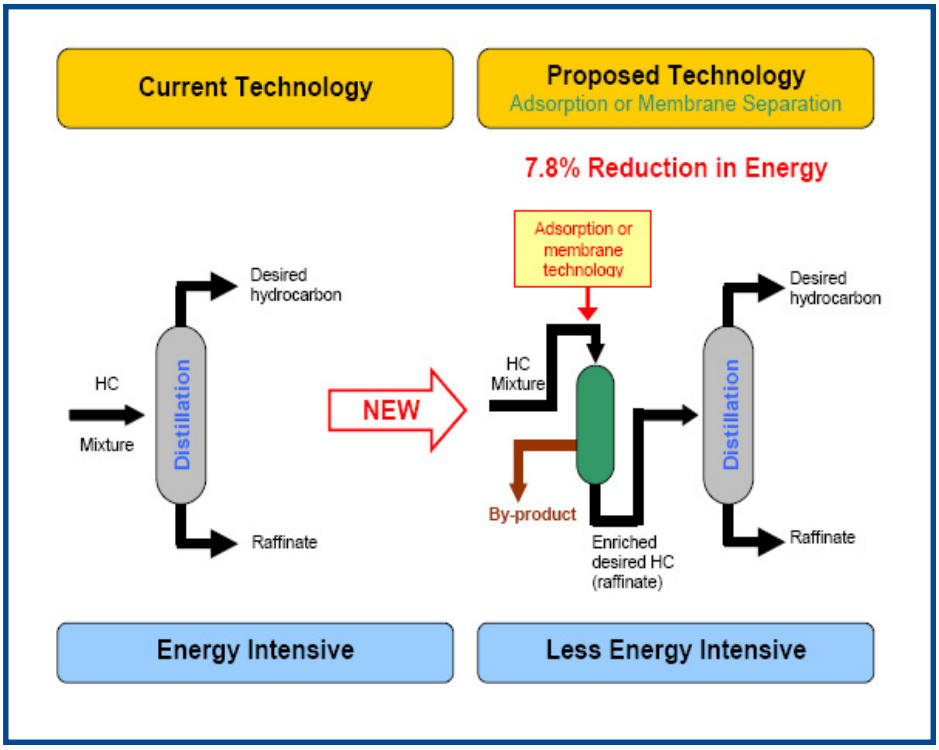
Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations

Zeolite Separation Technology Can Enable More Efficient Production of Hydrocarbons

Today's dominant C_2-C_5 hydrocarbon (HC) separation technologies are extractive and cryogenic distillation. Cryogenic C_2-C_5 distillation is a non-regenerative process that is highly energy intensive and harmful to the environment. These energy-intensive separations have motivated the petrochemical industry to explore alternative separation technologies, reflected in the large number of patents issued in the last 10 years (54 in the U.S. alone). The patented technologies to date represent only incremental improvements in the energy intensity of the distillation. Separation processes using bulk or membrane zeolites have primarily relied only on size exclusion to achieve physical separation of molecules. However, size exclusion alone is inadequate for separation of many commercially important HCs with similar boiling point and similar-sized molecules in the mixtures. The project team realized the opportunity to enhance the selectivity of zeolites by modifying their adsorptive property in order to change the interaction of the diffusing molecules with the internal pores and the external surface of the zeolite structure. The focus of this project was the surface and framework modification of the commercially available zeolites for significant enhancement in current HC separation. The R&D team targeted separation of linear from branched hydrocarbons, in particular isoprene from C_5 streams. It is anticipated that the results will provide the basis of knowledge to enable this technology for additional hydrocarbon and chemical separations.



Current versus proposed technology for the adsorption or membrane-based separation

Benefits for Our Industry and Our Nation

Employment of this technology in hydrocarbon separation of C_2-C_5 would have the following potential benefits:

- 7.8% reduction in energy consumption for hydrocarbon separations in the U.S.
- Estimated energy savings of 39×10^{12} Btu per year
- Reduction of volatile organic compounds, carbon dioxides, carbon monoxides, and nitrogen oxides (NO_x)

Applications in Our Nation's Industry

This technology will result in improved production efficiency of isoprene and more efficient separation of other hydrocarbons, reducing energy consumption in the chemicals and petrochemical industries.

Project Description

The goal of this project was to develop modified zeolite for energy-efficient, adsorption-based separation of isoprene and other similar olefins from HC streams. The success of this project resulted in an enabling technology for future adsorbents, materials for membranes, and the potential development of shape-selective catalysts.

Barriers

The technical hurdles overcome by this project were

- enhanced selectivity and lifetime of modified membranes for industrial streams,
- determined the precise combination for zeolite and carbon deposition parameters that would be successful for the separation of n-pentane from isoprene, and then n-pentane from isoamylenes, and
- recognized the potential for increased fouling and decreased ability to regenerate the materials due to the increasingly complex feedstreams.

Pathways

The objectives of this project were achieved through

- analyzing commercially available zeolites,
- developing modified zeolite adsorbents and membranes,
- conducting pilot bench-scale testing of bulk modified zeolites and membranes,
- performing simultaneous economic analysis for implementation of technology, and
- studying modified zeolite membranes at elevated temperatures in binary and four-component stream.

Results

- Performed HC adsorption/desorption experiments which directed the focus to developing and optimizing modified FAU and MFI zeolite membranes
- Utilized bulk carbonization to passivate the zeolite activity toward organic adsorption/decomposition
- Confirmed acid site deactivation of zeolites by performing NH3-TPD (Temperature Programmed Desorption) experiments
- Identified protonated MFI zeolite membrane as the most promising material for isoprene/n-pentane separations
- Demonstrated 4.1% enrichment of n-pentane over isoprene in a binary mixture using a modified and protonated MFI membrane on stream
- Demonstrated that the spent membranes restored to original separation capabilities
- Demonstrated that in four-component streams, a modified MFI zeolite membrane had high selectivities for n-pentane and 1-3 pentadiene over isoprene but virtually no separation for the 2-methyl-2-butene/isoprene pair

Commercialization

The project team successfully tested in an industrially relevant four-component HC stream. The stream components were the four major components found in Goodyear's stream. The membranes can be easily scaled-up and designed for "tube and shell" design modules. The modules can be designed along the lines of Mitsui's alcohol dehydration commercialized process. A well-known support tube manufacturer, Pall Corporation, has been consulted for designing and building the modules for commercialization.

Project Reports

This project was completed in October 2006. The final report is available on the Industrial Technologies Program website: http://www.eere.energy.gov/industry/imf/completed_rd.html

Project Partners

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A Strong Energy Portfolio for a Strong America

Energy efficiency and clean, renewable energy will mean a stronger economy, a cleaner environment, and greater energy independence for America. Working with a wide array of state, community, industry, and university partners, the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy invests in a diverse portfolio of energy technologies.

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