ADMINISTRATIVE INFORMATION

1. **Project Name:** Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations

2. **Lead Organization:**

Goodyear Chemical
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4. **Project Partners:**

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5. **Date Project Initiated:** April 23, 2002

6. **Expected Completion Date:** October 23, 2006

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:**

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

8. **Technical Barrier(s) Being Addressed:**

The primary *technical hurdle* in this work is finding the precise combination of zeolite and carbon deposition parameters that will be successful for the separation of *n*-pentane from isoprene, and then *n*-pentane from isoamylenes. Additional potential *hurdles* relate to scale up and industrial usage, such as potential fouling, deactivation, and material regeneration. It is expected that increasingly complex feed-streams are likely to increase fouling and decrease the ability to regenerate the materials, but these will not be known quantities until actual industrial testing is initiated. In the worst-case scenario, however, we anticipate that these materials can be regenerated and re-used in a similar manner as industrial zeolite catalysts. Fortunately, successful preliminary work has indicated that this separation is possible using differential adsorption on a carbon-modified zeolite. Furthermore, a great deal of groundwork concerning carbon deposition in zeolites has already been performed[1,2,3,4], allowing us to focus on a relatively small number of variables. Selective desorption can be an issue with some adsorbent materials, and it is recognized in this research that studies will need to be performed regarding this issue. However, based on previous work[1], these materials will possess significantly different adsorption energies such that both pressure and temperature can be readily used to achieve selective desorption, and therefore successful separations of the hydrocarbons considered in this project.

9. **Project Pathway:**

A strong team has been assembled to attack the aforementioned technical barriers. The intended pathway includes utilizing University of Colorado's (U. Colo.) strong tubular membrane program and adapting this with carbon modified zeolites prepared by Sandia National Laboratories (SNL) and tested at NM Tech University (NMT). The newly assembled membrane utilizes the strengths from both organizations and will be rigorously tested using actual plant C_5 streams by Goodyear Chemical. Through an iterative fashion, the generated data will be forwarded to Burns & McDonnell for economic process modeling. In addition, a well-known support tube manufacturer (Pall Corporation) has been consulted for commercialization.

10. **Critical Technical Metrics:**

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

Metrics:

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

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:**

[1] J. Antes, Z. Hu, W. Zhang, and K.J. Huttinger, Carbon 37 (1999) 2031.
[2] H.S. Cerqueira, P. Ayrault, J. Datka, P. Magnoux, and M. Guisnet, Journal of Catalysis 196 (2000) 149.
[3] H.G. Karge, W. Niessen, and H. Bludau, Applied Catalysis A: General, 146 (1996) 339.
[4] P. Andy, D. Martin, M. Guisnet, R.G. Bell, and R.A. Catlow, J. Phys. Chem. B, 104 (2000) 4827.

- Modified numerous zeolites (including Y, L, ZSM-5, Beta) by varying cation-loading, surface-modifying temperatures and durations, Si/Al ratios, carbonization levels.
- Modified materials were characterized and evaluated for separations using BET surface analyzer and Temperature Programmed Desorption (TPD) of branched & linear C_5 hydrocarbons. TPD was used to measure the catalytic acid sites and sorptive strengths by NH_3 and pyridine sorption.
- Analytical methods completed for separation/permeation at Goodyear.
- Constructed pilot plant unit at Goodyear (capable of evaluating packed beds, disks, and membrane tubes) and also at SNL for C_5 separation experiments.
- Conducted preliminary testing of separation abilities of various carbonized pellet disks and bulk material in Goodyear flow reactor. Pellet disk appears to be too porous and allowing all gases to pass through. Supported zeolite disc and/or tube membranes are necessary for testing.
- Started synthesizing self-supported, titania coated stainless steel-supported and alumina-supported Zeolite Y, ZSM-5 and silicalite membranes. The surface modification of supported membranes ongoing.
- Awarded an increase in FY03 and FY04 funds for this OIT/IMF project. The increase will allow the scope of the project to increase by adding university, an additional industrial partner, and lab-modeling efforts into the project. This will allow for the acceleration of the program to bring modified zeolites to commercialization and implementation.
- Wrote and signed the new Statement of Work between SNL and U. Colo. (Dr. Richard Noble) for OIT/IMF enlarged project. Their primary tasks are to produce zeolite membranes and conduct on-line testing of the membranes and the separation/selectivity process. Intellectual Property rights continue to be worked out between new three-way partnership between SNL, Goodyear and U. Colo.
- Modeling of Zeolite Adsorption Isotherm studies started with Dr. Marcus Martin of SNL to better understand the structure/property relationship of the modified zeolites and their enhanced hydrocarbon selectivity.
- Held review meeting at Sandia, CA in March, 2004 with both Goodyear Executive and Chemical Leadership Teams.
- Held a meeting between SNL (Tina Nenoff) and U. Colo. (Rich Noble) at the American Chemical Society National Meeting, Anaheim, CA, in April, 2004.
- Fourth year of CRADA funded by DOE/ITP.
- CRADA extended between SNL and Goodyear.
- Increased funding for program established by DOE/ITP PM to Sandia. (additional $200K for the 4th year of CRADA)
- Modified membranes optimized by both internal and external zeolite pore organic modification.
- Membranes tested on binary systems (50/50 n-pentane/isoprene) at varying temperatures and pressures both in the lab and at Goodyear Chemicals.
- Goodyear Chemicals testing done in small pilot plant unit, built specifically for this CRADA.
- With unmodified MFI zeolite membranes, maximum separation factors of 25-35 were obtained between RT and 70°C in the lab.
- With unmodified and modified MFI zeolite membranes, maximum enrichment of a binary mixture is 4.1% or the equivalent of 7.8% with an internal pore modification (from SNL) tested at Goodyear.
- Regeneration studies of the membranes restored spent membranes to original separation capabilities.

12. **Future Plans:**

The remaining milestones to be accomplished are to:

- Separation testing at variable temperatures and pressures with a modified zeolite MFI membrane using an industrially relevant 4-component hydrocarbon mixture containing isoprene.
- Feedback of results to Goodyear, NMTech and Burns & McDonnell.

- Complete detailed economic benefits from adsorption technology.
- Final reports to be written by Sandia (Nenoff) for DOE and Sandia (SAND report).

13. **Project Changes:**

The project was extended to a fourth year with generous DOE/ITP funding; the CRADA extension was signed by Sandia and Goodyear Chemical Company.

14. **Commercialization Potential, Plans, and Activities:**

Commercialization of this technology relies on the research and development of novel modified zeolite materials for advanced energy efficient separation processes for the petroleum and chemical industries with the help of future ITP funding. Successful research and development of these materials and their final commercialization into separation processes is guaranteed with the ensemble of varying skills from this project team. These skills include the industrial separations expertise of Goodyear, the advanced industrial process modeling of Burns & McDonnell, and the research and development expertise of SNL, NM Tech and Univ. CO. It is envisioned that the successful completion of this research will position this project team for a future ITP proposal, which will be used to completely develop a commercially viable process. The integration of materials research, process development, and engineering analysis, *via* direct feedback, will streamline commercialization of this technology. *Current and potential collaborating strategies* are inherent to this proposal because each industrial partner has different skill sets. It is expected that during the commercialization stages of an ITP-funded proposal, Pall Corporation will be a new team member. Their contribution in the future ITP proposal will be the adaptation of this technology to membrane based separations, while licensing strategies, economic analysis, and potential market barriers and will be addressed by all partners of this future ITP proposal. Finally, the necessary validation to other chemical industries for this technology will be twofold. The economic benefits obtained through the *minimization of energy and waste* under industrial process conditions, will be demonstrated *via* economic modeling by Burns & McDonnell, and the technical feasibility of this will be demonstrated *via* pilot-plant trials by Goodyear. After the completion of this ITP proposal, ITP funding will be sought for material development of process separations relying on pressure swing adsorption and membranes.

15. **Patents, Publications, Presentations:**

- Nenoff, T.M.; Kartin, M.; Thoma, S.G.; "Enhanced Selectivity of Zeolites by Controlled Carbon Deposition" **US Patent # 7,041,616**; May 9, 2006.
- Nenoff, T.M.; Kartin, M.; Dong, J.H.; "Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations", (open/closed presentations) at the DOE/ITP annual review meeting (Chicago, IL June **2005**).
- Ulutagay-Kartın, M.; Cornelius, C. J.; Nenoff, T. M., "Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations", American Institute of Chemical Engineers 2003 Annual Meeting, San Francisco, CA, Nov. 16-21, **2003.**
- Ulutagay-Kartın, M.; Cornelius, C. J.; Nenoff, T. M., "Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations", 226th. American Chemical Society National New York, NY, Sept. 7-11, **2003**.
- Attended and presented (poster and talk) at the DOE/OIT/IMF annual review meeting (Golden, CO, June **2003**).
- Nenoff, T.M.; Thoma, S.G.; Kartın, M., " Enhanced Selectivity of Zeolites by Controlled Carbon Deposition." Sandia National Laboratories, SD-6865/S96542, patent pending **2003**.

- Sandia (and Goodyear team members) presented a status overview to the Executive Team and the Chemical Senior Leadership Team of The Goodyear Tire & Rubber Company in February **2003** at Goodyear Corporate Headquarters in Akron, Ohio.
- Ulutagay-Kartın, M.; Thoma, S.G.; Cornelius, C.; Nenoff, T.M., "Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations." Abstracts of papers of the American Chemical Society Aug. 18, **2002**, *224*, *pt.1*, pp. U439-U440.
- Attended and presented (poster and talk) at the **2002** DOE/OIT/IMF annual review meeting (Albuquerque, NM).
- M. Ulutagay-Kartın, S. Thoma, C. Cornelius, T. M. Nenoff, "Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations", 3rd. NLCat 2002, Pacific Northwest National Laboratory, Richland, WA, May 22-23, **2002**.

16. **Budget History and Projection, $000:**

Project Year	ITP	Industry (note cash, in-kind, labor)	Other
PY-I	198	198	
PY-II	301	301	
PY-III	301	301	
PY-IV	200	10	