PERP Program
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Chem Systems' Process Evaluation/Research Planning program has published a new report, ***Ethylene via Catalytic Ethane Dehydrogenation (98/99S9)***.

Ethylene is typically obtained from non-catalytic steam cracking of saturated hydrocarbons such as ethane and propane and alternatively from the thermal or steam cracking of heavier liquids such as naphtha and gas oil. Steam cracking produces a variety of other products, including diolefins and acetylene. The latter are costly to separate from the ethylene, usually by extractive distillation and/or selective hydrogenation of the acetylene back to ethylene.

The dehydrogenation of paraffins is equilibrium-limited and hence requires high temperatures. Using this approach and conventional separation methods, both Houdry (Lummus) and UOP have commercialized the catalytic dehydrogenation of propane to propylene. A similar concept is possible for ethane dehydrogenation, but to date an economically attractive commercial process has not been developed. Recent work in the area of catalytic dehydrogenation of ethane has produced some promising results. Various companies are engaged in this research including Dow and BP. This report reviews the results of a patent issued to Dow and analyzes the economics of a speculative process for the production of ethylene via this route.

In order to achieve reasonable economic conversion, high temperatures are a prerequisite to dehydrogenating paraffins for the production of olefins. Higher paraffins are easier to dehydrogenate and processes exist for this purpose (e.g. UOP’s Oleflex and Lummus’ Catofin processes). Although high temperatures are achievable and indeed are commonplace for processes such as steam cracking, the difficulty is one of selectivity. Higher temperatures bring dividends in conversion at the cost of selectivity losses to side reactions including cracking and coking.

Dow has been awarded a patent that produces ethylene as an intermediate in a two step process producing ethylbenzene from ethane. Although Dow has not announced plans to commercialize this technology, this report has evaluated the Dow approach based on a speculative process design. The process involves contacting ethane in a dehydrogenation zone with a catalyst comprising a mordenite zeolite yielding a dilute ethylene stream. This stream is then contacted with benzene in an alkylation zone under reaction conditions such that ethylbenzene is formed. The dehydrogenation reaction (i.e. ethane to ethylene) is the area of interest for this report.

The Dow invention produces a product stream containing predominantly ethylene and unreacted ethane without the formation of unwanted impurities such as acetylene and diolefins. The reactor contains a mordenite zeolite catalyst, optionally containing gallium, zinc, or a platinum group metal, the latter being preferably platinum or ruthenium. Mordenites useful for the dehydrogenation process of this invention possess a silica to alumina molar ratio ranging between 10 and 500, preferably between 10 and 100. For comparison purposes, the dominant commercial propane and butane dehydrogenation processes use platinum on alumina (Oleflex) or chromia/alumina (Catofin). The patent results are summarized below.

DEHYDROGENATION OF ETHANE OVER MORDENITE CATALYSTS
(Dow Patent: WO96/34843)

Example	1	2	3	4
Catalyst	Ga-Mor	Zn-Mor	Ru-Mor	Mor
SiO_2/Al_2O_3	23.8	19	19	112
Temperature, ^oC	700	700	700	700
Pressure, kPa	101	101	101	101
GHSV, hr^{-1}	1,200	1,200	1,100	1,200
Ethane conversion, wt%	14	50	48	14
Ethylene selectivity, wt%	85.6	85.2	86.1	85.6

The conversion of ethane in the patent examples ranged from 14 to 50 percent. This is somewhat lower than the once-through ethane conversions found in high severity steam cracking operation (e.g. 60-70 weight percent). Since the ethane is recycled to extinction, the lower conversion results in significant ethane “traffic” throughout the plant. Speculative process flow plans and economics have been prepared for a one billion pound peryear ethylene plant basedon catalytic ethane dehydrogenation. These results are compared to a similarly-sized conventional ethane steam cracker.