page 22
• Energy Saving Calculation	Page 44
• Conclusions	Page 55
• Patents/Publications	Page 56
• References	Page 56
• Appendix	Page 58

List of Figures and Tables

Figure 1	TEM micrographs showing a zeolite before (left) and after (right) the incorporation of mesopores	Page 8
Figure 2	Catalytic performance of catalysts based on a meosoporous zeolite (RiveCat) and a conventional zeolite	Page 9
Figure 3	Cumulative and pore size distribution of rived and unrived Y zeolite (top) and pore volume dependence on citric acid amount (bottom)	Page 12
Figure 4	XRD powder diffraction patterns of unrived and rived Na-Y (CBV100) samples at different citric acid treatment levels	Page 13
Figure 5	Effect of pH on crystallinity of NaY, NaX and NaA zeolites	Page 13
Figure 6	XRD powder pattern of unrived and rived X samples at different levels of citric acid treatment	Page 14
Figure 7	Argon adsorption isotherms and the corresponding DFT cumulative and differential pore size distribution of an unrived 5A zeolite (blue)) and rived 4A zeolites by the normal riving procedure (red) and the modified procedure (green)	Page 15
Figure 8	TEM images of an unrived NaA zeolite crystal. The picture on right is a digital blown-up of the blue box region in the picture on the left	Page 16

Figure 9	TEM images of a rived Na-A sample by the normal procedure. The picture on right is a digital blown-up of the blue box region in the picture on the left	Page 17
Figure 10	TEM images of a rived Na-A sample by the modified procedure. The picture on right is a digital blown-up of the blue box region in the picture on the left	Page 17
Figure 11	Cumulative and differential pore size distribution of NaY rived with NaOH and NH ₄ OH	Page 18
Figure 12	Micropore and mesopore (20-80 Å) volumes of rived NaX showing that ~10g of 50% NaOH per 100 g of starting NaX zeolite is optimal. Similar effects were also found for riving of NaY and NaA zeolites	Page 18
Figure 13	Current preparation process scheme for laboratory adsorbent particles	Page 20
Figure 14	A schematic of the pulse test unit built and used in this project	Page 22
Figure 15	Comparison of Pulse Test Experiments on Commercial NaX(left) and Rived NaX (right) at 50°C, 100 mL/hr, and 25% feed	Page 25
Figure 16	Comparison of pulse test results on Commercial NaX (left) and Rived NaX (right) at 50°C, 100 mL/hr, and 4% feed	Page 27
Figure 17	Arrhenius plot showing temperature dependence of C ₃ H ₆ transport in Rived and Unrived NaX zeolites	Page 30
Figure 18	Propylene adsorption isotherms on Commercial NaX (top), Rived NaX (middle), and In-house UnRived NaX (bottom) zeolites	Page 33
Figure 19	Propane adsorption isotherms on Commercial NaX (top), Rived NaX (middle), and In-house Unrived NaX (bottom)zeolites	Page 34
Figure 20	Pulse test results on UnRived NaY zeolite (left) and Rived NaY zeolite (right) at 50°C, 100 mL/hr, and 25% feed concentration	Page 36
Figure 21	Pulse test results on UnRived NaY zeolite (left) and Rived NaY zeolite (right) at 50°C, 100 mL/hr, and 4% feed concentration	Page 36
Figure 22	Arrhenius plot showing temperature dependence of C ₃ H ₆ and C ₃ H ₈ transport in Rived and Unrived NaY zeolites	Page 39
Figure 23	Propylene adsorption isotherms on Rived NaY (top) and Unrived NaY (bottom)	Page 41
Figure 24	Propane adsorption isotherms on Rived NaY (top) and Unrived NaY (bottom)	Page 42
Figure 25	Schematic of True Moving Bed adsorption system and corresponding liquid composition profiles	Page 44

Figure 26	Schematic of Simulated Moving Bed adsorption system	Page 45
Figure 27	Schematic of a hypothetical integrated 4-bed SMB unit for processing 6000 BPSD C_3 stream	Page 47
Figure 28	Region of complete separation in the (m_2, m_3) plane, $K_A = 1.5$, $y_A^F = 0.175$, $K_B = 0.2$, $y_B^F = 0.075$, $K_D = 2.0$, $y_D^F = 0.75$	Page 48
Table 1	Micropore and mesopore volumes of rived and unrived NaX	Page 14
Table 2	Properties of the unrived and rived Na-A zeolite samples compared to unrived and rived Na-Y samples	Page 16
Table 3	Properties of unrived and rived A zeolites	Page 19
Table 4	Properties of the zeolites and the adsorbent particles prepared from the corresponding zeolites	Page 20
Table 5	Packed column properties for different adsorbents	Page 23
Table 6	Test conditions for all adsorbents	Page 24
Table 7	Tabulated pulse test results for Commercial NaX (top), In-house Unrived NaX (middle), and Rived NaX (bottom)	Page 28
Table 8	Tabulated pulse test results for In-house Unrived NaY (top) and Rived NaY (bottom) adsorbents	Page 37
Table 9	Calculations for a hypothetical SMB process: Subscripts F = Feed, R = Raffinate, D = Desorbent, E = Extract	Page 50
Table 10	Comparison of energy savings of SMB process using hexane (top), pentane (middle), and iso-pentane (bottom) as desorbent. Last column are corresponding numbers for conventional C_3 splitter	Page 52

Executive Summary:

Due to the very small relative volatility difference between propane and propylene, current propane/propylene separation by distillation requires very tall distillation towers (150-250 theoretical plates) and large reflux ratios (up to 15), which is considered to be the most energy consuming large-scale separation process. Adsorptive separation processes are widely considered to be more energy-efficient alternatives to distillation. However, slow diffusion kinetics/mass transport rate through the adsorbent bed often limits the performance of such processes, so further improvements are possible if intra-particle mass transfer rates can be improved.

Rive Technology, Inc. is developing and commercializing its proprietary mesoporous zeolite technology for catalysis and separation. With well-controlled intracrystalline mesoporosity, diffusion kinetics through such mesoporous zeolite based catalysts is much improved relative to conventional zeolites, leading to significantly better product selectivity. This “proof-of-principle” project (DE-EE0003470) is intended to demonstrate that Rive mesoporous zeolite technology can be extended and applied in adsorptive propane/propylene separation and lead to significant energy saving compared to the current distillation process.

In this project, the mesoporous zeolite Y synthesis technology was successfully extended to X and A zeolites that are more relevant to adsorbent applications. Mesoporosity was introduced to zeolite X and A for the first time while maintaining adequate adsorption capacity. Zeolite adsorbents were tested for liquid phase separation performance using a pulse flow test unit and the test results show that the separation selectivity of the mesoporous zeolite adsorbent is much closer to optimal for a Simulated Moving Bed (SMB) separation process and the enhanced mesoporosity lead to >100% increase of overall mass transport rate for propane and propylene. These improvements will significantly improve the performance of an adsorptive separation unit for propane/propylene separation compared with traditional zeolite adsorbents. The enhanced transport will allow for more efficient utilization of a given adsorbent inventory by reducing process cycle time, allowing a faster production rate with a fixed amount of adsorbent or smaller adsorbent inventory at a fixed production rate. Smaller adsorbent inventory would also lead to significant savings in the capital cost due to smaller footprint of the equipments.

Energy consumption calculation, based on the pulse test results for rived NaX zeolite adsorbent, of a hypothetical moderate-scale SMB propane/propylene separation plant that processes 6000 BPSP refinery grade propylene (70% propylene) will consume about 60-80% less energy (both re-boiler and condenser duties) compared to a C3 splitter that process the same amount of feed. This energy saving also translates to a reduction of 30,000-35,000 tons of CO₂ emission per year at this moderate processing rate. The enhancement of mass transport achievable by introduction of controlled mesoporosity to the zeolite also opens the door for the technology to be applied to several other adsorption separation processes such as the separation of xylene isomers by SMB, small- and large scale production of O₂/N₂ from air by pressure swing adsorption, the separation of CO₂ from natural gas at natural gas wellheads, and the purification of ultra-high purity H₂ from the off gas produced by steam-methane-reforming.

Introduction:

Propane and propylene separation is currently achieved by distillation process. This process (C3 split) is often cited as the most energy-consuming separation operation.[1] About half of the propylene produced in the US (~41 billion pounds/year) comes from C3 splitters in petroleum refineries (the other half as co-product from ethylene plants, i.e. steam crackers). The main source of propylene within oil refineries is from fluid catalytic cracking units (FCCU) for production of gasoline. “Refinery Grade Propylene” typically contains ~70% propylene (balance being propane and trace impurities). Due to the very small relative volatility between propane and propylene (b.p. -43 and -48 °C at 1 atm, respectively), separation of the two by distillation requires very large towers and high reflux ratios. Chemical Grade Propylene (92-94% purity) and Polymer Grade Propylene (>99.3% purity) are the main products from the C3 splitters, the latter being preferred due to its higher market demand and economic value. In the front-end energy consumption calculation carried out by Adsorptech (Appendix), a hypothetical refinery C3 splitter producing 40 million pounds of Polymer Grade Propylene per year would require 2790 BTU/lb propylene in reboiler duty and 2774 BTU/lb propylene in condenser duty.

This situation has spurred advanced research in more energy efficient separation methods over the last several decades—especially alternatives to distillation—much of it through DOE/OIT-industry collaborations or other government funding. These alternatives include gas phase pressure swing adsorption (PSA),[2, 3] vacuum swing adsorption (VSA),[4, 5] kinetic adsorption separation,[6] and simulated moving bed (SMB) adsorption.[7] The traditional PSA and VSA systems have been found to suffer from large mass transfer resistances leading to long step cycles in the VSA case, and poor propylene recoveries (<30%) in the PSA and kinetic separation cases.[8] The SMB process has attracted attention for this separation as it has been successfully applied to a number of large petrochemical separation processes such as *p*-xylene separation from its isomers, *n*-paraffins from branched and cyclic hydrocarbons, olefins from paraffins, glucose-fructose separation in the sugar processing industry, and several new applications in the pharmaceutical and fine chemical industries.[8]

Assuming the adsorptive separation technology under this development (specifically the SMB process utilizing the mesoporous zeolite based adsorbents) can fully satisfy the requirements for product purity (99.5% propylene) and productivity (40 million lbs propylene per year), the front-end energy consumption calculation (Appendix) showed that the energy consumption would be reduced to 666 BTU/lb propylene in reboiler duty and 656 BTU/lb propylene in condenser duty, roughly 75% reduction.

Zeolites are microporous crystalline aluminosilicates having pores of molecular dimensions, typically <12 Å (thus the name “molecular sieves”). Due to their unique porous properties (uniform and regular pore sizes, high surface areas, strong acidities and high thermal/hydrothermal stability), they are widely used in ion-exchange, adsorption, separation and catalytic applications. However, the micropores can impose diffusion limitations due to the restricted access and slow mass transport to and from active sites located within the micropores. This phenomenon represents the major drawback in most industrial applications of zeolites, especially in catalytic reactions such as fluid catalytic cracking. In adsorptive

separation processes, the narrow size of the micropores could also limit the diffusion of the molecules that need to be separated, reducing the flow and increasing the energy needed to maintain good production. A typical solution to this problem is to optimize the size (and shape) of the zeolite crystals and the adsorbent particles to reduce diffusion path length. However, there is a practical limitation on how small the crystals (and more importantly the adsorbent particles) can be because of increasing difficulty in manufacturing of small zeolite crystals and increasing pressure drop in adsorption towers with decreasing adsorbent particle size. Intracrystalline mesoporosity introduced by the “riving” process will greatly reduce the diffusion limitation while the crystal size remains unchanged.

Rive Technology, Inc. is developing and commercializing the proprietary mesoporous zeolite technology in catalysis and separation.[9-13] The technology, called “riving”, introduces additional, controlled mesoporosity (pore size > 2 nm) into zeolite crystals through a simple, surfactant-assisted method of nanoengineering, thus improving mass transport inside the small crystals where reactions (or separation) take place. The transmission electron micrographs (TEM) of a typical zeolite before and after the incorporation of the mesopores (Figure 1), clearly shows the more accessible structure of the modified version. In the micrograph on the left, the crystal lattice of the zeolite is observed as straight horizontal parallel lines. However, no porosity is observed (the magnification is too low to see the micropores). On the contrary, the micrograph on the right (corresponding to a mesoporous zeolite), both the crystal lattice and the additional mesoporosity are observed, indicating a much more accessible crystalline structure. In the inset of the micrograph of the mesoporous zeolite (taken at high magnification) the crystal lattice (going in diagonal) and the mesopore (as pale holes inside the structure) are clearly present.

Figure 1. TEM micrographs showing a zeolite before (left) and after (right) the incorporation of mesopores

The advantage of the intracrystalline mesoporosity of rived zeolites is evidenced by the improved catalytic performance of the FCC catalysts made from the mesoporous zeolite. Rive's recent development proved that the intracrystalline mesopores make the catalysts more capable of cracking large hydrocarbon molecules, and enable valuable primary cracked products, like gasoline and diesel molecules, to more readily escape the catalyst before they are over-cracked to less valuable light gases and coke (Figure 2).

Figure 2. Catalytic performance of catalysts based on a mesoporous zeolite (RiveCat) and a conventional zeolite

In addition, Rive's proprietary technology has the following advantages:

- The amount of mesoporosity introduced can be tailored very precisely, and can therefore be optimized for a particular separation and process.
- Mesoporosity can be incorporated into a range of zeolitic materials, which will allow us to identify an optimal material for the separation of propane / propylene.
- The introduction of mesoporosity does not change the main macroscale physical chemical properties of the zeolite or the crystal size or shape. The properties of the zeolite are usually optimized for each separation process, so maintaining those properties is important.
- The technology is low cost and easily manufactured. Based on our experience in developing mesoporous zeolite catalysts for the refining industry, we expect to develop an adsorbent that is commercially cost competitive.

The objective of Rive Technology's project (DE-EE0003470) is to explore the application of the company's proprietary mesoporous zeolite technology to large-scale, energy-intensive

separations in the chemical industry. The project will focus on the separation of propane from propylene utilizing zeolite-containing adsorbents with enhanced mesoporosity in a Simulated Moving Bed (SMB) process in comparison to the energy-intensive distillation process used today.

Materials Preparation and Characterization:

1. Riving of zeolites Y, X and A

Rive Technology has developed and optimized over the past few years a chemical process, referred as “riving”, to introduce controlled intracrystalline mesoporosity into Y (Faujasite) zeolite. Typically, the starting NaY zeolite (e.g. Zeolyst CBV100) is slurried into de-ionized water and was added mineral acid (nitric acid or sulfuric acid) to adjust the pH to ~5.9. Then 10% citric acid (or other aluminum chelating acid) at a certain dosage level (e.g. 4 miliequivalents (meq.)/g zeolite) is added over a period of 1 hour. Following filtration and rinsing with de-ionized water, the solid is re-slurried into de-ionized water and was added certain amount of cetyltrimethylammonium bromide or chloride solution (CTAB or CTAC), e.g. at 0.5 g CTAB/g zeolite level. Then certain amount of concentrated NH_4OH or NaOH solution is added to the reaction mixture. The pH of the mixture is typically about 10-11. The mixture is then heated to 80 °C in an oven with or without stirring for an extended period of time (e.g. 24 hours) before it is filtered and washed with hot de-ionized water to remove the excess surfactant. The occluded surfactant templates are typically removed by careful calcination. A typical calcination of rived zeolite involves loading certain amount of dried surfactant-containing zeolite into a custom-made calcination tube that has a gas inlet and outlet, flowing nitrogen through the sample at 6 cc/min, heating the sample in a muffle furnace from room temperature to 150 °C slowly at 5 °C/minute and holding for 1 hour, then heating up to 550 °C at 5 °C/minute and holding for 2 hours, switching the nitrogen to dry air at 6 cc/min and holding at 550 °C for another 2 hours, and cooling under dry air flow to room temperature.

The rived zeolites are typically characterized by X-ray diffraction (PANalytical Cubix Pro X-ray Diffractometer with a 1.8 kW Cu-target X-ray tube), N_2 (and/or Ar) gas adsorption/desorption (Quantachrome Quadrasorb-SI Surface Area/Pore Size analyzer), and X-ray fluorescence spectrometry (PANalytical Axios Wavelength Dispersive X-ray Fluorescence Spectrometer). Multi-point BET surface areas are calculated using N_2 adsorption results that range at 0.005 to 0.03 P/P₀. Pore size distribution is calculated from all adsorption results using NLDFT model. External surface areas (the total area of the true crystal external surface and the mesopore surface) are calculated from N_2 adsorption results using t-plot analysis. The unit cell size of the remaining crystalline framework is calculated from the X-ray diffraction results following ASTM D3942. Relative apparent crystallinity of the rived zeolite is calculated from the X-ray diffraction results following ASTM D3942 and referred to the starting CBV100 (NaY).

Argon adsorption measurements show that most of the mesoporosity introduced during riving are in the 40 Å range (Figure 3 top). With increasing amount of citric acid (meq/g), higher mesopore volumes can be introduced. Apparently, the mesopore size is controlled by the size of the surfactant used and the mesopore volume is controlled by the acid wash severity. The increase in mesopore volume is accompanied by a decrease in the micropore volume as shown in Figure 3 (bottom). The increase in mesopore volume is not proportional to the decrease in micropore volume. As a result, riving results in a net increase in the total pore volume (Figure 3, top).

Figure 3. Cumulative and pore size distribution of rived and unrived Y zeolite (top) and pore volume dependence on citric acid amount (bottom)

XRD powder patterns (Figure 4) confirm that rived Y zeolite retains the faujasite structure with decreasing crystallinity.

Figure 4. XRD powder diffraction patterns of unrivied and rived Na-Y (CBV100) samples at different citric acid treatment levels

The silica to alumina molar ratios (SAR) of Y, X and A are 5, 2.5, and 2, respectively. Due to the difference in their chemical compositions, dealumination of X and A zeolites by acid (e.g. citric acid or nitric), which is typically accompanied by destruction to the zeolite crystalline structures, is expected to be much more facile and much less selective than dealumination of Y. This is manifested by the vast difference of their stability in nitric acid (Figure 5). While Y zeolite retains 95% of the original crystallinity at pH 3, X retains only 23% and A already becomes a gel at pH 4. Therefore, more careful control of the acid wash conditions is recognized to be the key to successful “riving” of X and A zeolites.

Figure 5. Effect of pH on crystallinity of NaY, NaX and NaA zeolites

Under very similar reaction conditions as for NaY, NaX zeolite can be rived to different degrees by controlling the acid treatment severity (Table 1).

Table 1. Micropore and mesopore volumes of rived and unrived NaX

Citric Acid (meq/g zeolite)	MicroPV (0-20 Å) cc/g	MesoPV (20-300Å) cc/g	% Crystallinity
0 (unrived)	0.43	0.03	100
3.0	0.38	0.11	89
4.5	0.38	0.14	84
6	0.31	0.18	68

Rived Na- X zeolites retain faujasite structure (Figure 6). The relative crystallinity also follows the severity of the citric acid treatment (Table 1).

Figure 6. XRD powder pattern of unrived and rived X samples at different levels of citric acid treatment

When “riving” of NaA zeolite was first attempted using the normal procedure that has been developed for Y zeolite, very little mesoporosity (20-80 Å) was introduced as shown by Argon adsorption measurements (Figure 7). TEM analysis of the A zeolite sample revealed that the crystals were broken into very small pieces, suggesting that A zeolite was partially damaged during the process (Figure 8-10). TEM results also revealed that the large mesopores (>140 Å) observed in Ar adsorption measurement are probably the interparticle voids between the small broken pieces of the A zeolite crystals. XRD analysis showed that the sample still maintains significant crystallinity while Ar adsorption showed no micropore volume (Table 2). This difference suggests that X-ray diffraction comes from the undamaged A zeolite crystals in the sample. It should be noted that 4A zeolite will not adsorb Ar or N₂ due to the small pore

openings that restrict the diffusion of the probe (N_2 or Ar) molecules into the micropores under the experimental conditions (low partial pressure and low temperatures) while a Ca-exchanged sample showed ~ 0.28 cc/g micropore (0-20 Å) volume from N_2 adsorption measurement.

Figure 7. Argon adsorption isotherms and the corresponding DFT cumulative and differential pore size distribution of an unrived 5A zeolite (blue)) and rived 4A zeolites by the normal riving procedure (red) and the modified procedure (green)

The typical riving procedure was then modified (will disclose the details later due to proprietary reason). At the same acid wash severity (4 meq citric acid per gram of A zeolite), the sample treated by this new procedure showed significant mesoporosity within the 20-80 Å size range (Table 2). X-ray diffraction showed that the sample retained $\sim 75\%$ of the original crystallinity.

Argon adsorption showed 0.12 cc/g microporosity, lower than the X-ray crystallinity predicts (~0.21 cc/g), suggesting that the “riving” is not uniform. Some crystals may have been well “rived” while the others are not rived at all. The unrived A zeolite will not contribute to the micropore volume measured by Ar adsorption. This is substantiated by TEM analysis. It is very interesting that at a lower acid wash severity (2 meq citric acid per gram zeolite), the X-ray crystallinity match the micropore volume retention very well. It is possible in this case that the “riving” is more uniform and even at this small degree of “riving” (~0.05 cc/g mesoporosity introduced) it seems that the material readily takes up Ar (untreated 4A zeolite does not take up Ar under the same experimental conditions and show zero micropore volume). The new “riving” process is currently under evaluation for patent application.

Table 2. Properties of the unrived and rived Na-A zeolite samples compared to unrived and rived Na-Y samples

Zeolite	%Cryst. (XRD)	UCS (Å)	Micro (0-20 Å)	%Cryst. (MicroPV)	Meso (20-80 Å)	Meso (20-300 Å)
4A (Na-A)	100	24.61	0		0.04	0.05
5A (Ca-A)	N/A	N/A	0.28	100	0.01	0.01
Rived 4A- Normal Procedure (at 4 meq/g zeolite)	62	24.63	0	0	0.03	0.13
Rived 4A-New Procedure (at 4 meq/g zeolite)	75	24.63	0.12	43	0.12	0.15
CBV100 (Na-Y)	100	24.71	0.37	100	0.03	0.04
Rived CBV100 (at 4.5 meq/g zeolite)	68	24.64	0.28	76	0.27	0.28

Figure 8. TEM images of an unrived NaA zeolite crystal. The picture on right is a digital blow-up of the blue box region in the picture on the left

Figure 9. TEM images of a rived Na-A sample by the normal procedure. The picture on right is a digital blown-up of the blue box region in the picture on the left

Figure 10. TEM images of a rived Na-A sample by the modified procedure. The picture on right is a digital blown-up of the blue box region in the picture on the left

To control the purity of cations in the rived zeolites and also to avoid the instability of HY, HX or HA that form during calcination (to remove surfactant template) of the $\text{NH}_4\text{-Y}$, $\text{NH}_4\text{-X}$, $\text{NH}_4\text{-A}$ zeolites, concentrated NH_4OH used in the riving processes described above is replaced by 50% NaOH .

Figure 11 shows the cumulative and differential pore size distribution of NaOH and NH_4OH rived NaY (both pre-treated with 4.5 miliequivalent/g of citric acid). NaOH riving gives similar (or slightly better) results than NH_4OH . In terms of pore size distribution, there is a slight uplift in both MicroPV (0-20Å) and MesoPV (20-300Å). Correlating with the high micropore volume in NaOH rived zeolite is the higher crystallinity of 78% compared to 57% for zeolite rived in NH_4OH .

Figure 11. Cumulative and differential pore size distribution of NaY rived with NaOH and NH_4OH

For riving of NaX zeolite, it was found that the amount of NaOH used could also affect the mesoporosity introduced (Figure 12).

Figure 12. Micropore and mesopore (20-80 Å) volumes of rived NaX showing that ~10g of 50% NaOH per 100 g of starting NaX zeolite is optimal. Similar effects were also found for riving of NaY and NaA zeolites

Replacing NH_4OH with NaOH in riving of NaA in the new riving procedure described above show that the mesoporosity is controlled by the acid treatment severity, similar to riving of NaX and NaY (Table 3). No microposity is observed for the as-rived samples because N_2 or Ar

cannot diffuse through the small pore openings (~ 4 Å). After ion exchange with Ca^{2+} , the microporosity can be measured and show that they decrease with increasing acid treatment level. Removal of surfactant templates by calcinations does not affect the crystallinity of the samples.

Table 3. Properties of unrived and rived A zeolites

	Citric Acid (meq/g zeolite)	MicroPV, cc/g (0-20 Å)	MesoPV, cc/g (20-135 Å)	%Cryst. (vs. Na-A)	UCS (Å)
Na-A (4A)	0	0	0.01	100	24.60
Ca-A (5A)	0	0.39	0.01	90	24.62
Rived-1	4	0	0.09	84	24.59
Rived-2	6	0	0.15	70	24.59
Rived-1 (Calc.)	N/A	0	0.08	85	24.56
Rived-2 (Calc.)	N/A	0	0.15	71	24.55
Rived-1 (Ca^{2+} exch.)	N/A	0.26	0.11	64	24.61
Rived-2 (Ca^{2+} exch.)	N/A	0.19	0.21	49	24.52

In summary, Rive's proprietary technology in making mesoporous Y zeolite is successfully extended to make mesoporous X and A zeolites. The mesopore volume can be easily controlled by the amount of citric acid used in the pre-treatment step before surfactant and base treatment.

2. Binding of zeolites to form adsorbent particles

Zeolites, typically a few hundred nanometers to a few micrometers in size, cannot be used directly in adsorptive separation or testing because the pressure drop through the compacted bed would be too high.

Typically, the zeolite is mixed with some kind of "adhesive", e.g. clay, and compressed or extruded to form certain shape and size. For the pulse testing, particles of 20-60 mesh (~ 250 -840 micron) are typically used. After experimenting with different formulations and particle forming processes, it is found that a mixture of 80 wt% hydrated zeolite and 20% hydrated Attagel 50 with additional 10-25 wt% de-ionized water can be pressed using a hydraulic press at ~ 12000 -15000 psi pressure to form reasonably strong pressed pellets, which can then be carefully calcined at 650 °C for 2 hours under flowing dry air to set the binder (Attagel 50). The pressed pellets then are crushed in a grinder and sieved to the desirable size range (20-60 mesh). The particles made by this process are of irregular shape and have reasonable bulk density and good mechanical strength to sustain the pulse testing. After calcinations, the particles are washed with dilute NaOH solution to remove any possible proton sites formed

during the calcinations step. Before testing, the adsorbents are typically activated at 250 °C under flowing nitrogen for 2 hours (Figure 13).

Figure 13. Current preparation process scheme for laboratory adsorbent particles

Table 4. Properties of the zeolites and the adsorbent particles prepared from the corresponding zeolites

	%Crystal	UCS (Å)	MicroPV (0-20 Å, cc/g)	MesoPV (20-300 Å, cc/g)	BET (m ² /g)	ESA (m ² /g)	Hg-PV (cc/g)	Total PV (cc/g)	SAR
Commercial NaX Adsorbent	68	24.95	0.25	0.05	709	33	0.32	0.62	2.81
Unrived NaX Zeolite	100	24.97	0.37	0.01	888	26	N/A	N/A	2.46
Unrived NaX Adsorbent	68	24.97	0.25	0.04	632	31	0.31	0.60	2.95
Rived NaX Zeolite	70	24.96	0.27	0.12	767	119	N/A	N/A	2.96
Rived NaX Adsorbent	46	24.94	0.17	0.12	499	90	0.42	0.71	3.35
Unrived NaY Zeolite	100	24.66	0.38	0.02	949	21	N/A	N/A	5.22
Unrived NaY Adsorbent	72	24.62	0.31	0.07	794	41	0.56	0.94	5.63
Rived NaY Zeolite	89	24.58	0.32	0.11	903	173	N/A	N/A	6.41
Rived NaY Adsorbent	71	24.55	0.25	0.09	700	95	0.61	0.95	7.01

It was determined to use moderately rived zeolites with ~ 0.12 cc/g 20-300 Å MesoPV for preparation of the “rived” adsorbents in order to minimize the impact on adsorbent capacity (MicroPV). The adsorbent particles (and the rived and unrived zeolites that go into the particles) are characterized by XRD, XRF, nitrogen adsorption/desorption, and mercury porosimetry. The results are listed in Table 4 above. Since only Y and X zeolites are considered for SMB process and pulse testing, results on A zeolites are excluded from this table. As a comparison, a commercial adsorbent made from NaX zeolite, crushed and sieved to the same 20-60 mesh size, is also included in the table (and tested too in pulse test). The total pore volume of the adsorbent particles is calculated by adding the 0-300 Å pore volume from N_2 adsorption measurements and the pore volume of 300 Å - 1 μ m from mercury intrusion measurements (Hg-PV).

In summary, the unrived NaX adsorbent prepared in Rive laboratory compares well with the commercial NaX adsorbent in terms of porosity and surface areas. The properties of the laboratory prepared adsorbents (unrived and rived) generally correspond well with the properties of the zeolites inside. The rived adsorbents (NaX or NaY) show lower MicroPV/crystallinity and higher MesoPV and ESA (~ 2 to 3 times) than the unrived counterparts.

Pulse Test Unit and Adsorbent Testing:

1. Pulse test unit

Bench-scale, batch-wise pulse test units, which were invented by UOP,[14] provide a convenient way to evaluate/screen various adsorbents. The chromatographic separation test results can provide important information about the separation selectivity and kinetics, which can be used to provide meaningful directional projection of the performance of the adsorbents in a continuous SMB process. In order to operate at pressures high enough (>200 psig) to ensure all chemicals (propane, propylene, desorbent and tracer) remain in liquid phase under the test conditions, Rive Technology hired Guild Associates, an Ohio company specializing in adsorption system integrations, to customize and build a pulse test unit for this project. Figure 14 depicts a schematic of the pulse unit built. The unit consists of two tanks with one containing the feed mixture to be separated (70:30 wt% C_3H_6 : C_3H_8) diluted in varying amounts of desorbent (hexane) and the other tank containing the pure desorbent, a Valco 6-port Valve to direct flow through the system, a mass flow controller for accurately monitoring the rate at which the fluid is sent through the system, a thermostated convection oven that contains a steel column packed with the adsorbent used for the experiment, back pressure regulator, and an Agilent Technologies 7890A Gas Chromatograph (GC) equipped with a Valcobond Capillary column for on-line analysis of the effluent fluid mixture from the PTU. High Purity H_2 was used as the carrier gas for the GC. Separate gas cylinders for N_2 and air were also connected to the PTU to allow for purging the system with gas.

Figure 14. A schematic of the pulse test unit built and used in this project

2. Column packing, pulse testing and results treatment

The adsorbent to be tested was ground and sieved between a mesh size of 20 and 60, corresponding to particle sizes of 0.853 mm and 0.251 mm respectively. The adsorbents were heated to 250°C for 2 hours under flowing air to remove all moisture. The adsorbent was then allowed to gain ~4-5% wt. moisture by exposing it to the ambient air prior to being packed in the adsorbent bed.

The adsorbent bed is a 116.8 cm long coiled steel tube of 0.95cm OD that was packed with a sample of adsorbent, usually around 40-45 g. Prior to packing, the volume of the empty tube was measured by filling it with liquid water, and then pouring the water into a graduated beaker and measuring the volume of water the column contained. The volume of the empty column was 55 mL. The empty tube was also filled with pressurized Helium at 50 psig, and then depressurized to ambient pressure. The volume of gas exiting the column upon depressurization was measured by water displacement from a graduated cylinder, and this measurement was used to determine packed column void fractions of the different adsorbents.

The column was tapped as it was packed with adsorbent to ensure good packing of the adsorbent in the bed. The bulk density of the adsorbent, ρ_b (g/cm³), was measured from the mass of adsorbent packed in the filled column divided by the empty volume of the column. The bed void fractions, ϵ , were measured by pressurizing the packed columns with Helium to 50 psig and depressurizing to ambient pressure while measuring the volume of water displaced from a graduated cylinder. ϵ is equal to the ratio of volume of gas out from the packed column to volume of gas out from the empty column. A summary of measured bulk densities and column void fractions appears in Table 5. This table also contains information on the relative crystallinity, the unit cell size (UCS), and the silica:alumina ratio (SAR) as well. The crystallinity and UCS were measured in an XRD unit, with the crystallinity measured relative to CBV500 (USY) zeolite. The SAR was measured from XRF data.

Table 5. Packed column properties for different adsorbents

Sample	Notes	ρ_b , g/cm ³	ϵ	%Crystallinity	UCS	SAR
RP52-18X-20x60	Commercial NaX	0.75	0.73	68	24.96	2.81
RP52-22X-D	In-house Unrived NaX	0.71	0.73	68	24.97	2.95
RP52-19X-D	Rived NaX	0.61	0.76	49	24.912	3.35
RP52-23Y-D	In-house Unrived NaY	0.6	0.79	72	24.62	5.60
RP52-24Y-D	Rived NaY	0.54	0.83	71	24.55	7.00

As can be seen from the table, as expected due to the introduction of mesopores into the Rived samples, the bulk density is lower and the packed column void fraction is higher for the Rived adsorbents. The packed column was then placed inside of the convection oven and the experiments were then ready to be performed. To carry out the experiments, the system was

pressurized to 200 psig under flowing pure desorbent at a rate set by the mass flow controller. The oven temperature was set at the desired temperature. The 9 mL sample line is filled with the feed and desorbent mixture. Table 6 gives the different experimental temperatures, flow rates, and sample line compositions used for all adsorbents tested. The desorbent of choice at this time has been chosen to be hexane. The GC sampling is set at a rate of 1 sample per 2 minutes, and the switch valve is set so that the desorbent flows through the mass flow controller and through the sample line to push the sample through the column. As the experiment proceeds, the more strongly adsorbed species (propylene) is retained on the adsorbent and takes longer to travel through the column, while the less strongly adsorbed component (propane) emerges from the column first.

Table 6. Test conditions for all adsorbents

Column Temperature (°C)	Flow rate (mL/hr)	C ₃ mixture %
30	50	4
	70	4
	100	4
50	50	4
	70	4
	100	4
50	50	25
	70	25
	100	25
70	50	4
	70	4
	100	4

Figure 15 shows an example of a pulse test result comparing the separation performance of Rived and Unrived NaX zeolite at a temperature of 50°C, flowrate of 100 mL/hr, and feed concentration of 25%. This Figure shows the normalized height of the GC detector response as a function of volume of desorbent passed through the column. The first peak observed has a sharp Gaussian shaped peak and corresponds to propane exiting the system, which is the less strongly adsorbed component. The second peak to emerge has a sharp rise to its peak maximum, followed by a tailing decrease to the baseline. This peak is propylene, the more strongly adsorbed species. The peak has a long tail that is more pronounced on the commercial NaX sample, and this is due to the high concentration of C₃H₆ used in this particular experiment. The principles of chromatography are to use a low enough concentration of adsorbate to

operate where the fluid-solid equilibrium relation is linear (Henry's Law region), which will result in a Gaussian peak shape. At higher concentrations, the equilibrium relationship deviates from linearity and causes the peak tail that we observe in the pulse test. The peak asymmetry was measured for the chromatograms by taking the ratio of b/a at 10% of the maximum peak height.[15] For a Gaussian peak, $b/a = 1$. A measure of the peak broadening (due to adsorption kinetics) is obtained by looking at the peak width at half height, and is given by $\Delta w_{1/2}$ on the Figure. The other values on the figure are $V_{C_3H_8}$, $V_{C_3H_6}$, and V_T , which are respectively the retention volumes of propane, propylene, and a tracer component. The retention volume of each component is rigorously calculated by taking the zeroth and 1st statistical moments, μ_0 and μ_1 respectively, of the peak as [16]

$$\mu_0 = \int_0^{\infty} h_i dt \quad 1$$

$$\mu_1 = \frac{1}{\mu_0} \int_0^{\infty} h_i t dt \quad 2$$

$$V_i = Q\mu_1 \quad 3$$

where h_i is the height of the chromatograph response at time t , and Q is the volumetric flowrate. μ_0 gives the total area under the peak.

Figure 15. Comparison of Pulse Test Experiments on Commercial NaX(left) and Rived NaX (right) at 50°C, 100 mL/hr, and 25% feed

An issue that is integral to analyzing pulse test data is performing a tracer run using a non-adsorbing component to measure the retention volume of a component that simply passes through the column without adsorbing. The tracer experiments are performed as follows. The feed tank is filled with toluene and the sample line is filled. The experiment is started using isobutane as the carrier fluid and after a few minutes, a second pulse of toluene is sent through the system. The effluent is monitored until a toluene band is observed in the GC. For these experiments, only one band is observed as most of the toluene has adsorbed on the adsorbent surface. A second feed tank replaces the toluene tank that contains ~1.5% ethane dissolved in

isobutane, and a standard pulse test as described previously is run. The ethane is observed to emerge from the column at generally 4-6 minutes earlier than the propane peaks observed in the separation experiments. Isobutane was found to be a suitable purge fluid for the tracer experiments as a longer hydrocarbon molecule interacts too strongly with the toluene-saturated adsorbent, displacing toluene and allowing the ethane to adsorb, and therefore does not give an accurate measurement of system dead volume.

Once the tracer run was established, the pulse test experiment data could be used to calculate the Equilibrium adsorption selectivity from the relative retention volumes. First the retention factors for each component are calculated as

$$k'_i = \frac{V_i - V_T}{V_T} \quad 4$$

and the adsorption selectivity is calculated by

$$S = \frac{k'_{C_3H_6}}{k'_{C_3H_8}} \quad 5$$

A relative measure of the equilibrium constants, K_A , for propane and propylene can be calculated from μ_1 [16] by carrying out the experiment at different flow rates using the following equation: [17]

$$\frac{\Delta\mu_1 - \frac{t_{inj}}{2}}{\frac{1-\varepsilon}{\varepsilon}} = K_A \left(\frac{L}{v} \right) \quad 6$$

In this equation, $\Delta\mu_1$ is the difference between the component and tracer 1st moment, t_{inj} is the sample injection time, L is the column length, ε is the packed column void fraction, and v is the fluid velocity. K_A is a dimensionless equilibrium constant. To obtain K_A , the left hand side is plotted vs. L/v , and the slope of the line passing through the origin is equal to K_A .

The pulse test experiments also give information to the overall transport diffusivity (mass transfer resistance) on the adsorbent material. First, the 2nd central moment of each peak is calculated using the 1st moment by:

$$\mu_2 = \sigma^2 = \frac{1}{\mu_0} \int_0^\infty h_i(t - \mu_1)^2 dt \quad 7$$

The 2nd central moment is also called the variance of the peak response, and it is used to calculate the height equivalent to a theoretical transfer plate, HETP, by

$$HETP = \frac{\sigma^2}{\mu_1^2} L \quad 8$$

where L is the column length. A low HETP is desirable for a high column efficiency. Using the HETP values measured at different flow rates, a Van Deemter [18] approach is used where HETP is plotted vs. the fluid velocity, v , to give the following relation:

$$HETP = \frac{2DL}{v} + 2 \frac{\varepsilon}{1-\varepsilon} \frac{1}{15K_A} \frac{R_p^2}{D} v \quad 9$$

Here, D_L is the axial dispersion coefficient, R_p is the adsorbent particle radius, and D is the overall transport diffusivity, calculated as cm^2/s . The slope of these plots along with the previously calculated equilibrium constants allows for a measure of the overall transport diffusivity for each adsorbate on the adsorbent.

3. Test results on rived and unrived NaX zeolites

The above calculations are suitable for a linear equilibrium relationship, and it was believed that the concentration of propylene was too high to validate this assumption. Pulse Test experiments were carried out at lower feed concentrations (4%) at the conditions listed in Table 6. Figure 16 shows an example of the results using 50°C , 100 mL/hr , and 4% feed (same as Figure 15 but different feed concentrations). When compared with Figure 15, we can see that the retention of propane remains relatively unchanged while that for propylene is extended, increasing the selectivity. This is consistent with the fact that maximal selectivity is achieved when operating at sufficiently low concentrations approaching the linear equilibrium relation region.[17] The peak tailing for both materials is reduced, and that of the Rived NaX is greatly reduced and has a much more symmetric shape than its UnRived counterpart. This reduction in peak tailing also allows the sample to be fully eluted using much less desorbent and hence a shorter time.

Figure 16. Comparison of pulse test results on Commercial NaX (left) and Rived NaX (right) at 50°C , 100 mL/hr , and 4% feed

The differences between the Rived and Commercial NaX samples were consistently the same for every Pulse Test experiment carried out, and Figures 15 & 16 give a good representation of the difference between the two materials; therefore none of the other test results will be shown. It should also be noted that the Commercial NaX and In House Unrived NaX zeolites showed almost the same adsorption characteristics and will not be shown. Table 7 summarizes all of the experimental results on the different NaX zeolites, and includes measures of peak tailing, $\Delta w_{1/2}$ (min), measured relative K_A , selectivity, the height equivalent to a theoretical transfer plate (HETP), and measured overall transport diffusivity, D (cm^2/s). As can be seen from the table, the effects of Riving on the X zeolite are as follows:

- Lower relative dimensionless Equilibrium constants for propylene.

- 30-50% reduction in $\Delta w_{1/2}$ for propylene at all conditions.
- 30-50% reduction in calculated 2nd central moment, σ^2 , at all conditions.
- ~2-3 x's increased overall transport diffusivity for propylene at all conditions.
- Lowered selectivity that is a weaker function of temperature.

Table 7. Tabulated pulse test results for Commercial NaX (top), In-house Unrived NaX (middle), and Rived NaX (bottom)

RP52 18X CG20x60 Commercial NaX zeolite										
Component	Bed T (°C)	Flow rate (mL/hr)	Feed %	$A_{s,10\%}$, Peak Asymmetry	$\Delta w_{0.5}$ Chromatogram peak width at half-height	σ^2 Peak 2nd moment	HETP	Measured Equilibrium constant, K	Overall Transport Diffusivity D (cm ² /s)	Selectivity
C3H6	30	50	4	3.3	31.8	231.3	0.36	4.4	1.9E-05	9.3
	30	70	4	3.1	23.8	134.1	0.43			
	30	100	4	2.9	17.5	72.3	0.49			
	50	50	4	3.1	24.7	136.0	0.32	3.4	2.7E-05	8.0
	50	70	4	2.8	19.6	89.0	0.38			
	50	100	4	2.7	13.9	50.6	0.46			
	50	50	25	4.9	29.2	165.6	0.55	2.3	3.9E-05	6.6
	50	70	25	4.4	21	92.5	0.62			
	50	100	25	4.0	15.6	50.3	0.69			
	70	50	4	2.3	21.4	107.5	0.31	2.6	6.6E-05	7.0
	70	70	4	2.1	15.9	59.6	0.35			
	70	100	4	2.1	11.4	30.4	0.38			
C3H8	30	50	4	1.0	16.2	35.8	0.35	0.3	1.1E-04	-
	30	70	4	1.0	11.3	18.4	0.36			
	30	100	4	1.0	7.7	9.3	0.38			
	50	50	4	1.0	15.2	34.1	0.35	0.2	1.5E-04	-
	50	70	4	1.0	10.8	17.3	0.35			
	50	100	4	1.2	7.6	8.9	0.38			
	50	50	25	0.9	15.1	30.4	0.32	0.2	1.5E-04	-
	50	70	25	0.9	7.5	15.3	0.33			
	50	100	25	1.1	7.5	8.0	0.36			
	70	50	4	0.8	15.6	32.4	0.33	0.2	8.2E-04	-
	70	70	4	0.9	11.3	17.2	0.37			
	70	100	4	1.0	7.7	8.6	0.39			

RP52 22X D In house UnRived NaX zeolite										
Component	Bed T (°C)	Flow rate (mL/hr)	Feed %	A _{s,10%} , Peak Asymmetry	Δw _{0.5} Chromatogram peak width at half-height	σ ² Peak 2nd moment	HETP	Measured Equilibrium constant, K	Overall Transport Diffusivity D (cm ² /s)	Selectivity
C3H6	30	50	4	3.5	32.8	298.2	0.42	4.9	2.2E-05	9.0
	30	70	4	3.3	26.3	182.4	0.49			
	30	100	4	3.1	20.9	102.7	0.54			
	50	50	4	3.1	27.8	185.7	0.37	3.7	6.1E-05	7.2
	50	70	4	2.8	19.7	97.4	0.39			
	50	100	4	2.8	14.7	51.5	0.42			
	50	50	25	5.9	30.0	335.1	0.96	2.6	7.6E-05	5.6
	50	70	25	5.4	21.5	168.1	0.98			
	50	100	25	4.5	18.7	84.3	1.02			
	70	50	4	2.6	22.6	114.6	0.31	2.8	7.1E-05	6.3
	70	70	4	2.3	16.6	63.0	0.34			
	70	100	4	2.4	12.1	33.5	0.37			
C3H8	30	50	4	1.0	16.1	35.0	0.33	0.4	6.2E-04	-
	30	70	4	1.1	11.3	19.0	0.36			
	30	100	4	1.1	7.7	9.8	0.38			
	50	50	4	0.95	15.7	35.0	0.34	0.3	2.6E-03	-
	50	70	4	1	11.6	17.5	0.34			
	50	100	4	1.0	7.7	8.6	0.35			
	50	50	25	0.95	15.3	32.7	0.32	0.3	1.5E-03	-
	50	70	25	1	10.3	16.8	0.33			
	50	100	25	0.94	8.2	8.4	0.35			
	70	50	4	0.87	16.2	33.5	0.33	0.3	1.9E-03	-
	70	70	4	0.89	10.8	17.1	0.35			
	70	100	4	0.89	7.7	8.5	0.36			

RP52 19X D CG20x60 Rived NaX zeolite										
Component	Bed T (°C)	Flow rate (mL/hr)	Feed %	$A_{s,10\%}$ Peak Asymmetry	$\Delta W_{0.5}$ Chromatogram peak width at half-height	σ^2 Peak 2nd moment	HETP	Measured Equilibrium constant, K	Overall Transport Diffusivity D (cm ² /s)	Selectivity
C3H6	30	50	4	1.9	20.9	90.2	0.28	2.7	7.8E-05	5.7
	30	70	4	1.9	15.5	50.1	0.31			
	30	100	4	1.7	11.6	27.1	0.35			
	50	50	4	1.7	19	63.5	0.25	2.0	1.1E-04	5.3
	50	70	4	1.6	13.8	36.1	0.29			
	50	100	4	1.4	10.2	19.5	0.32			
	50	50	25	4.1	20.4	87.8	0.43	1.5	1.0E-04	4.3
	50	70	25	3.3	14.3	47.7	0.47			
	50	100	25	3.0	10.8	25.4	0.52			
	70	50	4	1.2	17.5	51.2	0.25	1.5	1.9E-04	5.2
	70	70	4	1.3	12.7	28.2	0.27			
	70	100	4	1.3	9	14.7	0.30			
C3H8	30	50	4	1.0	15.1	35.2	0.33	0.3	1.8E-03	-
	30	70	4	1.0	11	18.3	0.34			
	30	100	4	1.0	10	9.2	0.36			
	50	50	4	1.0	15.8	34.0	0.33	0.2	3.6E-03	-
	50	70	4	1.0	11.5	17.6	0.34			
	50	100	4	1.0	8.1	8.7	0.36			
	50	50	25	0.8	14.2	28.4	0.28	0.2	1.3E-03	-
	50	70	25	0.9	10.4	15.6	0.31			
	50	100	25	1.0	7.4	8.0	0.34			
	70	50	4	0.9	15.5	33.2	0.34	0.1	1.0E-02	-
	70	70	4	1.0	11.1	17.1	0.35			
	70	100	4	1.0	7.8	8.3	0.36

Figure 17. Arrhenius plot showing temperature dependence of C₃H₆ transport in Rived and Unrived NaX zeolites

An interesting feature to be noted is that the propane peaks remained relatively unchanged at all conditions tested on the Rived and UnRived Materials. This is most likely that for very fast diffusing species, chromatographic measurements are not very suitable for these calculations. It can be concluded that propane transport is very fast on both Rived and UnRived materials. The diffusivities at the low concentration runs (4%) were plotted on an Arrhenius plot as functions of temperature ($\ln D$ vs. $1/T$). The slope of this plot gives the value of the activation energy to diffusional resistance, $-E_D/R$, and the plot appears linear for propylene in Figure 17. This figure only shows the propylene adsorption data on Rived, Commercial UnRived, and In-House UnRived NaX as the propane was deemed too fast to obtain accurate measurements. The resulting values of E_D were respectively found to be 26.6, 26.0, and 19.1 kJ/mol on the Commercial NaX, the In House Unrived NaX, and the Rived NaX, respectively. This lower diffusional activation energy on the Rived NaX confirms that the propylene molecule encounters less restriction to motion within the NaX particle, and therefore exhibits higher rates of transport.[19]

Gas phase adsorption isotherms of propylene and propane were measured independently on the samples of Rived and UnRived NaX by Thermogravimetric Analysis (TGA). A small sample (~40 mg) of adsorbent was placed in the pan of the TGA unit and initially heated to 400°C under flowing N_2 and held there until the measured sample mass remained constant. The sample was then cooled to the desired adsorption temperature and exposed to a different partial pressures of either propane or propylene. At each partial pressure, the mass was allowed to stabilize, and then the partial pressure of hydrocarbon was increased. The total system pressure was 1 atm. After the final isotherm point was measured, the sample was again heated to 400°C, and the sample mass was observed to stabilize at the initial mass (that following the first heat treatment) indicating complete reversibility of the adsorption of either propane or propylene. The crystallinity of the samples appears in Table 5. Figures 18 & 19 show the respective corrected propylene and propane adsorption isotherms measured on the Rived NaX and UnRived NaX samples. These plots all measure the adsorbed phase loading in mol gas adsorbed/g adsorbent plotted as a function of the gas phase partial pressure. Due to the exothermic nature of adsorption, a higher capacity is achieved for a given gas phase partial pressure at lower temperatures.

The adsorbents containing Rived NaX zeolite displayed a decrease of ~20% capacity for both propylene and propane compared to the UnRived NaX adsorbent samples. The heats of adsorption which are the strength with which the adsorbate is bound to the adsorbent were estimated from the adsorption isotherms using thermodynamic relations.[20] The heats for propylene and propane on the Commercial and UnRived materials were very similar and estimated to be ~-43.1 kJ/mol and -31.4 kJ/mol respectively. These values correspond well with other measured values over 13X reported by other literature sources (-42.5 and -35.8 kJ/mol,[21] -46.1 and -32.9 kJ/mol [22]) The corresponding heats for propylene and propane on the Rived samples were estimated to be -41.0 kJ/mol and -31.8 kJ/mol respectively. It should be noted that better estimates of the heats of adsorption from the isotherms would be obtained if more low pressure sorption data were available at low adsorbate loadings. The heats of adsorption are often decreasing functions of surface coverage, and the largest heat is that obtained at zero coverage.[17] A better and more accurate method for heat of adsorption

measurements would be to use the Sorption Isotherm Technique (SIT) which incorporates the use of a calorimeter to precisely measure the heat evolved due to adsorption as a function of the adsorbate loading.[22] Such a study is beyond the scope of this work.

Figure 18. Propylene adsorption isotherms on Commercial NaX (top), Rived NaX (middle), and In-house UnRived NaX (bottom) zeolite adsorbents

Figure 19. Propane adsorption isotherms on Commercial NaX (top), Rived NaX (middle), and In-house Unrived NaX (bottom) zeolites

In summary, the riving of NaX zeolite (intracrystalline mesoporosity) impacted the results of the pulse tests in the following ways:

- Lower relative dimensionless Equilibrium constants for propylene
- 30-50% reduction in $\Delta w_{1/2}$ for propylene at all conditions
- 30-50% reduction in calculated 2nd central moment, σ^2 , at all conditions
- ~2-3 x's increased overall transport diffusivity for propylene at all conditions
- Lowered selectivity that is a weaker function of temperature
- No clear distinction in kinetics of propane adsorption can be deduced as it is very fast on all materials

An Arrhenius plot of the measured diffusivities as functions of temperature showed that the diffusional activation energy for propylene was lowered from 26.6 kJ/mol on the commercial NaX sample to 19.1 kJ/mol on the Rived NaX sample. This reduction in diffusional activation energy shows that the propylene molecule experiences much more freedom to move within the Rived NaX zeolite.

The adsorption isotherms of the Rived NaX adsorbent shows that the adsorption capacity of both propylene and propane are ~20% lower than those observed on the UnRived NaX samples. The lower crystallinity observed on the Rived NaX adsorbent sample tells that some of the zeolite was damaged in making the adsorbent particles. The decrease that is observed on the Rived NaX adsorbent particles could be overcome by either using a higher percentage of the Rived NaX zeolite in the adsorbent-binder mixture, or by reducing the amount of damage to the zeolite in preparing the samples. The heats of adsorption on the commercial sample of NaX were determined to be -43.1 and -31.4 kJ/mol respectively for propylene and propane, while on the Rived sample they were determined to be -41.0 and -31.8 kJ/mol respectively.

4. Test results on rived and unrived NaY zeolites

Following the experiments on the NaX zeolites, the exact same sets of experiments listed in Table 6 were carried out on samples of In-house Unrived NaY and Rived NaY zeolite based adsorbents. No commercial sample was available for testing. The bulk density, ρ_b , and packed column void fractions, ϵ , appear in Table 5. The same procedure described before for packing the adsorbent bed was used for the NaY samples. Figure 20 shows the pulse test results from runs on the UnRived and Rived NaY zeolites at 50°C, 100 mL/hr, and 25% feed concentration. As with the NaX, the position of the propane remains relatively unchanged, but broadening of the propane peak was observed, indicating slower kinetics on the NaY compared to NaX. It is interesting that “riving” effect (introduced mesoporosity improving diffusion kinetics) can be observed for the narrower propane peak on rived NaY zeolite. The propylene peak on the commercial sample is broad, and Riving reduces the retention time and sharpens this peak as

well. However, at this high feed loading (25% concentration), there is still significant peak tailing on both the Rived and UnRived NaY for propylene.

Figure 20. Pulse test results on UnRived NaY zeolite (left) and Rived NaY zeolite (right) at 50°C, 100 mL/hr, and 25% feed concentration

Figure 21 shows the pulse test results on the UnRived and Rived NaY zeolites at 50°C, 100 mL/hr, and 4% feed concentration. The retention volume of propane is relatively unchanged but that for the propylene has been pushed to further retention volumes due to the lower concentration of feed. Table 8 summarizes all of the experimental results on the UnRived and Rived NaY zeolites, and includes measures of peak tailing, $\Delta w_{1/2}$ (min), measured K_A , selectivity, the height equivalent to a theoretical transfer plate (HETP), and measured overall transport diffusivity, D (cm^2/s).

Figure 21. Pulse test results on UnRived NaY zeolite (left) and Rived NaY zeolite (right) at 50°C, 100 mL/hr, and 4% feed concentration

Table 8. Tabulated pulse test results for In-house Unrived NaY (top) and Rived NaY (bottom) adsorbents

RP52 23Y D In house UnRived NaY zeolite										
Component	Bed T (°C)	Flow rate (mL/hr)	Feed %	A _{s,10%} , Peak Asymmetry	$\Delta w_{0.5}$ Chromatogram peak width at half-height	σ^2 Peak 2nd moment	HETP	Measured Equilibrium constant, K	Overall Transport Diffusivity D (cm ² /s)	Selectivity
C3H6	30	50	4	1.4	40.9	294.6	0.52	5.6	2.2E-05	5.4
	30	70	4	1.4	30.5	168.7	0.59			
	30	100	4	1.3	22.2	91.8	0.66			
	50	50	4	1.5	33.3	211.7	0.52	4.2	4.0E-05	4.7
	50	70	4	1.4	25.4	122.7	0.59			
	50	100	4	1.5	18.0	61.6	0.63			
	50	50	25	2.5	37.8	258.1	0.83	3.3	5.9E-05	4.4
	50	70	25	2.8	28.0	135.0	0.86			
	50	100	25	2.6	20.1	70.5	0.91			
	70	50	4	1.3	28.0	144.3	0.49	3.1	6.7E-05	4.3
	70	70	4	1.4	20.7	79.5	0.53			
	70	100	4	1.4	15.2	41.8	0.57			
C3H8	30	50	4	1.1	19.6	69.1	0.56	0.8	2.2E-04	-
	30	70	4	1.1	14.0	38.7	0.62			
	30	100	4	1.0	10.2	19.8	0.66			
	50	50	4	1.06	18.8	66.8	0.57	0.7	3.9E-04	-
	50	70	4	1.03	13.8	34.3	0.58			
	50	100	4	1.1	9.4	17.8	0.63			
	50	50	25	1.03	17.0	53.0	0.49	0.5	2.4E-04	-
	50	70	25	1	12.9	29.2	0.54			
	50	100	25	1.09	9.9	17.0	0.64			
	70	50	4	1.03	17.6	56.6	0.52	0.5	4.9E-04	-
	70	70	4	1.06	12.6	30.6	0.55			
	70	100	4	1.06	9.1	16.0	0.59			

RP52 24Y D In house Rived NaY zeolite										
Component	Bed T (°C)	Flow rate (mL/hr)	Feed %	$A_{s,10\%}$ Peak Asymmetry	$\Delta w_{0.5}$ Chromatogram peak width at half-height	σ^2 Peak 2nd moment	HETP	Measured Equilibrium constant, K	Overall Transport Diffusivity D (cm ² /s)	Selectivity
C3H6	30	50	4	2.0	23.7	138.2	0.31	5.7	4.4E-05	5.0
	30	70	4	1.9	18.1	76.6	0.34			
	30	100	4	1.8	13.6	42.2	0.39			
	50	50	4	1.6	21.1	99.6	0.28	4.5	9.2E-05	4.5
	50	70	4	1.9	15.7	54.4	0.31			
	50	100	4	1.7	11.1	27.9	0.34			
	50	50	25	4.0	27.3	164.9	0.63	3.3	8.0E-05	3.9
	50	70	25	0.0	19.5	89.4	0.69			
	50	100	25	3.4	13.1	44.8	0.72			
	70	50	4	1.5	19.4	71.7	0.27	3.3	1.2E-04	4.2
	70	70	4	1.6	13.3	39.3	0.30			
	70	100	4	1.7	9.9	20.7	0.33			
C3H8	30	50	4	1.1	15.5	38.2	0.30	0.8	7.7E-04	-
	30	70	4	1.1	10.5	19.9	0.31			
	30	100	4	1.1	7.7	10.1	0.33			
	50	50	4	1.08	14.4	35.1	0.29	0.7	9.4E-04	-
	50	70	4	1.14	10.3	18.5	0.30			
	50	100	4	1.2	7.7	9.7	0.32			
	50	50	25	1	15.0	33.5	0.29	0.5	7.2E-04	-
	50	70	25	1.08	10.5	18.4	0.32			
	50	100	25	0.92	7.5	9.6	0.35			
	70	50	4	0.875	15.3	32.8	0.29	0.5	1.4E-03	
	70	70	4	1.07	10.5	17.1	0.30			
	70	100	4	0.96	7.2	8.7	0.32			

As can be seen from the table, the effects of Riving the Y zeolite are as follows:

- 30-50% reduction in $\Delta w_{1/2}$ for propylene at all conditions
- ~20% reduction in $\Delta w_{1/2}$ for propane at all conditions
- 30-50% reduction in calculated 2nd central moment, σ^2 , at all conditions for both propylene and propane
- ~2x's increased overall transport diffusivity for propylene at all conditions and ~3x's increased overall transport diffusivity for propane at all conditions
- Slightly lowered selectivity that is a weaker function of temperature

The diffusivities at the low concentration runs (4%) were plotted on an Arrhenius plot as functions of temperature (ln D vs. 1/T). The slope of this plot gives the value of the activation energy to diffusional resistance, $-E_D/R$, and the plot appears for both propane and propylene in Figure 22. The resulting values of E_D for propylene were respectively found to be 23.6, and 20.6

kJ/mol on the In-house Unrived NaY and the Rived NaY, respectively. The E_d values for propane we respectively determined to be 17.3 and 12.5 kJ/mol on the In House NaY, and the Rived NaY. This lower diffusional activation energy on the Rived NaY confirms that both the propylene and propane molecules encounters less restriction of motion within the NaY particle, and therefore displays higher rates of transport.[19]

Figure 22. Arrhenius plot showing temperature dependence of C_3H_6 and C_3H_8 transport in Rived and Unrived NaY zeolites

Gas phase adsorption isotherms of propylene and propane were measured independently on the samples of Rived and UnRived NaY by Thermogravimetric Analysis (TGA). A small sample (~40 mg) of adsorbent was placed in the pan of the TGA unit and initially heated to 400°C under flowing N_2 and held there until the measured sample mass remained constant. The sample was then cooled to the desired adsorption temperature and exposed to different partial pressures of either propane or propylene. At each partial pressure, the mass was allowed to stabilize, and then the partial pressure of hydrocarbon was increased. The total system pressure was 1 atm. After the final isotherm point was measured, the sample was again heated to 400°C, and the sample mass was observed to stabilize at the initial mass (that following the first heat treatment) indicating complete reversibility of the adsorption of either propane or propylene. Figure 23 shows the adsorption isotherms for propylene on the samples of Rived and In-house UnRived NaY. Figure 24 shows the adsorption isotherms for propane on the same samples of NaY. Due to the exothermic nature of adsorption, a higher capacity is achieved for a given gas phase

partial pressure at lower temperatures. The effect of Riving on the NaY zeolite was almost negligible on the equilibrium adsorption capacity. From Figures 23 and 24, it can be seen that the effect of Riving on the NaY zeolite for propylene adsorption is negligible, with maybe a very slight decrease at the measured isotherm temperatures. The same is true for the adsorption capacity of propane on the Rived and UnRived NaY zeolites. This would explain why there is very little change in experimentally measured selectivities for the Rived vs. UnRived NaY zeolites.

Figure 23. Propylene adsorption isotherms on Rived NaY (top) and Unrived NaY (bottom)

Figure 24. Propane adsorption isotherms on Rived NaY (top) and Unrived NaY (bottom)

An attempt was made to calculate the heats of adsorption for both propylene and propane from the adsorption isotherm data, but upon analysis it was deemed that more sorption data would be required to get an accurate measure of these quantities. Here again the use of calorimetry would be a great aid in accurately quantifying heats of adsorption as functions of surface loading.

In summary, the “riving” of NaY zeolite impacted the results of the pulse tests in the following ways:

- 30-50% reduction in $\Delta w_{1/2}$ for propylene at all conditions
- ~20% reduction in $\Delta w_{1/2}$ for propane at all conditions
- 30-50% reduction in calculated 2nd central moment, σ^2 , at all conditions for both propylene and propane
- ~2x's increased overall transport diffusivity for propylene at all conditions and ~3x's increased overall transport diffusivity for propane at all conditions
- Slightly lowered selectivity that is a weaker function of temperature

An Arrhenius plot of the measured diffusivities as functions of temperature showed that the diffusional activation energy for propylene was lowered from 23.6 kJ/mol on the commercial NaY sample to 20.6 kJ/mol on the Rived NaY sample. The diffusional activation energy for

propane was also reduced from 17.3 kJ/mol on the UnRived NaY to 12.5 kJ/mol on the Rived NaY. These reductions in diffusional activation energy show that both the propylene and propane molecules experience much more freedom to move within the Rived NaY zeolite.

The adsorption capacity of both propylene and propane on the Rived and UnRived NaY adsorbents were negligible. This would explain why there is very little change in experimentally measured selectivities from the pulse tests for the Rived vs. UnRived NaY adsorbents. The sorption data collected for both Rived and UnRived NaY was incomplete to get meaningful measures of the heats of adsorption on these materials.

Energy Saving Calculation:

A hypothetical moving bed adsorption system is shown in Figure 25 along with the corresponding liquid-phase composition profile. The solid adsorbent is continuously circulated in a closed loop and flows up through the adsorber. Liquid flows counter currently to the solid flow. The fluid mixture to be separated, A + B, is fed at the feed port. The feed may also be diluted with the desorbent, D. Here, A is the more strongly adsorbed species. Raffinate is withdrawn from the system below the feed entry point and consists of the less strongly adsorbed component, B, and desorbent, D. Only a portion of flowing liquid is withdrawn as the rest continues to flow into the next bed. Extract is withdrawn from above the feed port and consists of the more strongly adsorbed A along with D. As with the Raffinate, only a portion of liquid is withdrawn at this point. The placement of feed/desorbent introduction and extract/raffinate withdrawal results in the formation of 4 generic zones that each performs a different function. Following the zone numbers in Figure 25, zone 1 serves to adsorb A from the liquid, zone 2 serves to purge B from the solid, zone 3 serves to desorb A from the solid, and zone 4 serves as a buffer to prevent component B from contaminating the extract component A.

Figure 25. Schematic of True Moving Bed adsorption system and corresponding liquid composition profiles

Several practical issues arise from flowing solids such as particle attrition and obtaining uniform flow of liquid and solid in beds of large diameter. The fluidized bed system also suffers from mass transfer inefficiency as a prohibitively large number of beds may be necessary to achieve a desired separation performance.

To overcome these challenges, the movement of solid can be realized by maintaining a stationary bed and periodically shifting the positions at which the feed, desorbent, extract, and raffinate streams enter and leave. This port shifting simulates the flow of solid countercurrent to liquid flow, hence the name Simulated Moving Bed. The commercial application of SMB is

shown in Figure 26 where the adsorbent is in a fixed bed and a circulating pump is used to pump the liquid from the bottom of the column to the top. A rotary valve directs the flow of fluid appropriately through the bed. Distributors within the bed allow for appropriate introduction and withdrawal of the four streams from the bed. Smaller SMB systems may use extensive systems of switch valves instead of the complicated rotary valves. The number of beds in SMB applications can vary from 4 up to 24 beds, the latter of which may require more than 100 different rotary valves to achieve the desired switching performance. Due to the switching of ports, the circulating pump must shift its pumping rate to accommodate the necessary flow rate for whatever zone is above it. Sequential samples taken from the liquid circulating pump can trace the composition profile in the entire bed. In SMB the temperature is set to achieve rapid mass transfer or achieve a desired adsorbent selectivity. Pressure is not a critical operating variable, but is set sufficiently high to avoid vaporization of the fluid.

Figure 26. Schematic of Simulated Moving Bed adsorption system

The raffinate and extract products withdrawn from the SMB system are subsequently fed to a set of distillation columns for recovery of the products A & B, and for solvent recovery back into the SMB process. Solvent recovery is critical to avoid excessive make-up of desorbent to the system. The major consumption of energy in an SMB process is this subsequent extract/raffinate recovery. Therefore choice of desorbent is a critical issue in energy consumption of the system.

As the proposed energy saving consumption comparison is between a C3 splitter (already simulated in the front-end calculation in Appendix) and an adsorptive separation system using rived zeolite based adsorbents, it is not necessary to take into consideration of the improved diffusion kinetics for the rived compared to the unrived and rigorous SMB process simulation is not necessary. Therefore, the energy consumption of a SMB separation process herein can be carried out by the well-developed Equilibrium Theory for simulated moving bed adsorption.[24-

29] This section is based on the work presented in these references. In this analysis, the operation of a 4-bed SMB unit is approximated by the established equivalence of a True Counter-Current (TCC) adsorption unit where fluid and solid flow counter-currently to one another as depicted in Figure 25. Local equilibrium is assumed to prevail at all times and locations in the column, hence there is no resistance to mass transfer in the system or axial mixing (this assumption, of course would be more valid for a rived adsorbent than an unrived adsorbent under the same operating conditions). Complete separation is achieved, so that only propylene and desorbent appear in the extract, and only propane and desorbent appear in the raffinate, which are then further separated by distillation.

The key parameters for design of the steady state system have been demonstrated to be the flow rate ratios, m_j , in the different sections of the unit. These flow ratios are defined as

$$m_j = \frac{\text{net fluid flow rate}}{\text{adsorbed phase flow rate}} = \frac{G_j t^* - A L \varepsilon \rho_f}{A L \rho_s \gamma^\infty (1 - \varepsilon)} \quad 10$$

where G_j is the fluid mass flow rate through section j of the column, t^* is the switching time in the SMB unit, A is the column cross sectional area, L is the column length, ε is the packed column void fraction, ρ_f and ρ_s are the respective fluid and solid densities, and γ^∞ is the adsorbent saturation capacity in mass adsorbate/mass adsorbent. The bottom term of equation 10 represents the total mass of adsorbate that must be adsorbed during the step of the cycle. Determining these flow ratios provides boundaries for conditions in which complete separation can be achieved. This region can be graphically depicted by the proper choice of the variables (m_2 , m_3) to define the space where optimal and robust operation of the system can be realized to achieve complete separation. With these parameters properly chosen, the flow rates of the desorbent, extract and raffinate streams can all be calculated, along with the stream compositions, from the relative equilibrium constants (K_i) calculated from the pulse test experiments and the feed concentrations of propylene, propane, and desorbent. The flow rate of C_3 to the system was chosen as 6000 BPSD (same as in the front-end calculation in Appendix), which is equivalent to the flow rate of a C_3 stream obtained from a 50,000 BPSD FCC unit. In commercial SMB, the feed is often diluted with the desorbent so the feed stream contains 75% desorbent with a balance of mixture to be separated (C_3 mixture is 70:30 propylene: propane). The desorbent in this case was hexane, however, the actual value of the equilibrium constant for hexane was not experimentally determined. It is known that hexane adsorbs more strongly than either propane or propylene, so a value of K_D greater than $K_{C_3H_6}$ was arbitrarily chosen. Another assumption in the system is that the adsorption of each component follows the stoichiometric, constant selectivity isotherm model, which has been observed to hold fairly true for several systems of SMB interest as it does account for adsorbate-adsorbate interactions. This model is given as

$$\theta_i = \frac{K_i y_i}{\sum_{i=1}^3 K_i y_i} \quad 11$$

Where θ_i is the surface coverage of species i , and K_i & y_i are the dimensionless equilibrium constants and mass fractions of species i . Once the stream flow rates and compositions were calculated, the subsequent purification of propylene and propane by distillation were modeled

using ASPEN Plus to determine the energy inputs needed to produce 99.5% propylene and to recover the solvent from both extract and raffinate streams for recycle back into the SMB system. A schematic of this system is shown in Figure 27 and it consists of a 4-bed SMB unit, 2 distillation units for purifying the propylene and propane, and two heat exchangers for heat recovery from the hot desorbent recycle streams. The SMB unit operates $\sim 50^{\circ}\text{C}$ and 200 psig pressure (where we have collected Pulse Test Data). The distillation units operate at lower temperature ($\sim 37^{\circ}\text{C}$) and 200 psig, which is close to the operating conditions of a conventional C3 splitter.

Figure 27. Schematic of a hypothetical integrated 4-bed SMB unit for processing 6000 BPSD C3 stream

For a system governed by the stoichiometric adsorption isotherm (Equation 11) with desorbent present in the feed, the following procedure for determining the optimal values of the flow ratio's m_2 and m_3 is presented. For this system of a desorbent with stronger adsorption than either component to be separated the general relation $K_{\text{C}_3\text{H}_8} < K_{\text{C}_3\text{H}_6} < K_{\text{D}}$ holds true. The flow ratios of

sections 1 and 4 are independent of the values of m_2 and m_3 and are only bounded by the constraints

$$\frac{K_{C_3H_6}}{K_D} < m_1 < +\infty \quad 12$$

$$0 < m_4 < \frac{K_{C_3H_8}}{K_D} \quad 13$$

Figure 28. Region of complete separation in the (m_2, m_3) plane, $K_A = 1.5$, $y_A^F = 0.175$, $K_B = 0.2$, $y_B^F = 0.075$, $K_D = 2.0$, $y_D^F = 0.75$

Conservative restraints for the case of a strong desorbent have been identified as $m_1 > 1$. The construction of the separation region is based on certain mathematical projections that have been described in detail in the literature and will not be discussed here.[25, 26] Figure 28 shows the construction of the separation plot for the Rived NaX using the pulse test data at 50°C described in the previous experimental section. For complete separation, $m_3 > m_2$ so a lower bound of the region is the line $m_3 = m_2$. Several other bounds to the region appear on the plot and are depicted by the points, A, B, R, D, and W. The point at W indicates where optimum separation performance is achieved, but any (m_2, m_3) pair lying within the boundary of Figure 28 will lead to complete separation of propane and propylene. The values of these points are based from the measured equilibrium constants and the feed fractions of each component. Two

parameters, Ω_G and Ω_H , are first defined as the real, positive roots of the following quadratic equation:

$$\delta_F \Omega^2 - [K_A y_A^F (K_B + K_D) + K_B y_B^F (K_A + K_D) + K_D y_D^F (K_A + K_B)] \Omega + K_A K_B K_D = 0 \quad 14$$

$$\delta = K_A y_A^F + K_B y_B^F + K_D y_D^F \quad 15$$

where the subscripts A = C₃H₆, B = C₃H₈, and D=desorbent. y_i^F is the concentration of each species in the feed, and for the roots $\Omega_G > \Omega_H > 0$.

The points on the plot are given as follows:

$$\text{Point A: } \left(\frac{K_A}{K_D}, \frac{K_A}{K_D} \right) \quad 16$$

$$\text{Point B: } \left(\frac{K_B}{K_D}, \frac{K_B}{K_D} \right) \quad 17$$

$$\text{Point R: } \left(\frac{\Omega_H [\Omega_G (K_A - K_B) - \Omega_H (K_A - \Omega_G)]}{K_A K_D (\Omega_G - K_B)}, \frac{\Omega_H^2}{K_B K_D} \right) \quad 18$$

$$\text{Point W: } \left(\frac{\Omega_H [\Omega_G (K_A - K_B) - K_A (K_A - \Omega_G)]}{K_A K_D (\Omega_G - K_B)}, \frac{\Omega_H K_A}{K_B K_D} \right) \quad 19$$

The points on the plot are then connected by the following relations to finish construction of the (m_2 , m_3) separation region:

$$\text{Straight Line WD: } m_3 = \frac{\frac{\Omega_G \Omega_H (K_A - K_B)}{K_D} - K_A (\Omega_G - K_B) m_2}{K_B (K_A - \Omega_G)} \quad 20$$

$$\text{Straight Line WA: } m_3 = \frac{K_A (K_A - K_B) - K_A (K_D - K_B) y_B^F m_2}{K_D (K_A - K_B) - K_A (K_D - K_B)} \quad 21$$

$$\text{Curve RB: } m_2 = m_3 - \frac{(\sqrt{K_B} - \sqrt{K_D m_3})^2}{y_B^F (K_D - K_B)} \quad 22$$

$$\text{Straight Line AB: } m_2 = m_3 \quad 23$$

Using the experimental K values, the optimal operating conditions, (m_2 , m_3) was determined to be (0.11, 0.82).

Table 9 lists the calculated flow ratios, mass flow rates of feed, raffinate, desorbent, and extract streams, and corresponding purities (mass basis) of the raffinate and extract streams for these optimal operating conditions. The feed rate is based on a 6000 BPSD feed of 70:30 mixture of propylene: propane, diluted in desorbent:C₃ ratio of 3:1.

Table 9. Calculations for a hypothetical SMB process: Subscripts F = Feed, R = Raffinate, D = Desorbent, E = Extract

EQ constants & Feed concentrations		Flow Ratios		Calculated mass flow rates 6000 BPSD C3 mixture (kg/min)		Raffinate/Extract Purities	
K_A	1.53	m_1	1.10	G_F	1282	y_B^R	y_D^R
K_B	0.2	m_2	0.11	G_R	1321	0.073	0.927
K_D	2	m_3	0.82	G_D	1828	y_A^E	y_D^E
y_A^F	0.175	m_4	0.09	G_E	1788	0.125	0.875
y_B^F	0.075						
y_D^F	0.75						

Once the flow rates and purities of the extract and raffinate streams were calculated, ASPEN Plus process modeling software was used to determine energy inputs (Reboiler and condenser duties along with sizing) of the two subsequent distillations. The feed was assumed to be at 37°C and 200 psig. Target purities for the propylene and propane were both set at 99.5%. Equilibrium stage calculations were used in ASPEN's RadFrac distillation unit. The Peng-Robinson equation of state was used as it determines molecular interactions for hydrocarbons well. The column pressure drop was calculated by the model, and Murphee tray efficiencies of 70% were used. The number of equilibrium stages was set to a near optimum level to try to keep the column reflux ratio below 2, and the tallest column (Raffinate separation) was 22 EQ stages tall. The feed stage introduction point was manipulated until the minimum energy requirements were found. The energy duties for the reboilers and condenser units were recorded as BTU/lb C₃H₆ product. For the condenser duty, cooling water was assumed to be available with a 8.3°C ΔT , and from the calculated duties, the total gallons per minute of cooling water necessary per lb C₃H₆ was calculated. Once calculated, the necessary power requirements to pump the SMB feed, desorbent, extract, raffinate, and cooling water streams were calculated using a pump efficiency of 70%. The cost of electricity for these pumps was assumed to be \$0.09 per kWhr, and an electricity cost per ton of C₃H₆ product was calculated. CO₂ emissions were calculated for supplying the electricity to the pumps by assuming that refinery still gas could be used to generate power, with a carbon intensity of 1.135 lb CO₂ generated per kWhr of electricity produced. These rough numbers were obtained from general numbers for power generation found on the Energy Information Administration's web site.[30]

The bottoms products from both distillation units are to be recycled back to the SMB unit as seen in Figure 26, but are very hot ($T > 150^\circ\text{C}$). ASPEN was also used to recover heat from

these streams using phase-specific heat transfer coefficients. The amount of heat recovered from these streams was subtracted from the calculated reboiler duties to give a net BTU/lb C_3H_6 for the process. To supply this heat, it was assumed that refinery still gas would be used as fuel with a lower heating value of 20,267 BTU/lb still gas. The price of still gas, which is similar in heat content to natural gas, was assumed to be the market cost of natural gas obtained from the Energy Information Administration's web site and was \$3.76/MM BTU. The carbon emissions from firing the reboilers was calculated by using a carbon intensity of natural gas of 117 lbs CO_2 /MM BTU.

Several other cases were also investigated such as feeding the SMB unit a less diluted stream of C_3 feed (35% C_3 feed vs. 25% C_3 feed) and the use of desorbents other than hexane. The less diluted feed to the SMB unit resulted in higher purities of the extract and raffinate streams due to less desorbent present in the system and less energy demand for the subsequent purification of propylene and propane. Using the same calculated compositions for both 25% and 35% feed, other C_3 -desorbent separations were modeled using pentane and iso-pentane as the desorbent. The same calculations described above were performed for all these cases, and also at an elevated pressure of 265 psig. The same duties calculated for the extract and raffinate columns were compared with the numbers from a conventional C_3 splitter operating at 265 psig and was done by an outside source. Table 10 shows the cases studied using various desorbents. As can be seen from the tables the overall reduction in cost of supplemental energy required for the separation can be reduced by 60-80% depending on the conditions chosen, the desorbent selected, and proper heat integration of the process. An additional value that has not been quantified is the reduction in CO_2 emissions by the SMB process. The reduced energy requirements directly result in reduced CO_2 emissions, and as can be seen from the table, for a single separation system in a single year, 30,000-35,000 tons of CO_2 can be avoided each year by the SMB process compared to the conventional C_3 splitter. Assuming there is a price associated with carbon emissions of \$40/ton, this carbon emission reduction results in avoided penalties of \$1.2-1.4 million per year.

A comparison of the energy savings of Rived and UnRived adsorbents does not give a fair analysis due to the nature of the calculation performed. The main advantages of the Riving process are (for NaX zeolite) much enhanced kinetics at the sacrifice of some equilibrium adsorption capacity. For NaY zeolite, we observe enhanced kinetics with only a very slight decrease of the equilibrium adsorption capacity. The calculations performed here assumed that local equilibrium prevails, therefore eliminating the effects of kinetics. The kinetic advantage of the Rived zeolites cannot be realized by this calculation alone. However, it can be stated that the enhanced kinetics of the Rived zeolites makes the assumption of local equilibrium much more likely for the Rived adsorbents compared to the UnRived adsorbents. The enhanced kinetics will also make the SMB process much more efficient by better utilization of adsorbent inventory, and will lead to reduced size of adsorber beds. Another advantage of the Rived adsorbents was assessed by using the Ergun equation [31] in which the pressure drop per unit length through a packed column is given by:

Table 10. Comparison of energy savings of SMB process using hexane (top), pentane (middle), and iso-pentane (bottom) as desorbent. Last column are corresponding numbers for conventional C₃ splitter

Energy Duty	SMB system, 25% feed, hexane, 200 psig Rived NaX	SMB system, 35% feed, hexane, 200 psig Rived NaX	SMB system, 25% feed, hexane, 265 psig Rived NaX	SMB system, 35% feed, hexane, 265 psig Rived NaX	Conventional C3 splitter
Reboiler Duties					
net heat supply needed (BTU/lb C ₃ H ₆)	483	425	493	453	2790
Energy savings	82.7%	84.8%	82.3%	83.8%	
Additional Cost to fire reboilers (\$/ton)	\$ 3.63	\$ 3.19	\$ 3.71	\$ 3.41	\$ 21.0
Reboiler CO ₂ emisssons per ton C ₃ H ₆ (lb/ton)	113	99	115	106	653
Condenser Duties					
Total Condenser Heat Duty (BTU/lb C ₃ H ₆)	166	164	167	184	2774
Total cooling water consumption (gal/lb C ₃ H ₆)	1.3	1.3	1.3	1.5	22.27
Total Solvent makeup (lb/lb C ₃ H ₆)	7.1E-03	5.0E-03	7.1E-03	5.0E-03	--
Pump Electricty Cost (\$/ton C ₃ H ₆) Includes pumping feed, extract, Raffinate, Desorbent Streams & Circulating Cooling H ₂ O for condensers	\$ 2.11	\$ 1.54	\$ 2.76	\$ 2.01	\$ 2.41
CO ₂ emissions from pump powering (lb CO ₂ /ton C ₃ H ₆)	27	19	35	25	30
Total CO ₂ emissions (lb CO ₂ /ton C ₃ H ₆)	140	119	150	132	684
Avoided CO2 emissions in one year (tons)	33905	35204	33246	34412	--
net utility cost per ton of C ₃ H ₆	\$ 5.74	\$ 4.73	\$ 6.47	\$ 5.42	\$ 23.41
Utility cost reduction per ton of C₃H₆	75.5%	79.8%	72.4%	76.8%	--

Energy Duty	SMB system, 25% feed, pentane, 200 psig Rived NaX	SMB system, 35% feed, pentane, 200 psig Rived NaX	SMB system, 25% feed, pentane, 265 psig Rived NaX	SMB system, 35% feed, pentane, 265 psig Rived NaX	Conventional C3 splitter
Reboiler Duties					
net heat supply needed (BTU/lb C ₃ H ₆)	598	520	664	583	2790
Energy savings	78.6%	81.4%	76.2%	79.1%	
Additional Cost to fire reboilers (\$/ton)	\$ 4.49	\$ 3.91	\$ 4.99	\$ 4.38	\$ 21.0
Reboiler CO ₂ emisssons per ton C ₃ H ₆ (lb/ton)	140	122	155	136	653
Condenser Duties					
Total Condenser Heat Duty (BTU/lb C ₃ H ₆)	281	261	338	314	2774
Total cooling water consumption (gal/lb C ₃ H ₆)	2.2	2.1	2.7	2.5	22.27
Total Solvent makeup (lb/lb C ₃ H ₆)	7.1E-03	7.1E-03	7.1E-03	7.1E-03	--
Pump Electricty Cost (\$/ton C ₃ H ₆) Includes pumping feed, extract, Raffinate, Desorbent Streams & Circulating Cooling H ₂ O for condensers	\$ 2.30	\$ 1.68	\$ 3.03	\$ 2.21	\$ 2.41
CO ₂ emissions from pump powering (lb CO ₂ /ton C ₃ H ₆)	29.1	21.2	38.2	27.8	30.4
Total CO ₂ emissions (lb CO ₂ /ton C ₃ H ₆)	169	143	194	164	684
Avoided CO2 emissions in one year (tons)	32077	33701	30544	32375	--
net utility cost per ton of C ₃ H ₆	\$ 6.79	\$ 5.59	\$ 8.02	\$ 6.59	\$ 23.41
Utility cost reduction per ton of C₃H₆	71.0%	76.1%	65.7%	71.8%	--

Energy Duty	SMB system, 25% feed, IsoPentane, 200 psig Rived NaX	SMB system, 35% feed, IsoPentane, 200 psig Rived NaX	SMB system, 25% feed, IsoPentane, 265 psig Rived NaX	SMB system, 35% feed, IsoPentane, 265 psig Rived NaX	Conventional C3 splitter
Reboiler Duties					
net heat supply needed (BTU/lb C ₃ H ₆)	693	607	803	746	2790
Energy savings	75.2%	78.2%	71.2%	73.3%	
Additional Cost to fire reboilers (\$/ton)	\$ 5.21	\$ 4.56	\$ 6.04	\$ 5.61	\$ 21.0
Reboiler CO ₂ emissions per ton C ₃ H ₆ (lb/ton)	162	142	188	175	653
Condenser Duties					
Total Condenser Heat Duty (BTU/lb C ₃ H ₆)	376	347	476	477	2774
Total cooling water consumption (gal/lb C ₃ H ₆)	3.0	2.8	3.8	3.8	22.27
Total Solvent makeup (lb/lb C ₃ H ₆)	7.1E-03	7.1E-03	7.1E-03	7.1E-03	--
Pump Electricity Cost (\$/ton C ₃ H ₆) Includes pumping feed, extract, Raffinate, Desorbent Streams & Circulating Cooling H ₂ O for condensers	\$ 2.36	\$ 1.75	\$ 2.98	\$ 2.34	\$ 2.41
CO ₂ emissions from pump powering (lb CO ₂ /ton C ₃ H ₆)	29.8	22.1	37.6	29.5	30.4
Total CO ₂ emissions (lb CO ₂ /ton C ₃ H ₆)	192	164	226	204	684
Avoided CO₂ emissions in one year (tons)	30642	32382	28554	29886	--
net utility cost per ton of C ₃ H ₆	\$ 7.57	\$ 6.31	\$ 9.02	\$ 7.95	\$ 23.41
Utility cost reduction per ton of C₃H₆	67.7%	73.0%	61.5%	66.0%	

$$\frac{\Delta P}{L} = \frac{150V_s \mu (1-\varepsilon)^2}{D_p^2 \varepsilon^3} + \frac{1.75 \rho V_s^2 (1-\varepsilon)}{D_p \varepsilon^3}$$

24

where V_s is the fluid superficial velocity (m/s), μ is the fluid dynamic viscosity (Pa s), D_p is the adsorbent particle size (m), ε is the column void fraction, and ρ is the fluid density (kg/m³). Using the Glueckauf [32] approximation in which the overall mass transport rate, k (s⁻¹), is related to the diffusivity by

$$k = \frac{\Omega D}{D_p^2}$$

25

where Ω is a constant, generally 15. It can be calculated that to achieve the same mass transfer values observed on Rived NaX by using UnRived NaX, the particle size would need to be reduced by ~40%. Using the Ergun Equation, it can be calculated that holding all other numbers constant, this could nearly double the column pressure drop to achieve the same transport rates. Also, the increased porosity of the Rived adsorbents will allow for the use of smaller particles while still achieving the same pressure drop. This decrease of particle size will further enhance the mass transport.

In summary, a hypothetical SMB propane/propylene separation system was approximated as a True Countercurrent adsorption process using equilibrium theory to determine the steady state behavior of the SMB unit. The SMB unit would process a feed of 6000 BPSD C₃ mixture containing 70% propylene and 30% propane, which was further diluted in desorbent to a feed

fraction of 0.25. This calculation requires the relative equilibrium constants and feed compositions of propylene, propane, and desorbent (hexane, used in the experiments) to predict the complete separation of propane/propylene and the resulting purities of the SMB raffinate and extract streams. The equilibrium constant of the desorbent was assumed to be a value larger than that of either propane or propylene as it was not directly measured. The raffinate (containing propane and desorbent) and extract (containing propylene and desorbent) are subsequently separated in distillation units to obtain the pure products. ASPEN was used to model these separation units along with a heat recovery scheme, and the calculated energy duties were compared with the energy requirements of a conventional C_3 splitter. The energy consumption of the SMB process also included the necessary additional pumping power required for all the additional fluid streams involved in the SMB process. The energy calculation was performed for cases using hexane, pentane, and iso-pentane as the desorbent. Two different pressures (200 and 265 psig) and two different feed concentrations to the SMB unit (25% and 35%) were also investigated for each different desorbent.

The results showed that the energy requirements of the propylene/propane separation can be reduced by 60-80% depending upon the choice of desorbent, operating conditions, and implementation of a proper heat recovery system. The utility cost savings were quantified in terms of amount of fuel burned and amount of electrical energy needed for fluid pumping. An additional benefit is that this reduction of energy usage directly relates to reduced CO_2 emissions by the process. Future regulations may result in a cost penalty on CO_2 emissions, and the SMB process would alleviate some of that burden.

The comparison of Rived and UnRived zeolites for C_3 separation by an equilibrium based calculation does not give a true comparison of the advantages of the Rived zeolite as the enhanced transport through the Rived materials cannot be realized. It can be said that the equilibrium assumption is more likely to be true for the Rived material compared to the UnRived materials. The enhanced transport will lead to smaller adsorbent beds and more efficient utilization of adsorbent inventory. Smaller particles of Rived adsorbents can be used to further increase transport while maintaining a constant pressure drop due to the increased porosity of the Rived materials. It has been shown that use of an adsorption process for C_3 separations has the potential to drastically reduce the energy consumption of production of polymer grade propylene.

Conclusions:

1. The mesoporous zeolite Y technology was successfully extended to X and A zeolites that are more relevant to adsorbent applications.
2. The zeolites (mesoporous and conventional) were formed into adsorbent particles and the particles maintain enhanced mesoporosity and external surface area.
3. Pulse testing established that the enhanced mesoporosity inside the mesoporous zeolite based adsorbents leads to much increased (>100% increase) overall mass transport rate for propane and propylene.
4. Energy saving calculation shows that for a hypothetical SMB propane/propylene separation plant using the mesoporous NaX zeolite based adsorbents that process 6000 BPSD refinery grade propylene consumes 60-80% less energy, depending on the operation conditions, than a hypothetical C3 splitter operating at the same capacity. The energy saving also translates to a reduction of 30,000-35,000 tons of CO₂ emission per year.

Patents/Publications:

Patent applications are current in preparation for filing.

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Appendix:

Front-end energy consumption simulation by Adsoritech, Inc., NJ

1. Study procedure

- (i) Develop a design basis to benchmark a typical C3/C3= splitter column in a Refinery or Petrochemical complex. The design basis defines typical feed flowrate, pressure, temperature and composition.
- (ii) Use the above design basis to simulate a conventional C3/C3= column using a commercial process simulator and prior experience designing such a system.
- (iii) Make assumptions about the performance of the Propane-Propylene Adsorption system and use the process simulator to design the desorbent/propane and desorbent/propylene distillation columns.
- (iv) Compare the energy consumption of the conventional system from step 2 with newly designed separation system in step 3.
- (v) Tabulate the assumptions and create objectives to be determined experimentally by research team creating the molecular sieve material.

Key assumptions made for the study

- (i) The C3/C3= separation system is fed a mixture of 70:30 (wt. basis) of Propylene and Propane at 265 psig and 97 deg F. The flow rate of this stream is 6000 bpsd (50000 bpsd FCC unit).
- (ii) The product propylene must have polymer grade purity of 99.5% wt. basis.
- (iii) The C3/C3= adsorption system splits the feed stream with a 100% recovery of propane and propylene components in Raffinate and Extract streams respectively.
- (iv) The desorbent liquid used in the adsorbent is recycled from both the Raffinate and Extract distillation columns and along with some make up desorbent is fed into C3/C3= adsorption system in a feed to volume ratio of 2:1 (Desorbent : Feed).
- (v) A small amount of desorbent used in the process is lost with Propane and Propylene product streams from Raffinate and Extract distillation units.
- (vi) The desorbent used for the study is 1-Hexene.
- (vii) The desorbent is split in the same weight ratio with the propane and propylene stream as present in the feed downstream of the Adsorption system. (i.e. 70 % wt of desorbent mixing with propylene to form Extract stream and balance with propane stream to form Raffinate).

- (viii) Low pressure (LP) and medium pressure (MP) steam are available from Reboiler duty at 65 psig and 210 psig, with 30 deg F superheat.
- (ix) The cooling water is used in the distillation towers with 15 deg F temperature swing. (Supply at 77 deg F and Return at 92 deg F.)
- (x) Pumping energy of various streams in the above processes consumes some energy and has been neglected in this study.
- (xi) In addition to the above, reasonable pressure losses, exchanger temperature approaches, thermodynamic model choices etc were also made in the study but are not listed separately.

2. Tabulated summary results of the study simulations

Table 1: Major utility consumptions per pound of propylene product

Process scheme	Reboiler Duty Btu/lb of C3= product	Condenser Duty Btu/lb of C3= product	Steam usage lb/lb of C3= product	Cooling water US gal/lb of C3= product
Conventional C3/C3= distillation process	2790	2774	2.98 (LP Steam)	22.27 (DT=15 deg F)
Idealized C3/C3= Adsorption separation process	666	656	0.77 (MP Steam)	5.27 (DT=15 deg F)

Table 2: Energy saving projected to entire FCC feed stream in US (DOE database)

Year	FCC feed Stream average (Thousand Barrel per day)	Reboiler Energy saving Billion Btu/year @ 8500 stream hours per year	CO₂ Emissions equivalent Burning of barrels of oil per day
2007	5250	60145	19160
2008	4983	57087	18186
2009	4957	56788	18091

Source: <http://tonto.eia.doe.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=MCRCCUS2&f=A>

Table 3: Major Equipment sizes for 6000 bpsd C3/C3=separation duty

Process scheme	Column sizes	Duty for major exchangers (includes design margins) MMBtu/hr	Cooling water and steam consumptions	Rough order of magnitude cost Million USD
Conventional C3/C3= distillation process	16' diameter X 300 ft tall, 220 trays Double column system	220	48 tph LP Steam 11850 gpm CW	55-65
Idealized C3/C3= Adsorption separation process	4' diameter X 30 ft tall (16 trays) + 6' diameter X 30 ft tall (16 trays)	40	13 tph MP Steam 2900 gpm CW	10-15 (Excluding Adsorption system)

3. Process schematics

(1) CONVENTIONAL C3/C3= DISTILLATION COLUMN

PROPANE PROPYLENE SPLITTER SEPARATION SCHEME

(2) ADSORPTION BASED C3/C3= SEPARATION PROCESS

PFD 1: ADSORPTION SYSTEM

PFD 2: RAFFINATE COLUMN

PFD 3: EXTRACT COLUMN

PFD 4: DESORBENT COOLING & RECYCLE PUMP

4. Suggested experimental work for getting a better estimate of process design and energy estimates
- (i) The optimum desorbent type needs to be determined. The study suggests that in order to use lower temperature in the Raffinate and Extract columns it may be advisable to use a lower boiling point molecule or mixture of molecules. Such as C5 or C5 in mixture with C6.
 - (ii) The actual ratio of adsorbent carryover to the Raffinate and Extract columns needs to be determined. This ratio has been assumed to be in the same proportion as the ratio of C3 and C3= in the feed.
 - (iii) The assumption that 100% propane and propylene are recovered in the adsorption process is ideal. The actual carryover needs to be estimated or experimentally determined.
 - (iv) Based on the input from the experiments with data for diffusion and other adsorption parameters a better design estimate and process cycle for the adsorption system needs to be determined. This cycle and design can give a better cost estimate and the energy estimate for the process.
 - (v) The simulation done is very preliminary and the process to distill Raffinate and Extract can be further optimized with significant energy savings if studied in more detail.