Industrial Technologies Program

Biocatalytic Desulfurization of Petroleum

New Processing Method for Biocatalysts Will Help Petroleum Industry Meet EPA Goal of Ultraclean Fuels

Pending EPA regulation, sulfur levels in transportation fuels must be reduced by 90% or more below current levels. Hydrotreating is the main desulfurization process and although it is the preferred option of refineries, increasing capacity to meet new sulfur level restrictions may not be economical throughout the industry. Biological desulfurization offers an attractive alternative to conventional treatments due to its mild operating conditions (temperature and pH) resulting in energy savings, greater sulfur removal potential, greater process chemistry selectivity, and the anticipated use of lower quality feedstocks.

Until now, biocatalytic desulfurization has been limited by the narrow reaction specificity of current biocatalysts and the slow rate of desulfinase, one of the four enzymes involved in the desulfurization pathway. This project seeks to improve biodesulfurization on two levels. The first level is to improve the activity and broaden the substrate specificity of desulfinase, increasing and perhaps maximizing its effectiveness. The second level is to enable deeper desulfurization (compared to only desulfinase degradation) by a sequential or combinatorial approach using biological ring opening (biocracking) in addition to desulfinase degradation.

Oxidative Biodesulfurization Path

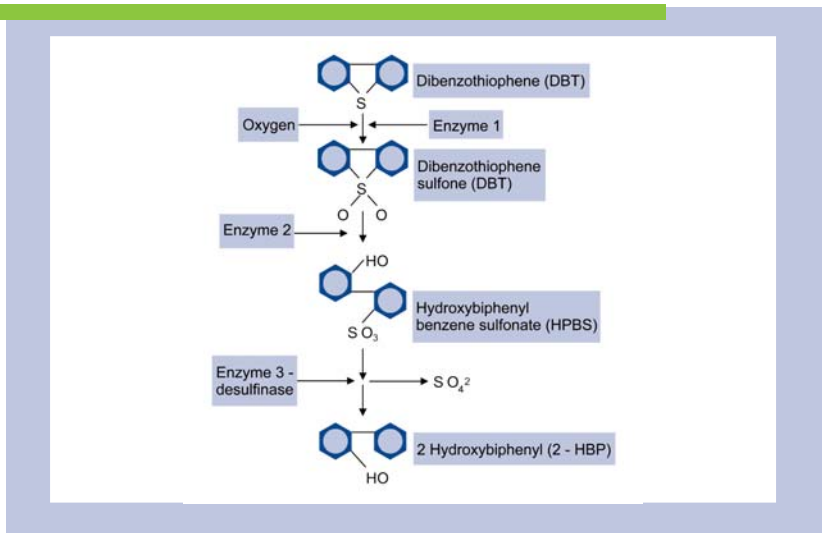

Diagram of the control technology that enables very low excess air in process heaters.

Benefits for Our Industry and Our Nation

- Reduced energy use
- Creates a more effective desulfurization process
- Enables refining of lower quality crude oils

Applications in Our Nation's Industry

This technology is expected to help meet the increased EPA standards of sulfur content in transportation fuels while cutting refining costs and allowing the use of lower quality crude in refineries.

Project Description

Goal: To develop a biocatalyst with higher activity and broader substrate specificity for desulfurization of petroleum feedstocks through directed evolution, and investigate the potential of biocracking for enhancement of sulfur removal.

The major hurdle preventing the biodesulfurization process from being developed into a commercial process is linked to the kinetics of the desulfinase enzyme. Directed evolution will be used to develop enzyme mutants which will be screened to select enzymes exhibiting improved specificity and activity. DNA sequencing will be performed on selected enzyme mutants to identify key amino acids responsible for the enzyme's efficiency. Biocracking catalysts will be developed on the assumption that ring opening can increase substrate solubility and decrease steric hindrance. The desulfinating enzyme would then have easier access to the carbon-sulfur bond, increasing effectiveness.

Milestones

- Exxon has developed the recombinant enzyme strain which was passed on to the University of Tennessee, Knoxville (UTK).
- Together with the Oak Ridge National Laboratory (ORNL), UTK performed directed evolution (through point mutagenesis using PCR) and assessed the substrate specificity. The enzyme did not desulfinate most of the model substrates (mostly thiophenes and sulfonates) but was more effective on diesel fuel. Further tests are needed.
- Exxon, UTK, and ORNL collaborated on determining the extent of biodesulfurization using the new enzyme. The mutant strains showed activity as much as 4 times greater than parent strains.
- For the promising mutants, UTK and ORNL performed DNA sequencing to identify the key amino acids responsible for the enzyme's efficiency. No differences in the genetic sequence were seen but the change in activity may be due to a mutation in the regulatory portion of the DNA sequence or the presence of a different copy number of the plasmid carrying the desulfinase gene in different strains. Further tests are needed.
- Development of the biocracking catalysts was performed solely by Texaco. The enzyme used demonstrated an ability to open rings in a variety of model substrates as well as in diesel and crude oil.

Project Partners

University of Tennessee
Knoxville, TN

ExxonMobil Corporate Strategic Research
Annandale, NJ

Texaco Upstream Technology
Houston, TX

Oak Ridge National Laboratory (ORNL)
Bioprocessing Research and Development Center Oak Ridge, TN

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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