

Methanol to Propylene: From Development to Commercialization

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Abstract

In the late 1990s the development of the so-called MTP[®] (methanol-to-propylene) process, a Lurgi Technology (by Air Liquide Global E&C Solutions) started. This constitutes a novel route to a valuable product that would not rely on crude oil as feedstock (as conventional propylene production does), but instead utilizes coal or natural gas and potentially biomass. These alternative feedstocks are first converted to synthesis gas, cleaned, and then converted to methanol. The development of the methanol-to-propylene conversion was achieved in a close collaboration between R&D and engineering. Two pilot plants at the R&D center in Frankfurt and a demonstration plant in Norway have been used to demonstrate the yields, catalyst lifetime and product quality and to support the engineering team in plant design and scale-up. Especially the last item is important as it was clear from the very beginning that the first commercial MTP[®] plant would already be world-scale, actually one of the largest propylene producing plants in the world. This required a safe and diligent scale-up as the MTP[®] reactors in the commercial plant receive about 7,000 times the feed of the demo unit and as much as 100,000 times the feed of the pilot plant. The catalyst used is a zeolite ZSM-5 that was developed by our long-term cooperation partner Süd-Chemie (now Clariant). At the end of 2010, the first commercial MTP[®] plant in Ningdong in the Chinese province of Ningxia was started up as part of a coal-to-chemicals complex owned by the Shenhua Ningxia Coal Industry Group. In this complex the complete chain starting from coal through to the final polypropylene product is realized. The customer successfully started the polymer-grade propylene production in April 2011 and then announced in May 2011 that he sold the first 1000 tons of polypropylene made with propylene coming from the MTP[®] unit. Following this successful start-up of the first commercial-scale MTP[®] unit, the same client decided to build another MTP[®] plant on the same site in close proximity to the first unit. The new contract with Air Liquide Global E & C Solutions was signed in late summer 2011. A growth in demand is seen as regionally differing but as steady on the global scale and large enough to justify a good number of MTP[®] projects in the next years. The feedstock side is also important with the emergence and rapid growth of unconventional gases, like tight and shale gas; prices have come down to a level where conversion to chemicals is much more profitable than sale as an energy carrier.

The process basics will be explained and it will be shown which technical and economical hurdles had to be taken in order to win the first projects and to establish the process in the marketplace.

Introduction

With this special Lurgi technology, Air Liquide Global E & C Solutions succeeded in developing a catalytic process to produce on-purpose propylene using natural gas, coal or biomass as feedstock. These alternative feedstocks are first converted to synthesis gas which is cleaned and then converted to methanol. Methanol in turn is converted to DME (dimethyl ether) which is used to produce a propylene-rich mixture containing various hydrocar-

bons. This new process was named Methanol-to-Propylene - MTP[®] and is based on a catalyst developed by Süd-Chemie AG (now Clariant).

Why propylene?

Propylene is a major petrochemical commodity with an annual production volume of about 80 million tons, the majority being converted to polypropylene, a polymer used for everyday applications such as food packaging, foils etc. Since demand of propylene is forecast to rise faster than production, on-purpose propylene processes (from alternative feedstocks such as natural gas, coal or biomass) will be required to close the so-called “propylene gap”. Figure 1 provides information about the additional propylene demand and the forecast for 2015.

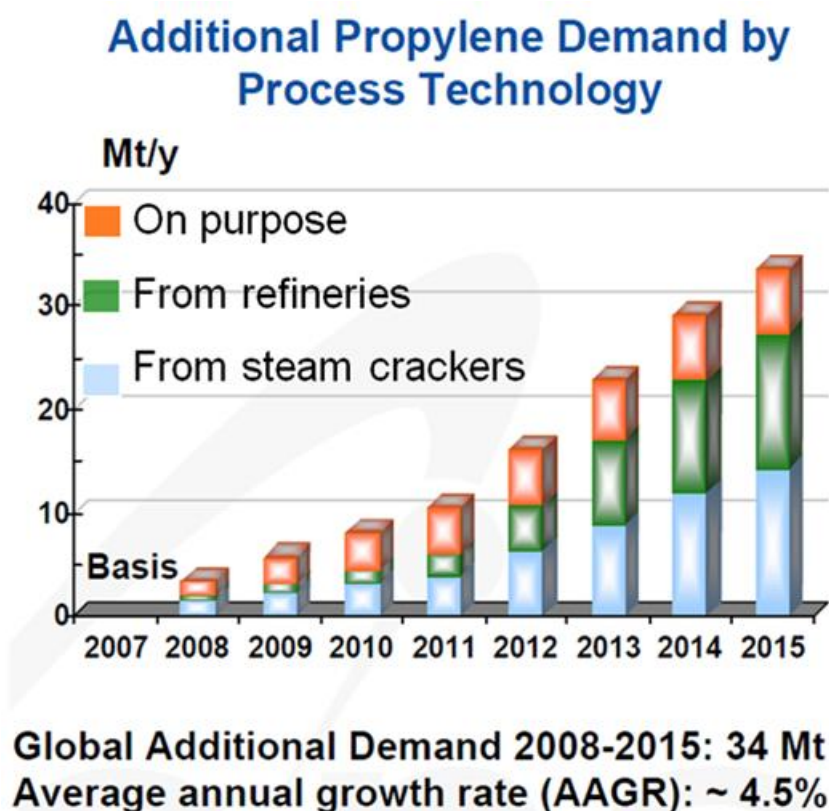


Figure 1: Additional propylene demand by process Technology (Petrotech – New Delhi, India, January 2009)

At present propylene is made predominantly from crude oil via steam cracking and the FCC process. In this process propylene is seen rather as a by-product the yield of which cannot be raised independently. Nowadays, shale gas plays an increasingly important role and in the USA, for example, the abundance of shale gas has caused natural gas prices to decouple from crude. This has recently pushed olefin producers to change from heavy to lighter feedstocks which results in a reduction of propylene production in crackers (www.platts.com, *Special Report: Petrochemicals*, September 5, 2011).

In the late 1990s many market studies already showed that the incremental demand increase for propylene would outpace the growth of ethylene, the major product from a steam-cracker. Following this trend the development of a Lurgi process for on-purpose propylene production started.

At that time the development of a new methanol process was completed, known as the Lurgi MegaMethanol[®] technology which delivers methanol at very low production costs in plants with a capacity of about 1.7 million tons of methanol per year or 5000 tons per day. With cheap methanol available in large quantities, the chemical conversion to value-added petrochemical commodities became interesting. Initial studies from the 1970s and 1980s examined the conversion of methanol to hydrocarbons. In 1999 the first Lurgi R&D program specifically on the topic methanol to propylene process was launched in Frankfurt am Main.

One important element of the MTP[®] process is a selective catalyst able to convert most of the methanol in propylene. From the outset the MTP[®] process had been based on a tailor made ZSM-5 zeolite catalyst supplied by Clariant.

With the Lurgi MTP[®] process, Air Liquide Global E & C Solutions is in a position to offer customers a complete chain of proprietary technologies. For a gas or coal-based complex the full process chain can be covered, including gasification, ASU, gas cleaning, CO shift, methanol synthesis and MTP[®] - a strategy that is known today as “Your One Stop Shop” (see figure 2).

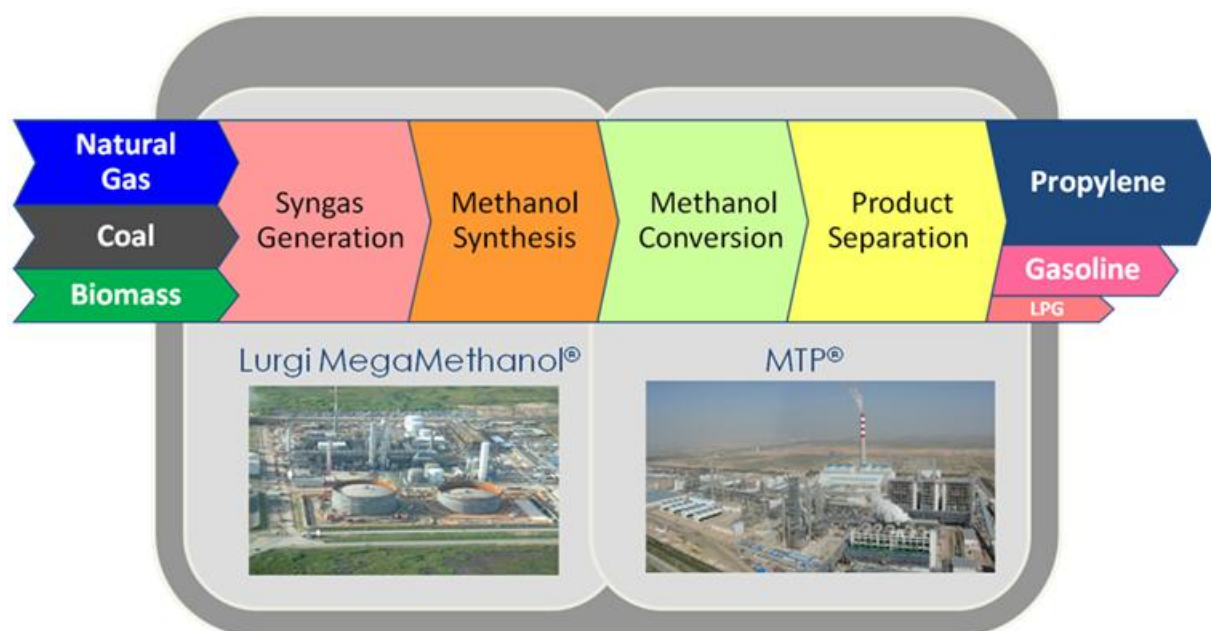


Figure 2: Lurgi processes from alternative feedstock to propylene production (Air Liquide Global E & C Solutions)

From the idea to the development of an innovative technology

The development of a new technology is never an easy task but it is often an exciting one. The methanol-to-olefins (MTO) reaction is very complex and since this reaction is exothermic, control of the temperature in the reactor is very important. One of the best known models used to describe this reaction is the “CH₂-Pool” (see figure 3) which describes the complex and interlinked network of possible reactions on the catalyst. As the aim of the new process development was to maximize the propylene yield, two tasks had to be completed: develop a catalyst that is highly selective for propylene (Clariant) and optimize the process and the process conditions such as temperature, pressure, partial pressures, presence of a diluent etc. to utilize the potential of the catalyst to its maximum (Air Liquide Global E & C Solutions).

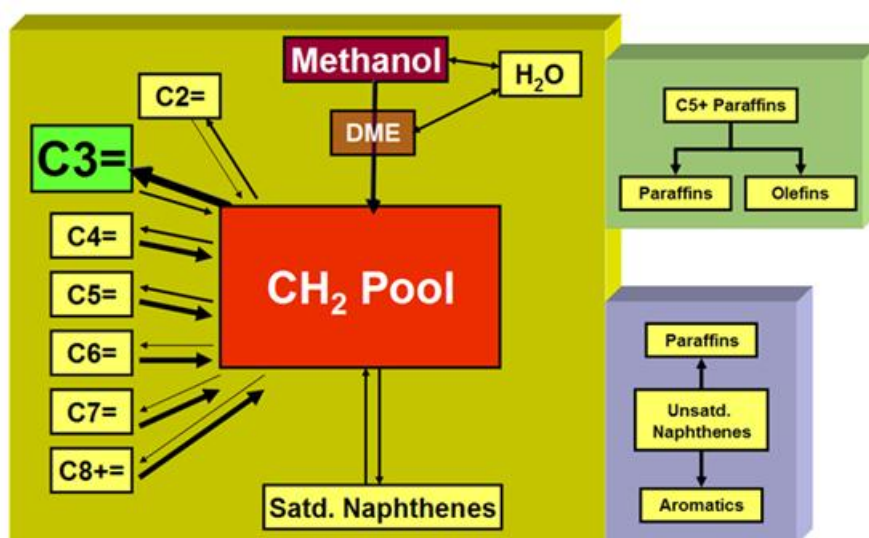


Figure 3: CH₂-Pool model to describe the MTO reaction

It had been reported in the late 1980s in the literature that methanol could be converted to light olefins. However, the use of an isothermal reactor working under vacuum was required to achieve any significant propylene yield. Because of the high temperature of the reaction (>400°C) a salt bath along with a bundled tube reactor was required, which is not only very expensive but also poses safety challenges.

UOP (now part of Honeywell) had also started to develop an MTO process using a SAPO-34 catalyst. Due to fast coking of the catalyst, the UOP MTO process uses two fluidized bed reactors of which one is continuously used in a regeneration mode. Despite good olefin yields this technology was not ideally suited to solve the impending problem of the propylene gap because propylene production in MTO always also involves a significant amount of ethylene production which can be produced more cost efficiently in ethane crackers. To date, the UOP process has not been industrially referenced.

The aim of the MTP[®] process was to address this deficit as the main product is propylene. Based on previous experiences, from the very beginning of this new development the reactor system was designed as a fixed bed reactor operating under adiabatic conditions to avoid complex and costly cooling systems. Steam was used as a diluting agent to control the exothermicity of the reaction and to limit the amount of coking.

However, the presence of steam required a stable catalyst to ensure longer lifetime since the dealumination of zeolites is a well-known cause of zeolite catalyst deactivation.

Close cooperation between engineering and R&D for scale-up

The MTP[®] process was developed in a close collaboration between R&D and the process engineering team. Two pilot plants at the Research & Technology Center (FRTC) in Frankfurt am Main and a demonstration plant in Norway have been used to demonstrate the yields, catalyst lifetime and product quality and to support the engineering team in plant design and scale-up. Especially the demonstration plant in Norway has been an important development step since it was clear from the very beginning that the first commercial MTP[®] plant would already be world-scale, actually one of the largest on-purpose propylene producing plants in the world. This is quite an achievement for a novel process which requires a safe and diligent scale-up as the commercial plant will see about 7,000 times more feed than the demo unit and as much as 100,000 times more feed than the pilot plant (see figure 4).

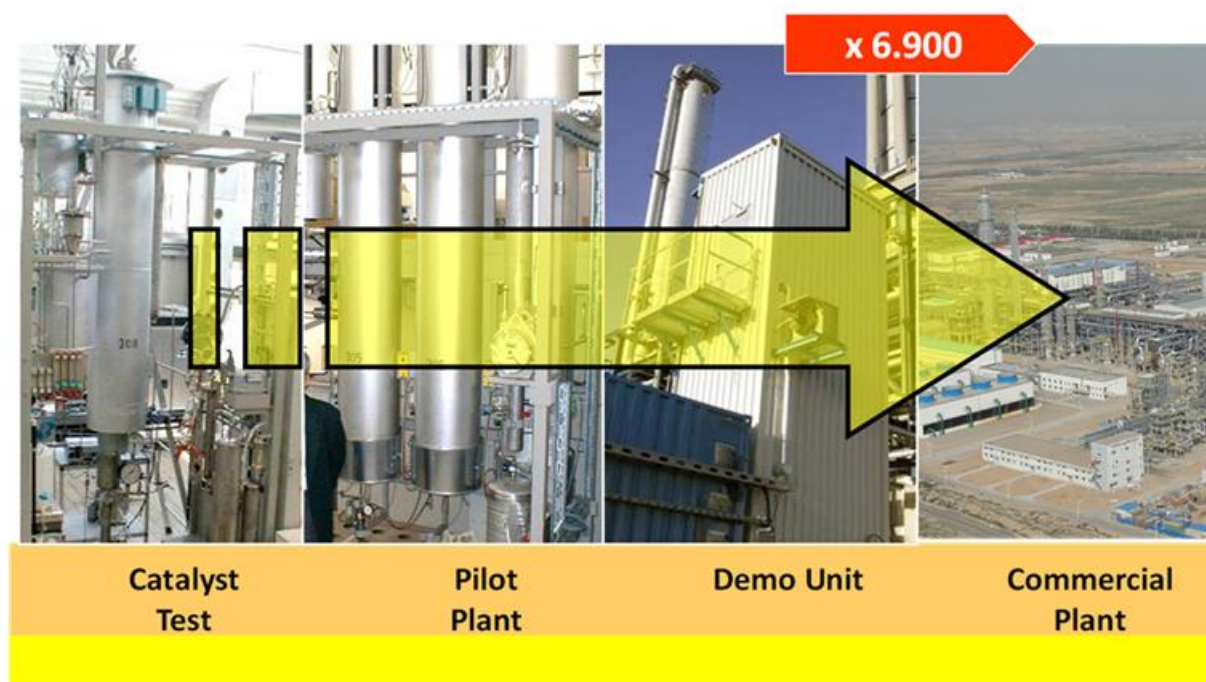


Figure 4: Scale-up from pilot plant to commercial plant

The first tests of the MTP[®] reaction with the Clariant catalyst were performed in 1999 at the FRTC in a catalyst test unit under idealized conditions (polytropic, once-through operation) to allow for a first optimization of the reaction temperature, pressure and space velocity. The first results proved to be promising and a larger-scale pilot plant was built to allow for adiabatic operation and the application of artificial recycle streams. As the results continued to match the targets with respect to propylene yield, it was decided to build a demonstration unit. Besides the demonstration aspect to potential customers, the main purpose of the demo unit was to actually prove the lifetime of the catalyst in the real environment of a commercial MTP[®] plant. The demonstration plant was built in Tjeldbergodden, Norway as a side-stream plant of a Statoil methanol plant using natural gas as feedstock and the demo unit was operated from January 2002 to April 2004. It delivered many useful data. Amongst others a catalyst lifetime of 8000 h was demonstrated.

Another very important milestone was achieved when propylene from the MTP[®] process was for the first time successfully polymerized into polypropylene in collaboration with Borealis, Norway (see Figure 5). It was demonstrated that “MTP[®] propylene” exhibits the same quality as “regular”, crude-oil based propylene and does not contain any new or harmful poisons for the very demanding polymerization catalysts. The successful production of on-spec polypropylene from MTP[®] propylene has proven the MTP[®] technology as a new, attractive route for on-purpose propylene production.

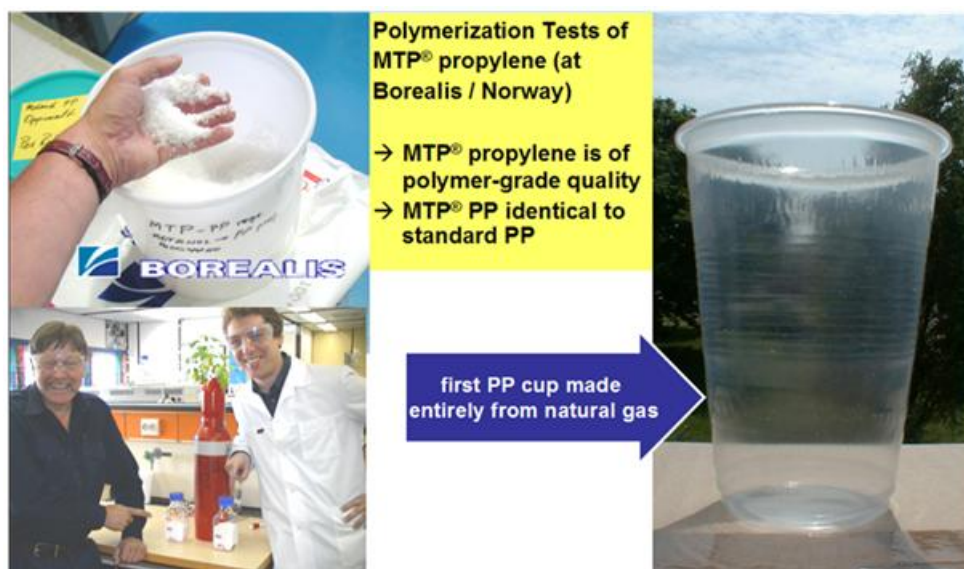


Figure 5: First polymerization tests of MTP® propylene (at Borealis / Norway)

As the key reaction parameters were successfully demonstrated, the scale-up process could be refined. The data obtained from the demonstration plant served as verification of the key concepts of reactor design. The detailed composition data collected of the MTP® reactor effluent over the full catalyst lifetime enabled the process engineering team to design a purification scheme. Based on the data from the demonstration plant the equipment materials were selected and product quality was defined. During the design of the pilot plant and demo unit care was taken to optimize them for a possible scale-up of the MTP® reactors. For example the bed heights in the smaller units were chosen to be identical to their projected commercial-size counterparts. In this respect the beds in the lab and demonstration plant can be seen as a cut out of the commercial MTP® reactor. The lab plant was then also optimized to have an ideal adiabatic multi-stage operation like in the commercial plant so as to get a good prediction of the temperature profiles and the resulting propylene yields and by-products.

Moreover, the knowledge acquired with this demonstration plant also served to optimize the pilot plant at FRTC in Frankfurt. In addition, the results from the refined purification design could be implemented for the recycle streams. Therefore, the composition and quality of the product from a MTP® reactor could be evaluated in the pilot plant under operating conditions similar to those of a commercial plant, including all the recycle streams occurring in a commercial MTP® plant. Based on these results the commercial-size design could be further refined.

Extensive experiments have been performed to characterize the by-products and identify parameters for their quality. In addition, the pilot plants serve to answer project-specific questions and to further develop the technology.

From development to start-up of commercial plant

Figure 6 shows a simplified scheme of the commercial MTP® process. The methanol feed, for example from a MegaMethanol plant, is sent to an adiabatic DME pre-reactor where the methanol is converted to DME and water. The high-activity, high-selectivity catalyst nearly achieves thermodynamic equilibrium. The methanol/water/DME stream is routed to the MTP® reactor together with steam and recycled olefins. Process conditions in the reactor are adjusted to guarantee similar reaction conditions and maximum overall propylene yield. Feeding small streams of fresh feed between the catalyst beds ensures maximum propylene yield and controls the operating conditions. The product mixture from the reactors is cooled and the product gas, organic liquid and water are separated. The product gas is compressed and traces of water, CO₂ and DME are removed. The cleaned gas is then further processed to polymer-grade propylene and polymer grade ethylene. Several olefin-containing streams are

sent back to the main synthesis loop as an additional propylene source.

MTP[®] gasoline and MTP[®] LPG are produced as co-products, contributing additional value to the economics of this technology. Water is recycled to steam generation for the process. The excess water from the methanol conversion is purged. This process water can be used as supplemental raw water in the petrochemical complex or for irrigation after appropriate and inexpensive treatment.

The 2+1 reactors concept allows regeneration as well as exchange of the catalyst without reducing the production. Regeneration has to be performed in-situ after the end of the cycle time when the catalyst is temporarily deactivated due to coke formation.

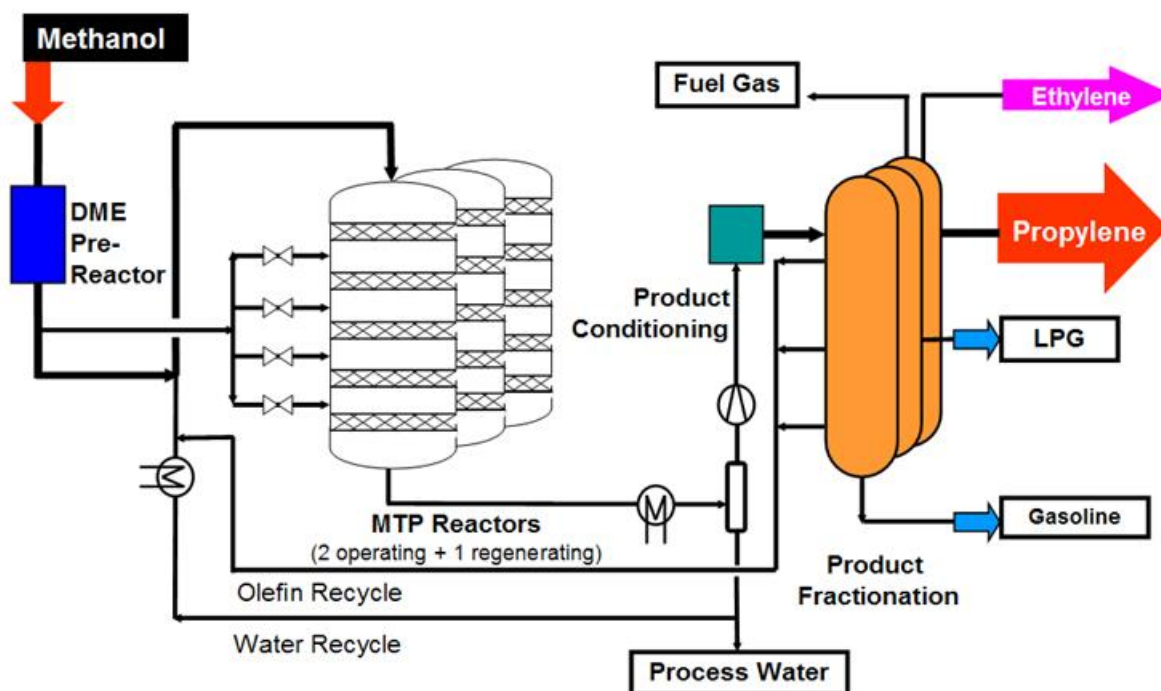


Figure 6: Scheme of the MTP[®] process

Based on the data collected from the pilot and demonstration plant and the design work from the engineering function, it was possible to offer the Lurgi MTP[®] process from mid 2005. The first two big MTP[®] commercial plants were ordered by the Chinese clients Datang International Power Generation and Shenhua Ningxia Coal Industry Group (SNCG) and both plants went on stream in late 2010.

In Ningdong in the Chinese province of Ningxia the first MTP[®] plant commenced commercial production as a part of a coal-to-chemicals complex owned by the Shenhua Ningxia Coal Industry Group (SNCG). In this complex the complete process chain from coal through to the final polypropylene product was realized. Air Liquide and its Engineering division Air Liquide Global E & C Solutions have provided not only the MTP[®] unit (including the world's largest reactor for DME production), but also the upstream air separation unit, as well as the technology packages (including proprietary equipment) for Rectisol[®] for syngas cleaning, sulfur recovery and, of course, the MegaMethanol unit as illustrated in figure 7. The production capacity of the plant is about 470,000 tons per year of propylene.

The sizes of the reactors, columns and splitters are impressive in comparison to those of the pilot plants. The length of the C3 splitter, for example, is close to 90 meters. In the control room, the operators are monitoring the complete MTP[®] unit. The client began polymer-grade propylene production in April 2011 and then announced in May 2011 that he sold the first 1000 tons of polypropylene made with propylene coming from the MTP[®] unit. Initially the MTP[®] plant could not be ramped up to 100% because of insufficient feedstock availability. The performance test run of the MTP[®] unit was successfully completed in May 2012. That was a big success for this new technology in view of the high complexity of the MTP[®] reaction and the high propylene quality required for the polymerization. Following this successful

start-up of the first commercial scale MTP[®] unit the same client decided to build another MTP[®] plant on the same site close to the first unit and signed a new contract with Air Liquide Global E & C Solutions in late summer 2011. The contract comprises the basic engineering, license and supply of proprietary equipment as well as services for procurement and technical advisory services on site.



Figure 7: SNCG coal to polypropylene complex (Ningdong, Province of Ningxia, China)

Outstanding performance by R&D and by the engineering teams composed of highly skilled and motivated people allowed realizing the MTP[®] concept and making it a success story. Hence the pilot plant at the R&D center delivered a very good prediction of yields and even product properties in comparison to the commercial plant. The product slate of the commercial plant is as expected, especially concerning the propylene yield as shown in figure 8.

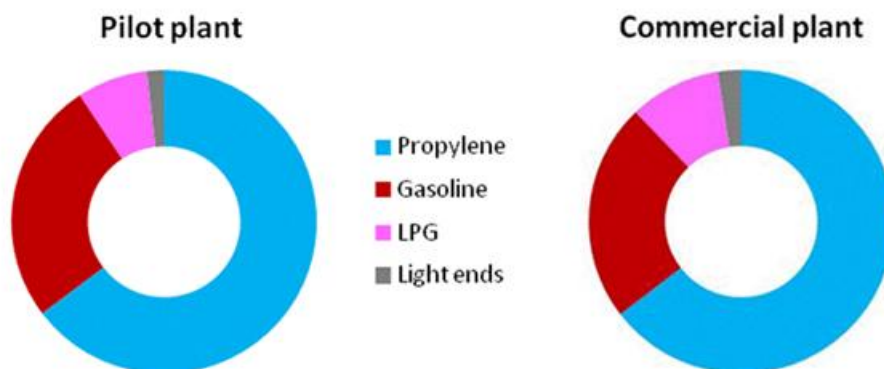


Figure 8: Comparison between product slate in pilot plant versus commercial plant

Conclusions

The successful development of the MTP[®] technology is the result of combination of imagination, expertise and know-how from the people working for Air Liquide Group. A scale-up of factor 7000 was successfully achieved and the performance of the commercial plant is very good and in line with the data obtained from the pilot plant.

Today the MTP[®] Process is a proven and commercially referenced technology that offers an attractive route for on-purpose propylene production independently from crude oil. Rising market demand for propylene and the shortage in conventional propylene produced from crackers as well as attractive gas prices resulting from the abundant shale gas reserves create an attractive environment for the MTP[®] technology.