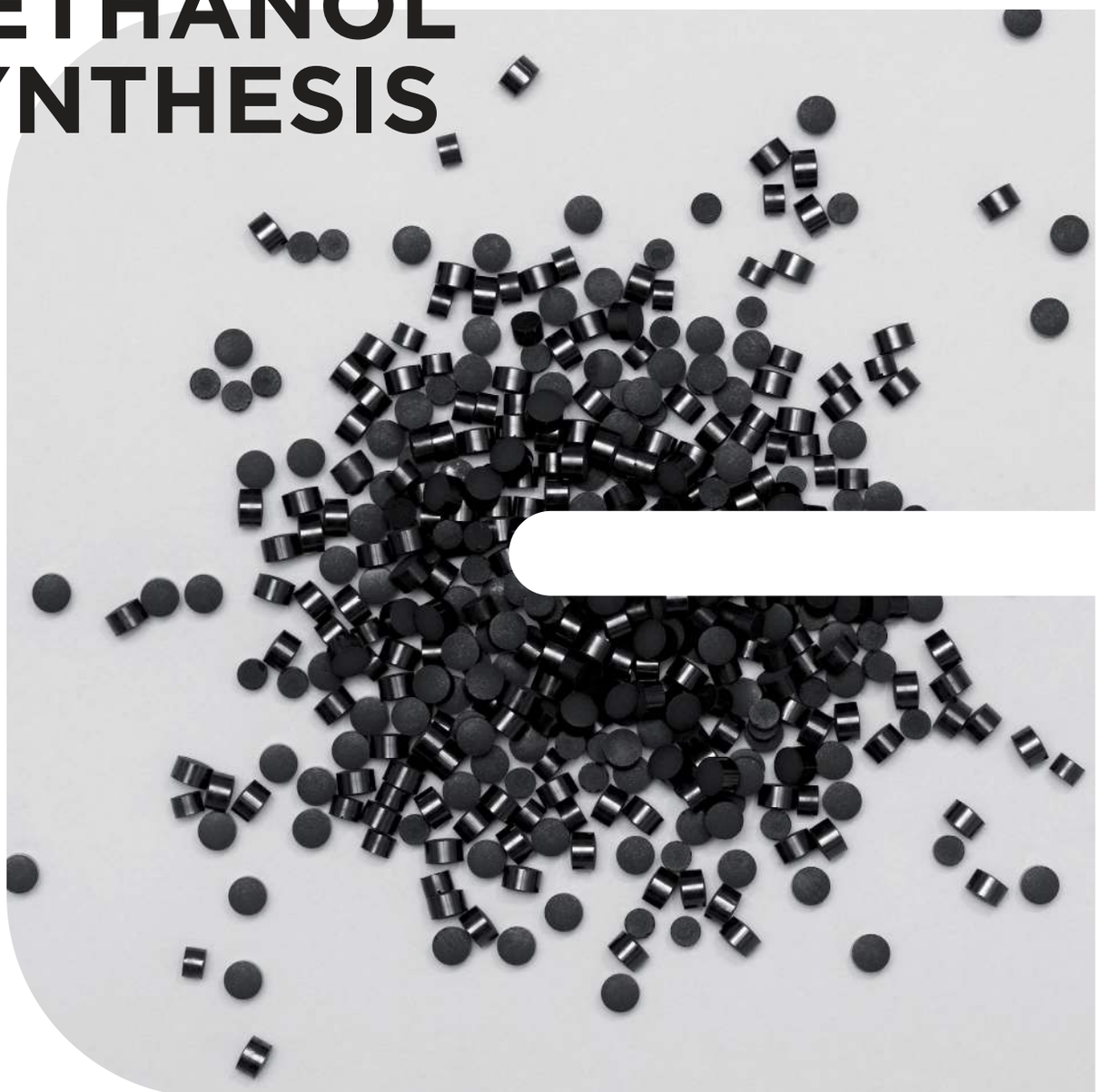
CLARIANT

Catalysts for **METHANOL SYNTHESIS**



what is precious to you?

Catalysts for Methanol Synthesis
INTRODUCTION

Catalysts
Clariant is a globally active specialty chemicals company, based in Muttenz, Switzerland.

Our strength in methanol technology grows from our roots in Süd-Chemie, a leading company in the development of process catalysts for chemicals markets. The broad portfolio of highly innovative catalyst products is now part of the Catalysts business unit of Clariant.

The Catalysts Business Unit is headquartered in Munich, Germany, and has 16 production sites and 11 R&D centers around the world. Our catalysts contribute significantly to value creation in our customers' operations, ensuring that finite raw materials and energy are used efficiently in the production of industrial chemicals, plastics, and fuels. Our products enable the use of alternative raw materials – such as natural gas, coal and biomass – as chemical and energy feedstocks, and are used to clean emissions from industrial processes and combustion engines to limit the impact on the environment.

We are committed to R&D and customer service to ensure that our products are well positioned to meet the global challenges of raw material scarcity, energy efficiency and responsible care for our environment.

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AT THE EUROPEAN CATALYST CENTER
The Heufeld site has both catalyst production and R&D.

Catalysts for Methanol Synthesis **APPLICATION**

Reactions

MegaMax® 800 catalyst is the next generation of methanol synthesis catalyst, with much higher activity and selectivity than previous catalysts. This catalyst is utilized for methanol synthesis from carbon monoxide, carbon dioxide and hydrogen.

$CO + 2H_2 \leftrightarrow CH_3OH$ $\Delta H_R = -91$ kJ/mol
$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ $\Delta HR = -49$ kJ/mol

Both methanol forming reactions are inter-connected with the water gas shift reaction:

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta HR = -42$ kJ/mol

The above equilibrium reactions are exothermic, so low reaction temperatures and high reaction pressures favor methanol yield. Figure 1 shows an equilibrium curve for methanol as a function of temperature and pressure.

Processes

Historically, methanol was produced at very high pressure – more than 300 bar. Catalyst development during the late 1960's and early 1970's enabled the process to be carried out at much lower pressures, from 40 to 100 bar (low pressure methanol process).

Today, industrial scale methanol synthesis is conducted either in isothermal or in adiabatic converters utilizing indirect or direct cooling. The main advantages of the low pressure process are:

- Lower investment and production costs
- Improved operational reliability and
- Much greater flexibility in the plant size

Older plant capacities ranged from 150 to 1,000 mtpd, while most modern plants have an average production capacity of 2,000 to 2,700 mtpd. Lurgi introduced MegaMethanol® plants in recent years, offering production capacities of 5,000 mtpd and higher in a single train. And its latest development, GigaMethanol®, enables production of up to 10,000 mtpd and is based on the high activity of MegaMax 800.

Feedstock

The hydrocarbon feedstocks used to produce methanol are:

- Natural Gas
- LPG
- Naphtha
- Residual Oils
- Coal, and
- Off-Gases.

These feedstocks can be processed by several routes – Steam Reforming, Partial Oxidation, and Gasification – to provide the required carbon oxides for the methanol synthesis. Figure 2 shows a typical flow sheet of the methanol synthesis loop design.

FIGURE 1 Methanol Equilibrium Chart

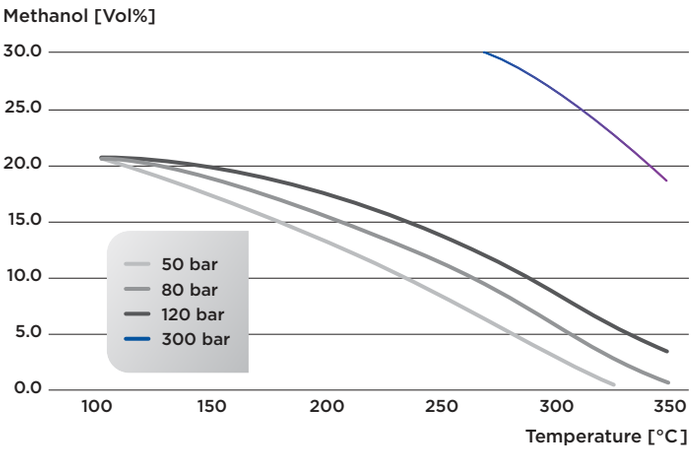
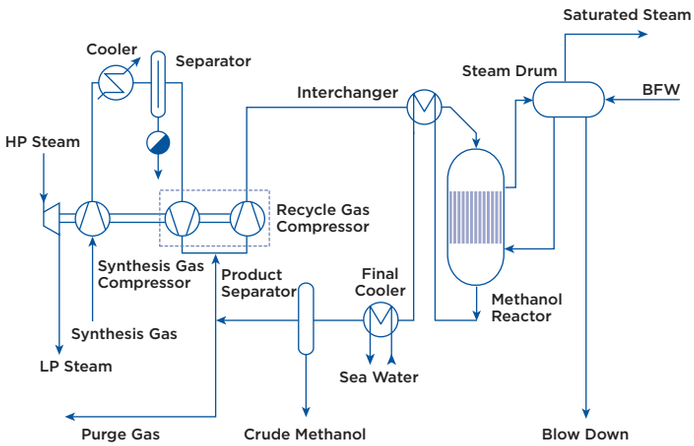


FIGURE 2 Flow sheet of the Methanol Synthesis Process Design



Catalysts for Methanol Synthesis
PRODUCT FEATURES

Performance

Clariant has studied Cu/Zn/Al chemistry in catalytic processes for many years, with internal R&D programs and with external universities. The first result of these collaborative activities was MegaMax 700, which offered improved activity, selectivity and poison resistance over previous catalysts. MegaMax 800 is the next generation methanol synthesis catalyst, proving even higher activity than previous generations and alternative catalysts on the markets.

MegaMax 800 builds on our wealth of experience in the methanol and syngas markets. This catalyst offers the flexibility to run in large and small production units, and with a variety of production technologies.

MegaMax 800 boosts productivity of older units and delivers the performance that you have come to expect from MegaMax products, including:

- High activity,
- High physical strength,
- High selectivity,
- Low temperature activity,
- Low pressure drop,
- Poison tolerance, and
- Longevity.

The typical operating conditions for methanol production using MegaMax 800 are:
Temperature: 190 - 315 °C, and
Pressure: 20 - 125 bar g.

Table 1 gives an overview of MegaMax 800 chemical composition and typical physical properties.

TABLE 1 Chemical Composition and Physical Properties of MegaMax 800

Composition	copper oxide, zinc oxide, alumina
Size and Shape	6 x 4 mm Tablets, 6 x 5 mm Tablets
Bulk Density	1.2 kg/l
Side Crush Strength	210 N

FIGURE 3 Activity Comparison MegaMax Series Catalysts

FIGURE 4 Predicted Performance of MegaMax 800

Activity

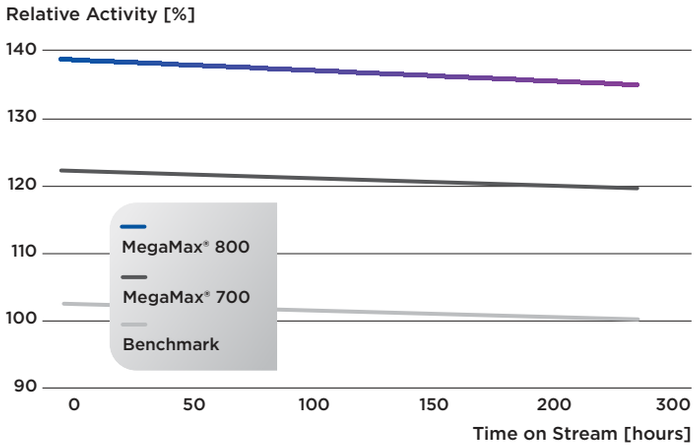
Optimal catalyst activity depends on the delicate balance between copper surface area, the number of active copper sites and copper crystallite size. The ideal formulation exhibits an extremely stable matrix with the optimum number of small copper crystals. To achieve long-term performance, it is also important to maintain this energy-rich state as long as possible, which means ensuring that sintering is suppressed as far as possible. These properties may be realized through a combination of catalyst precursors, catalyst composition and catalyst manufacturing techniques. By utilizing the latest research and applying state-of-the-art production technologies, Clariant has succeeded in:

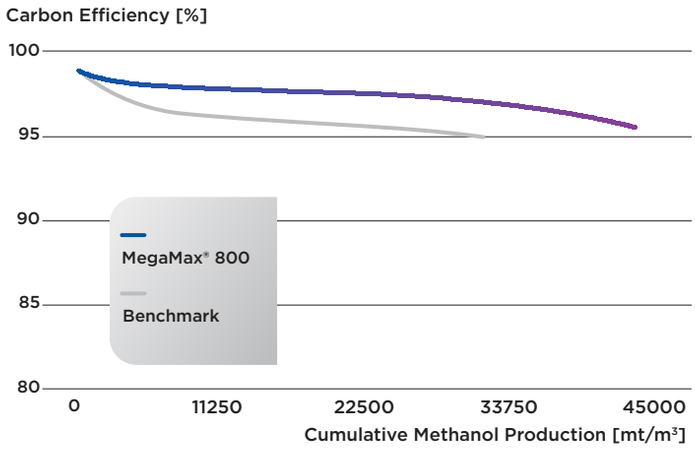
- increasing copper surface area,
- improving copper dispersion,
- decreasing copper crystallite size, and
- improving pore structure (pore volume and pore size distribution)

The novel MegaMax 700 methanol synthesis catalyst provided at least a 20% higher level of initial activity compared to a Benchmark synthesis catalyst, and MegaMax 800 offers a 35 - 40% boost over Benchmark (Figure 3).

The extremely high activity and productivity of the MegaMax Series catalysts allows new methanol plant designs, such as a MegaMethanol® plant (Lurgi), to operate using lower catalyst volumes per ton of methanol, while providing for high carbon and energy efficiency, all of which results in lower cost methanol production. And the high activity of MegaMax 800 has enabled the development of GigaMethanol, which allows production of up to 10,000 mtpd.

Because of its high stability, MegaMax 800 will maintain its high activity level for a lifespan as long as five years, with an expected cumulative methanol production of 45,000 metric tons per cubic meter of catalyst (Figure 4).





Catalysts for Methanol Synthesis **MEGAMAX**

Selectivity

The process conditions that influence selectivity are:

- Reaction temperature,
- CO_2 concentration at reactor inlet,
- Operating pressure, and
- H_2/CO ratio in make-up gas.

By far the most important factors are temperature and CO_2 concentration inlet the reactor. An increase in reaction temperature leads to a significant increase of by-product formation, but high CO_2 concentrations in the feed significantly reduce the by-product formation. Additionally, catalyst formulation also influences by-product formation.

In principal, the production of methanol and the formation of undesired by-products such as higher alcohols, esters, ethers and ketones occur through the same intermediate species on the active copper site of the catalyst. Therefore, with conventional catalysts, an increase in catalytic activity for methanol formation will also lead to increased by-product formation.

Our extensive research and development work established manufacturing techniques that produced a catalyst with a much higher activity level that also exhibited superior selectivity compared to existing catalysts. Consequently by-product formation over the entire life of MegaMax 800 is very low compared to existing catalysts.

Although by-product formation increases with time-on-stream as the reaction temperature is raised to compensate for activity decay, the extremely high selectivity of MegaMax 800 is maintained and outperforms that of Benchmark.

Mechanical Stability

The physical and mechanical properties of methanol synthesis catalysts have a significant impact on performance and longevity. The catalyst must be physically strong enough to withstand the abuse of the initial loading procedure, routine operation and potential process upsets. A mechanical breakdown of the catalyst pellet could result in an unacceptably high pressure drop and/or gas channeling, leading to a decreased methanol formation rate and ultimately the need for premature replacement.

Figure 5 illustrates typical side crush strengths of the MegaMax 800 catalyst compared to MegaMax 700 and a benchmark methanol synthesis catalyst. Note that MegaMax 800 shows an additional 15% improvement in crush strength over the excellent performance of MegaMax 700.

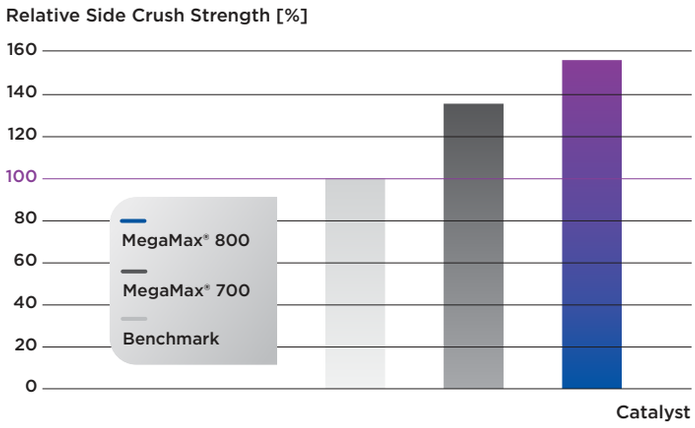
The extremely high crush strength of the catalyst in the oxide form allows easy handling, transportation and loading. Screening or sieving the catalyst prior to loading is usually not necessary.

The exceptional retention of catalyst strength after catalyst reduction is important to provide the necessary endurance for daily operation and protection against process upsets.

Catalyst Activation

The MegaMax 800 catalyst is shipped in the oxide state and is easy to commission. For details please refer to the Operating Manual for MegaMax 800. Additionally, the Catalysts business is always prepared to provide a technical expert to review procedures and assist with start up, and a self-contained hydrogen analyzer is available for tight control of reduction conditions. Our service will help to keep down-times short and assure a trouble-free start-up as far as possible.

FIGURE 5 Side Crush Strength of MegaMax 800



Catalysts for Methanol Synthesis **MEGAMAX**

Experience
Clariant has developed a series of methanol synthesis catalysts that have successfully operated in the widest possible spectrum of operating conditions and in a variety of reactor designs. Also the capacities of units using MegaMax vary widely from 50 tons per day to 10,000 tons per day.

Makeup Gas
The makeup gas analysis composition depends on the synthesis gas generation technology. Makeup gas can be characterized by its stoichiometric number. The stoichiometric number is defined as

$SN = (H_2 - CO_2) / (CO + CO_2)$

Steam Methane Reforming (SMR)
Most of the worlds methanol production is based on synthesis gas generated from steam reforming of either natural gas (Table 2) or naphtha. Depending on the reforming process, there is a wide variety of makeup gas compositions with varying stoichiometric numbers. CO_2 can be added to adjust the SN of a steam reforming process gas. The addition of CO_2 decreases the by-product formation across the catalyst and the amount of make-up gas needed per ton of production due to a better stoichiometric number. The make-up gas produced by the Lurgi combined reforming process (tubular steam methane reformer combined with oxygen blown autothermal reformer) results directly in the optimum SN of 2.05. Typical synthesis gas compositions from steam reforming are shown in Table 3.

Partial Oxidation (POX)
Partial oxidation of natural gas, heavy residual oil or coal results in a makeup gas that is very rich in CO, but contains little CO_2 and inerts. It is necessary to treat such a process gas with CO shift conversion followed by CO_2 removal and a sophisticated cleanup system to adjust the stoichiometric number and to remove the relatively high amounts of sulfur and heavy metals in the feedstock.

Independent of the loop design, the make-up gas composition determines the specific makeup gas consumption. Makeup gas consumption is defined as the kg-moles of makeup gas per metric ton of methanol in the crude methanol and is a measure of the plant efficiency, which also effects by-product formation in the loop.

The lowest specific makeup gas consumption is obtained with the optimum SN = 2.05, and the lowest inert level in the synthesis gas, i.e. using gasification gas (Table 4). The highest specific makeup gas consumption usually results in the case of steam reforming of natural gas without CO_2 addition. Such a synthesis gas is hydrogen rich with SN close to 3.0, which is quite high for efficient methanol production.

	SMR WITHOUT CO_2 ADDITION	SMR WITH CO_2 ADDITION	LURGI COMBINED REFORMING
[vol%]			
CO	14.2	14.6	20.6
CO_2	8.5	12.7	8.5
H_2	72.7	70.6	70.6
CH_4	4.3	1.9	2.2
N_2 + Ar	0.3	0.2	0.2
Stoichiometric Number	2.8	2.1	2.05

TABLE 2 Typical Compositions of Synthesis Gas from Steam Reforming

	MAKEUP GAS	REACTOR INLET
[vol%]		
CO	29.0	10.6
CO_2	2.4	3.5
H_2	69.9	73.0
CH_4	0.3	5.0
N_2 + Ar	0.4	7.9
Stoichiometric Number	2.15	4.93

TABLE 3 Typical Compositions of Partial Oxidation Gas

SPECIFIC MAKEUP GAS CONSUMPTION [kmole/mt]	
Gasification (residual oil)	95 - 105
Combined Reforming	110 - 120
Steam Reforming with CO_2 Addition	120 - 130
Steam Reforming without CO_2 Addition	140 - 150

TABLE 4 Specific Makeup Gas Consumption for different Synthesis Gas Processes

Catalysts for Methanol Synthesis **MEGAMAX**

Reactor Designs

Methanol synthesis reactors feature adiabatic multi-bed quench or indirect cooled converters, isothermal steam raising tubular reactors and tube (gas) cooled designs. MegaMax catalyst can be used in all of these reactor types.

Clariant developed computer models to simulate all of the following reactor designs on the basis of rate equations derived from the MegaMax series of methanol synthesis catalysts. These models are described in the Operating Manual for MegaMax 800.

Isothermal Reactor

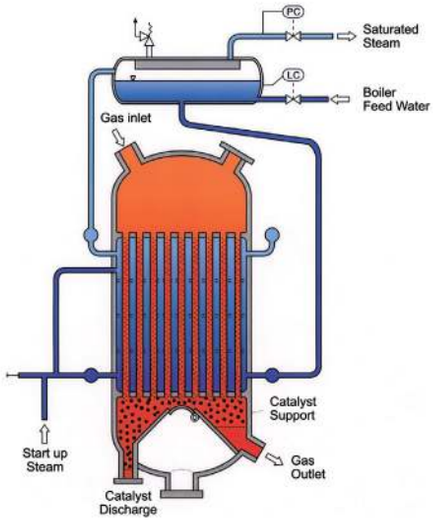
There are five different types of isothermal reactor designs:

1. LURGI tubular steam raising reactor with the catalyst in the tubes and boiling water on the shell side. The heat of reaction is utilized to produce process steam. (Figure 6)
2. Casale isothermal methanol converter that is either gas-cooled or steam-raising.
3. TOYO MRF-Z steam raising reactor with radial process gas flow mode.
4. LINDE steam raising spiral reactor with the catalyst on the shell side and steam produced inside the coils, which are built in spirals through the catalyst bed.
5. ICI tube cooled converter with the catalyst on the shell side and straight cooling tubes inside the catalyst bed.

Adiabatic Reactor

There are two different types of adiabatic reactor designs:

1. multi-bed quench (direct cooling) in Iozenge (Figure 7), ARC or CMD design, and
2. multi-bed with inter-stage heat exchange (indirect cooling).



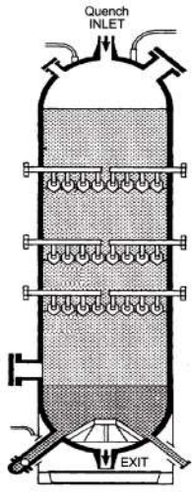


FIGURE 6 Lurgi Isothermal Reactor

FIGURE 7 ICI lozenge reactor

Operational Parameters

In commercial plants, there is normally a fixed feedstock, makeup gas composition and loop design. With all designs, the general rule is to always operate the methanol synthesis catalyst with the lowest reaction temperature possible, while maintaining the desired methanol production rate and quality.

The inherent loss in activity of any methanol synthesis catalyst over time in service can be compensated for by the following operating parameters:

- reaction temperature,
- quench gas distribution,
- operating pressure,
- recycle ratio (not possible with every design), and
- purge rate.

By-Products

In principle, the by-products formed during methanol synthesis are compounds such as higher alcohols, esters, ethers and ketones. Ketones and acetone are critical by-products in terms of achieving Grade AA methanol product.

As an example of the selectivity of MegaMax 800 catalyst, Table 5 lists typical levels of by-products in large scale industrial methanol plants (conditions: combined reforming, operating pressure = 80 bar g, steam jacket temperature = 232 °C).

IMPURITIES [ppm wt.]	
Ethanol	121
Total Higher Alcohols	342
Acetone	1
MEK	3
Total Ketones	6
Grand Total	568

TABLE 5 Typical By-Products in Crude Methanol

Catalysts for Methanol Synthesis **MEGAMAX**

Poisons

MegaMax 800 methanol synthesis catalyst is a copper-based catalyst so any constituent in the feed gas that reacts with copper acts as a poison. The primary deactivation mechanism for methanol synthesis catalysts is poisoning by trace levels of sulfur and chlorides in the feed gas.

To a lesser extent, the catalyst is also deactivated by thermal sintering of the copper crystals. Sintering results in the formation of larger copper crystallites with a corresponding reduction in copper surface area. In addition, solid particles such as dust in the feed and trace metals physically block the catalyst surface and lead to premature deactivation of the catalyst.

Sulfur – As with all copper based catalysts, the MegaMax 800 catalyst is deactivated by sulfur. The sulfur content in the synthesis gas (or nitrogen circulation) should be less than 0.05 ppm v as H_2S. A sulfur content of more than 0.8 wt% on the catalyst, deactivates the catalyst completely.

Iron – If iron in the form of iron carbonyls is carried onto the methanol synthesis catalyst, this catalyzes the Fischer-Tropsch reaction and consequently by-product formation increases. Iron and other heavy metals also block the active sites of the catalyst, thus reducing activity. Nickel has a similar deleterious effect on the catalyst performance.

Chlorine/Chlorides – Chlorine in any form, e.g. Cl_2, HCl or R-Cl, is a strong poison to the methanol synthesis catalyst. Copper chloride sinters quickly, which reduces the active copper surface area of the catalyst. Chlorine should be excluded completely from the system; chlorine content in the synthesis gas should be at a non-detectable level. Chlorides more than 500 ppm wt on the catalyst deactivates the catalyst completely.

Oil – Any carry-over of lubricating oil should be avoided as it is well known that these heavy hydrocarbons have a deactivating effect on methanol synthesis catalysts.

Steam – Steaming of methanol synthesis catalyst must be avoided as it leads to an accelerated growth of copper crystals and deactivates the catalyst prematurely.

Oxygen – Oxygen can also be considered a poison as oxygen contact with the reduced catalyst leads to partial re-oxidation followed by subsequent reduction by the process gas. These redox reactions affect the structure of the catalyst and lead to premature loss in crush strength and a rapid increase in pressure drop a rapid decrease in pressure. This can also lead to thermal sintering with a consequential loss in active copper surface area.

Sales and Technical Services

The Catalysts business offers its customers complete service regarding to the use of any of the catalysts it supplies. This service begins with supplying process information to the engineering contractor or the customer during the initial stages of design and construction of a plant; continues through start-up services when the plant is placed online; and subsequent follow-up service to assist the customer in maintaining optimum operating performance of the catalysts. This service is available to the customer throughout the life of the catalyst.

Our Technical Services Group offers a wide range of personnel with specific expertise in the areas of catalyst characterization, research, catalyst installation, start-up, plant operation and performance evaluations.

This in-depth knowledge allows us to provide the following services:

- Review of reactor system design
- Selection of proper catalysts
- Technical reviews of start-up/shut-down procedures
- Technical assistance for loading catalyst upon start-up and shut-down
- Routine performance evaluations
- Troubleshooting
- Catalyst life-projections
- On-site training seminars for engineering and operations personnel
- Chemical and physical analyses of spent catalyst
- Supply proprietary computer programs for catalyst performance evaluation

CLARIANT INTERNATIONAL LTD
Rothausstrasse 61
4132 Muttenz
Switzerland

CATALYSTS
syngas@clariant.com

CLARIANT.COM/CATALYSTS

Clariant Group

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