

CHEMSYSTEMS PERP PROGRAM

Alternative Routes to Propylene

Developing Technology & Costs of Producing propylene via (1) Steam Cracking/Dimerization/Metathesis process, (2) n-Propanol from glycerin byproduct of biodiesel production, (3) Raffinate-1 (butenes mix), (4) Oxidative Dehydrogenation of Propane. Existing Commercial Propylene Technology & Production Costs are also summarized. Regional Supply/Demand Forecasts are included.

PERP 08/09S8

Report Abstract

January 2010

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INTRODUCTION

Propylene supply has been a concern in recent years, mostly owing to strong demand growth for polypropylene (PP). The concern stems from the fact that propylene supply is linked to the vagaries and limitations of the production of other products - namely ethylene via steam cracking, and gasoline production from fluid catalytic cracking (FCC). The growing demand for propylene requires new ways for its production.

The petrochemical industry has reacted and technology developers have seen this potential supply gap as an opportunity and have developed several "on-purpose" propylene (OPP) production technologies. These approaches include propane dehydrogenation, olefin metathesis, selective butylenes (C_4 s) and carbon cuts (C_5) olefin cracking, methanol to olefins (MTO) and propylene (MTP) and enhanced FCC processes. All of these routes have been or will soon be exploited commercially to varying degrees. Furthermore, there is an emphasis on the development of routes to "green" or "bio-propylene".

Despite this overabundance of innovation, still more "on-purpose" propylene routes are under development. The challenge of developing alternative technologies is made more and more difficult because the commercial technologies such as steam cracking and catalytic dehydrogenation are well established and continuously subject to incremental improvements. However, they still suffer from thermodynamic limitations with respect to the paraffin conversion (which result in the need to operate at high temperatures, with consequences for coke formation, periodic regenerations, and the use of costly materials), and the need for large energy inputs (which in turn create an environmental impact).

DEVELOPING TECHNOLOGIES

New approaches are being worked on for the production of on-purpose propylene, a number of which are discussed herein including:

• Production of propylene from steam cracking of ethane followed by dimerization and metathesis

A major technology licensor has developed a procedure whereby an ethane cracker based complex can produce both ethylene and propylene products. Within the context of the overall process flow schemes, several process integrations are possible to improve economics. The technologies involved (steam cracking, dimerization, metathesis) are all commercial and are discussed in more detail in the report.

• Utilization of the glycerin obtained in the production of biodiesel to produce propylene via hydrogenation to *n*-propanol followed by dehydration

A speculative process employing a major oil producer's invention for producing n-propanol from byproduct glycerin and then taking it a step further by producing propylene via dehydration is reviewed in the report.

Propylene from raffinate-1 via isomerization and metathesis of butanes

A leading chemicals producer/licensor has developed a process for producing propylene (and isoprene if desired) from a feed stream comprising butene-1 and isobutylene. The feed stream is reacted in a catalytic distillation reactor containing an olefin isomerization catalyst to produce an overhead stream and a bottoms stream. The overhead stream is reacted in the presence of a metathesis catalyst to produce propylene and isoamylenes. If desired, isoprene can be produced. This technology is discussed further in the report.

• Oxidative dehydrogenation (ODH) of propane

Alkanes are typical feedstocks for transformation to alkenes, aromatics, and chemicals containing value added moieties. Dehydrogenation is a route to such transformations, but it is an endothermic process requiring significant energy input. Oxidative dehydrogenation (ODH) of propane to propylene is another route to on-purpose propylene. ODH of paraffins is an alternative to commercial industrial methods for olefin production – direct dehydrogenation and steam cracking. ODH of alkanes is exothermic, is not limited by thermodynamic constraints, and, is an attractive alternative to dehydrogenation. However, current ODH catalysts have limited activity and/or poor selectivity. The process development is discussed in further detail in the report.

• Following a review of recent patents, other technologies of interest are briefly outlined.

COMMERCIAL TECHNOLOGIES

Over 88 percent of the propylene produced in the world today is either as a byproduct from steam cracking or as a byproduct from gasoline production via FCC. On-purpose production of propylene includes propane dehydrogenation, olefin metathesis, selective butylenes (C_{4s}) and carbon cuts (C_5) olefin cracking, methanol-to-olefins (including methanol-to-propylene) and enhanced FCC processes. All of these routes have been or will soon be exploited commercially to varying degrees. The Figure below gives a breakdown of propylene capacity according to technology type.



Distribution of Propylene Capacity

• Commercial technology routes to produce propylene are briefly summarized in this section of the report.



ECONOMIC ANALYSIS

Cost of production estimates have been developed for production of propylene via the alternative routes discussed:

- Production of Propylene from Ethane via Steam Cracking, Dimerization, and Metathesis (includes cost of production estimate for ethylene from pure ethane feedstock via steam cracking, cost of production estimate for dimerization of ethylene to butene; and cost of production estimate for metathesis of ethylene and butene to produce polymer grade propylene).
- Production of Propylene Utilizing Glycerin obtained in the Production of Biodiesel (includes cost of production estimate for *n*-propanol via hydrogenation of crude glycerine and cost of production estimate for polymer grade propylene via dehydration of *n*-propanol).
- Production of Propylene from Raffinate-1.
- Production of Propylene via Oxidative Dehydrogenation of Propane.

Various sensitivities have been explored to illustrate the effects of variations in certain parameters on the base case economics presented in the previous section. These results can also be used to make approximate comparisons between cases for which detailed economics that have not been provided by adjusting for capacity differences, alternative feedstock valuation, etc. Therefore, the sensitivity of the development process economics as a function of pricing, capital investment and economy of scale are also analyzed.

• The economics of the various commercial routes to polymer grade propylene have been presented previously in PERP reports 06/07-3, *Propylene* and 07/08S5, *Olefins via Enhanced FCC Processes*. These have been summarized in the form of a bar chart displaying the cost of production elements (i.e., net raw materials, utilities, direct fixed costs, allocated fixed costs, depreciation and return on capital employed) for the following processes: Fractionation, PDH, High Severity FCC, Superflex (LCN), Superflex (Pyrolysis C₄s), MTP, MTO, MTO w/OCP and Metathesis (stand alone).

COMMERCIAL ANALYSIS

Propylene demand is approximately one-half the size of ethylene demand, and is the second most important olefin product, and like ethylene is a primary petrochemical precursor. In each region, polypropylene is the largest propylene derivative. Other propylene derivatives are briefly discussed in the report in terms of supply/demand for various regions.

The major applications of propylene are exemplified by the Figure below, which is the end-use demand for propylene in Western Europe.



West European Propylene Consumption

- Supply/Demand and Trade data are detailed and discussed for the United States, Western Europe and Asia Pacific regions.
- Tables giving extensive listings of propylene capacity for each of the regions are included
 the tables show company, company location, and specific plant capacity at that location and process technology employed at the plant.



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