A different game plan

Professor Gregory A. Funk, David Myers, and Bipin Vora, UOP, USA, discuss new technology for the production of ethylene and propylene from methanol.

Worldwide, ethylene and propylene are mainly produced by steam cracking of hydrocarbons such as ethane, LPG and naphtha, with the preferred feedstock varying significantly by geographical region. In the Middle East and North America, ethane has been favoured due to a significant price advantage. However, most other regions do not have access to low cost ethane and have had no other option but to use more expensive naphtha as their feedstock.

UOP’s advanced methanol to olefins (MTO) process is a new, innovative technology for producing ethylene and propylene from methanol. Since methanol can be made using a variety of different feedstocks, MTO opens up an entirely new pathway for the production of ethylene and propylene starting from low cost, alternative raw materials such as coal or natural gas (Figure 1).
Ethylene and propylene are two of the largest volume petrochemicals in the world. Ethylene is used in a variety of products including a variety of different plastics such as polyethylene (food packaging, house wares), polyvinylchloride (piping, construction materials), polyethylene terephthalate (bottles, films), and polystyrene (insulation, cups). Likewise, propylene is used in a variety of applications including polypropylene (films, packaging, automotive components), acrylonitrile (synthetic rubbers), propylene oxide (antifreeze, polyurethane foams) and many others.

Today, nearly all of the world’s ethylene is produced by steam cracking technology. Steam cracking uses high temperatures (800 °C - 900 °C) and steam to crack and dehydrogenate hydrocarbons into ethylene and other valuable byproducts. Propylene is one of the most important byproducts from steam cracking of propane and higher hydrocarbons. Approximately 55% of the world’s supply of propylene comes from steam cracking. Propylene is also supplied as a byproduct from fluid catalytic cracking (~35%) and propane dehydrosulfonation (~5%).

Over the past several decades, the manufacturing capacities for these chemicals have undergone remarkable transitions, with impressive growth in some regions and flat to declining production in others (Figure 2). Two of the most important factors shaping the development of most chemical markets are regional demand and feedstock cost and availability.

Driven mainly by the availability of low cost ethane, ethylene production capacity in the Middle East has grown significantly over the past 10 - 15 years. Similarly, after more than a decade of minimal growth, ethylene capacity in the Americas is increasing due to the availability of low cost ethane from shale gas and enhanced gas recovery technologies. Clearly, the availability of low cost feeds can be an important driver for the investment in new production capacity.

The Asia Pacific region has also experienced tremendous growth in ethylene production capacity. However, unlike the Middle East, this region does not possess an abundance of cheap ethane. With no other options available until recently, naphtha has been the predominant feedstock even though it has been up to more than five times more expensive than the ethane used in other regions. New technologies such as advanced MTO have the potential for changing the game by opening up new routes based on alternative, low cost feed stocks.

**Methanol to olefins technology**

Methanol is widely produced from natural gas or coal at locations with abundant reserves. By utilising methanol derived from these cost advantaged raw materials, MTO enables low costs of production for ethylene and propylene in regions that do not have large reserves of ethane. MTO can also help to fill the gap between propylene demand and supply from steam crackers and refineries by producing olefins at high ratios of propylene to ethylene.

The conversion of methanol to olefins and other hydrocarbons products has been widely studied. Initial work in the 1970s and early 1980s focused on conversion of methanol to gasoline range products and employed ZSM-5 type zeolites. Selectivity of methanol to ethylene and propylene over ZSM-5 was generally low, with selectivities favouring heavier more highly branched hydrocarbons and aromatics. This catalyst technology was utilised in the commercial development of the Mobil MTG Process. During the 1980s, a group of scientists at Union Carbide (the group later became part of UOP LLC) discovered a new class of materials, silicoaluminumphosphates (SAPO) molecular sieves. Of these, the discovery of SAPO-34 provided a technology breakthrough. SAPO-34’s unique pore size, geometry and acidity created a more selective route for methanol conversion to ethylene and propylene with reduced heavy byproducts.

As illustrated in Figure 3, SAPO-34 has a smaller pore size (approximately 4 Å) compared to that of ZSM-5.
The smaller pore size for SAPO-34 restricts the diffusion of heavy and branched hydrocarbons and therefore favours high selectivity to the desired light olefins. The optimised acidity of SAPO-34 reduces the amount of hydride transfer reactions relative to ZSM-5, thereby lowering the yield of paraffinic byproducts. A further advantage of SAPO-34 is that the majority of the $C_4 - C_6$ fraction produced is olefinic. As discussed later in this article, these olefinic compounds make the heavy byproduct suitable for upgrading by olefin cracking.

**Development of the advanced process**

In the early 1990s, UOP and Norsk Hydro A.S. formed an alliance to develop MTO technology. This collaboration with Norsk Hydro led to the development of the UOP/HYDRO MTO process. In developing the process, UOP built on its in house FCC experience for fluidised reactor and regenerator and known steam cracker art. Norsk Hydro’s interest in the MTO technology alliance with UOP is now a part of INEOS.

Unrelated to MTO at the time, ATOFINA was at work in the 1990s developing olefin cracking technology. Shortly after, in 2000, ATOFINA (which later became part of Total Petrochemicals and nowadays of TOTAL Refining and Chemicals) and UOP formed a joint alliance to further develop olefin cracking technology. This collaboration led to development of the Total Petrochemicals/UOP olefin cracking process.

The Total Petrochemicals/UOP olefin cracking process has been integrated with the UOP/HYDRO MTO process. This combination of processes is the basis for advanced MTO.

A major milestone for MTO commercialisation was the start up in 2009 of the semi commercial, fully integrated MTO demonstration unit (Figure 4) in Belgium, which successfully demonstrated the performance of the integrated UOP/Hydro MTO process with the Total Petrochemicals/UOP olefin cracking process.

**Process description**

The UOP/HYDRO MTO process utilises a fluidised reactor and regenerator system to convert methanol to olefins using a proprietary, SAPO-34 type catalyst.

The UOP/HYDRO MTO process can be operated on crude, or undistilled methanol, as well as with pure (Grade AA) methanol. The choice of feedstock quality generally depends on project specific situations because there can be advantages in either case. Figure 5 illustrates a simple flow diagram for the UOP Advanced MTO process.

The methanol feed is preheated and then introduced into the reactor. The conversion of methanol to olefins requires a selective catalyst that operates at moderate to high temperatures. The reaction is exothermic so heat can be recovered from the reaction. Carbon or coke accumulates on the catalyst and requires removal to maintain catalyst activity. The coke is removed by combustion with air in a catalyst regenerator system. A fluidised bed reactor and regenerator system is ideally suited for the MTO process because it allows for heat removal and continuous catalyst regeneration. The reactor operates in the vapour phase at temperatures between 650 to 1000 °F and pressures between 15 and 45 psig. A slipstream of catalyst is circulated to the fluidised bed regenerator to maintain high activity.
The reactor effluent is cooled and quenched to separate water from the product gas stream. The product gas is compressed and then unconverted oxygenates are recovered and returned to the reactor. The reactor provides very high conversion so there is no need for a large recycle stream. After the oxygenate recovery section, the effluent is further processed in the fractionation and purification section to remove contaminants and separate the key products from the byproduct components. Ethylene and propylene are produced as polymer grade products and sent to storage. The C4 - C6 fraction can be sent to the OCP reactor where it is selectively converted to light olefins, the majority of which is propylene. Typically the propylene to ethylene ratio in OCP reactor effluent is about 4:1. The OCP product is separated by fractionation, with the C3 and lighter fraction sent to the MTO product recovery section and the residual C4 plus fraction used as a byproduct fuel.

As shown in Figure 6, the Advanced MTO process, which is the integrated MTO-OCP processes, can produce propylene to ethylene product ratios between 1.2 and 1.8 to help meet the growing demand for propylene and additional flexibility is achievable with the technologies, if desired.4 In most regions of the world, either methane or coal are readily available at prices that make UOP’s advanced MTO process a better economic choice than naphtha cracking. Investment in MTO can be staged by first constructing and operating the MTO unit based on purchased methanol and then later constructing the gasification and methanol synthesis sections.

To date, UOP has licensed four MTO units with the first unit scheduled to come on stream at the end of 2013. All of these units are located in China and are based on either purchased methanol or coal. In total, more than 10 million tpy of combined ethylene plus propylene production capacity from MTO technologies is planned to come on stream in China by 2015.5

Conclusion

Regional demand and the regional availability and cost of key raw materials are some of the most important factors shaping the development of petrochemical markets. By opening up new production pathways that utilise low cost, alternative feedstocks, new technologies can change the game for chemical producers that do not have easy access to traditional feedstocks.

References