Methanol to Olefins (S-MTO) Technology

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July 2016 , Iran

中国石化
SINOPEC

MTO Reaction

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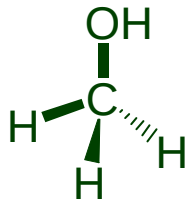
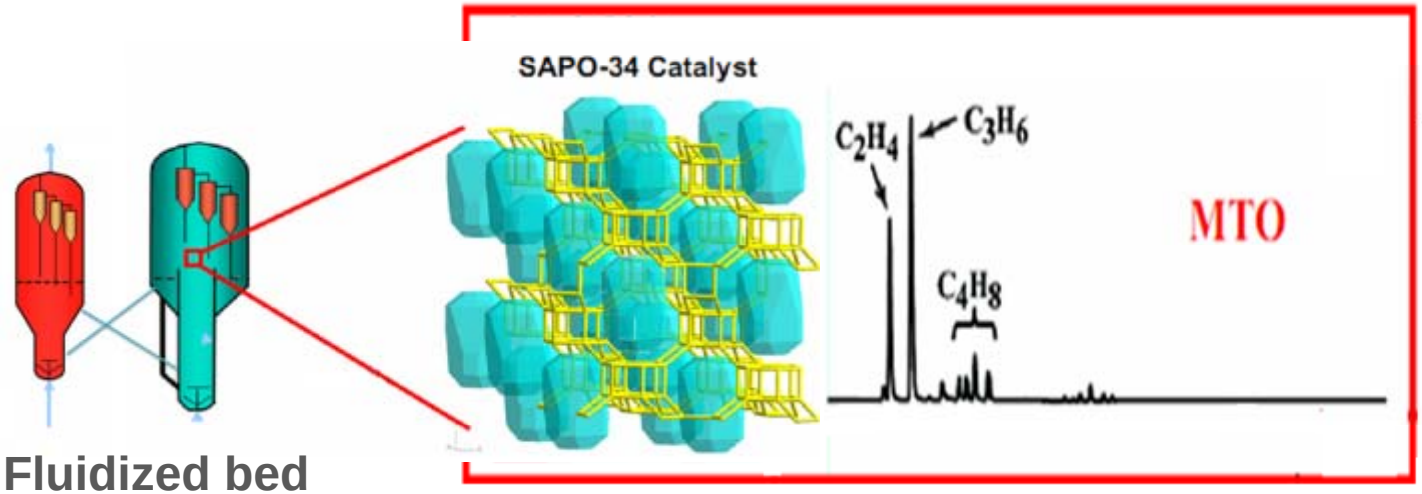


Methanol

SAPO-34

$H_2C{=}CH_2$ + $H_2C{=}CH{-}CH_3$ + $-[CH_2]_n-$ + H_2O

Ethylene | Propylene | Other Hydrocarbons | Water



Fluidized bed

High MeOH conversion & light olefins selectivity, strong exothermic, fast deactivation

Driving force

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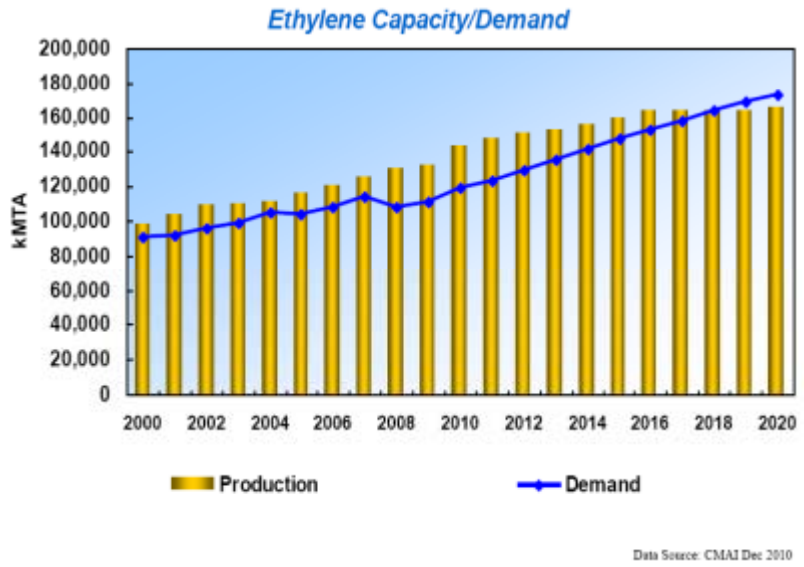
Ethylene and propylene are the most important feedstock in petrochemical industry.

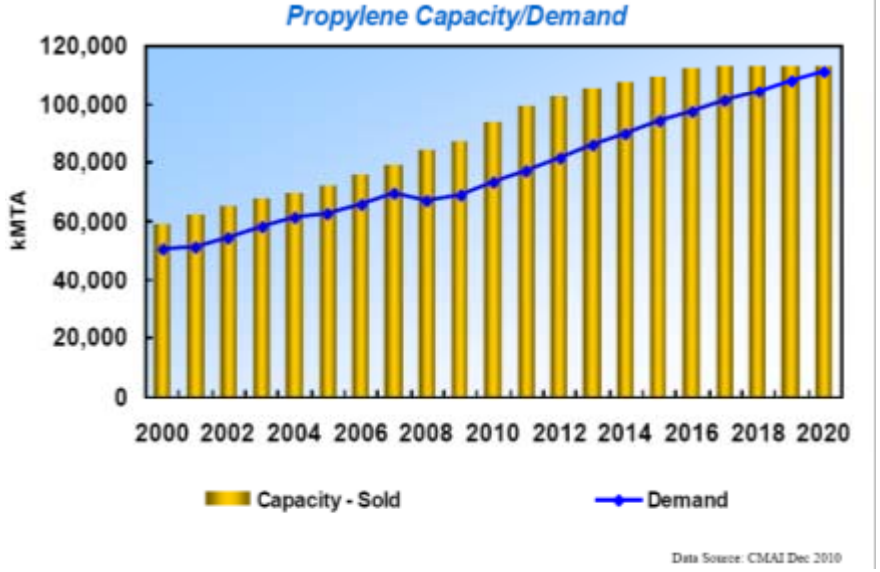
The world market continues to drive the demand for light olefins products.

Almost 90 million MTA of incremental light olefins needed between 2010 to 2020.

- **Ethylene – annual growth ~3.8%**



- **Propylene – annual growth ~4.2%**



Driving force

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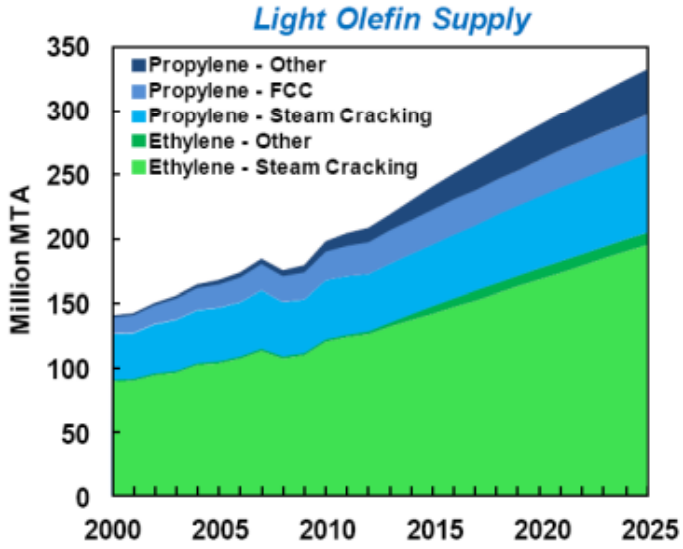
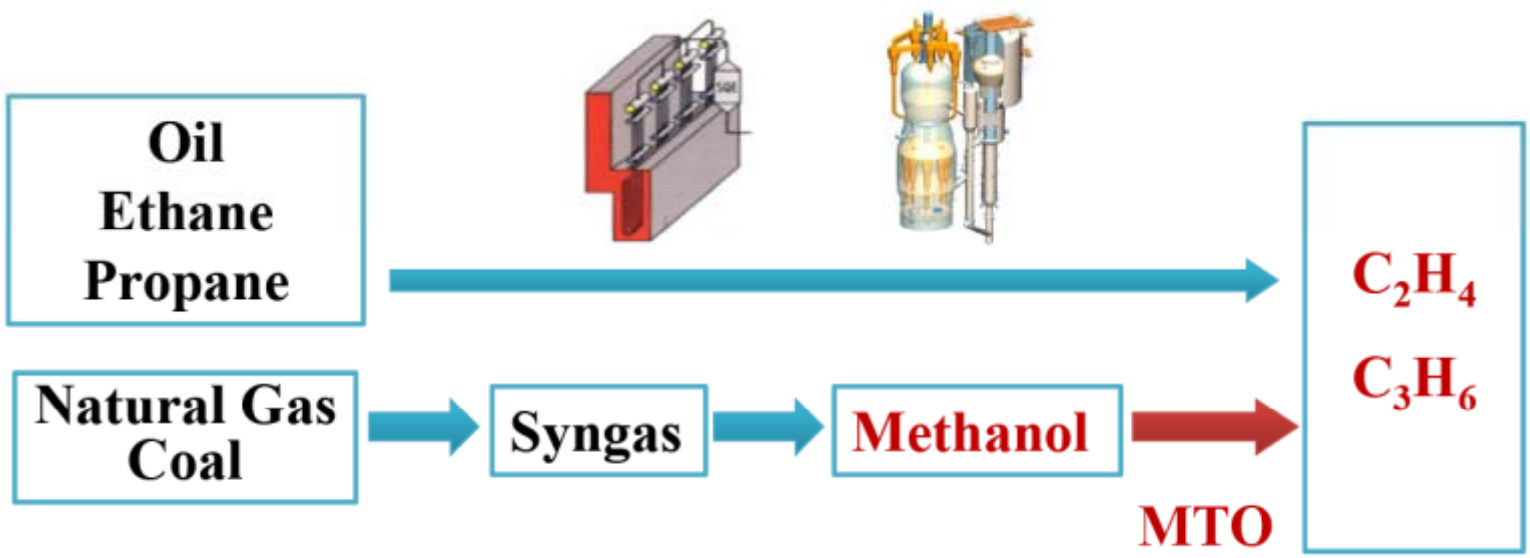
- Ethylene and propylene production are mainly based on oil.
- New technologies based on alternative feedstock to produce ethylene and propylene have been developed.
- Recently, light olefins production keeps growing share from other sources besides steam cracking and refineries.





Driving force

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Iran's Key Energy Statistics

		world rank
Crude Oil Proved Reserves 2015	158 Billion Barrels	4
Total Petroleum and Other Liquids Production 2014	3,377 Thousand Barrels Per Day	7
Proved Reserves of Natural Gas 2015	1,201 Trillion Cubic Feet	2
Production of Crude Oil including Lease Condensate 2014	3,236 Thousand Barrels Per Day	7
Total Electricity Net Generation 2014	253 Billion Kilowatthours	13

According to the Iran Petroleum Ministry, the proved natural gas reserves of Iran are about 1,200 trillion cubic feet (34 trillion cubic metres) or about 16% of world's total reserves

Gas to Olefins (GTO)

Significance of MTO process

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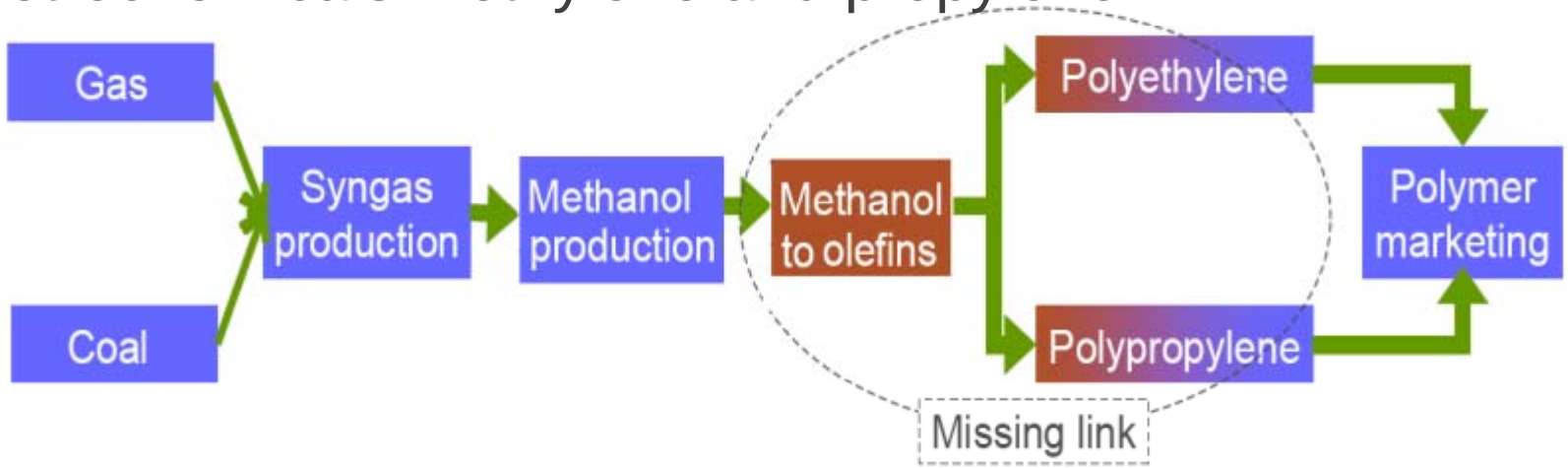
- MTO process becomes an important technology connecting natural gas and coal to the largest commodity petrochemicals – ethylene and propylene.



- MTO process could release the lack of petroleum and diversify the raw materials of light olefins production.
- MTO technology has gradually become a pillar of capacity additions of light olefins production.

R&D history of S-MTO

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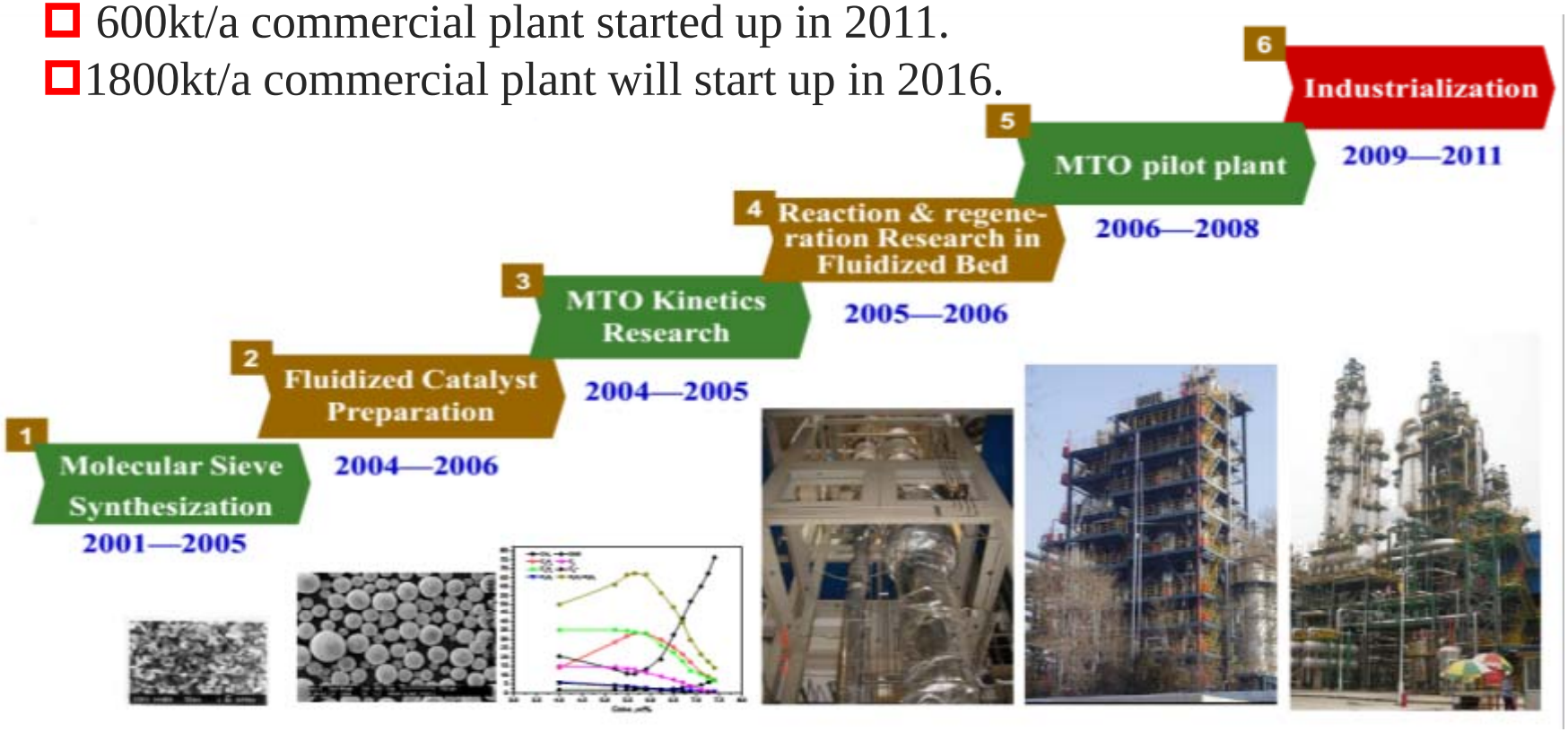
- SINOPEC started MTO research in 2000.
- Molecular sieve was synthesized and scaled up successfully in 2005.
- Parameters used for design were confirmed basically in 2006.
- Pilot plant was established and started up successfully in 2007.
- S-MTO technology came into being and ready for commercialization in 2008.
- 600kt/a commercial plant started up in 2011.
- 1800kt/a commercial plant will start up in 2016.



100t/d S-MTO pilot test-----Biggest MTO pilot plant

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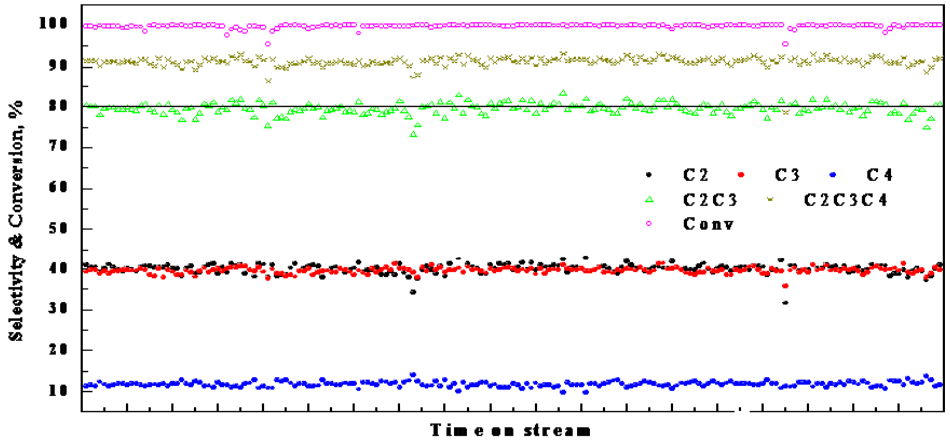
- Methanol conversion: 99.8%
- Sel. of ethylene + propylene: >80%



Light olefins yields at the outlet of the reactor are in line with expectations

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Zhongyuan 600kt/a S-MTO commercial plant

Site: Puyang City, Henan Province, China.

Construction period :14 months.

2011.10.9, started up successfully.

Qualified PE and PP were produced about 7 hours after MeOH feeding.

- **Methanol conversion: > 99.8%**
- **Ethylene+Propylene selectivity:~81%**
- **Catalyst loss： <0.25kg Cat./t Methanol**

Methanol load has reached 110% of the design load and ran steadily for almost two years.

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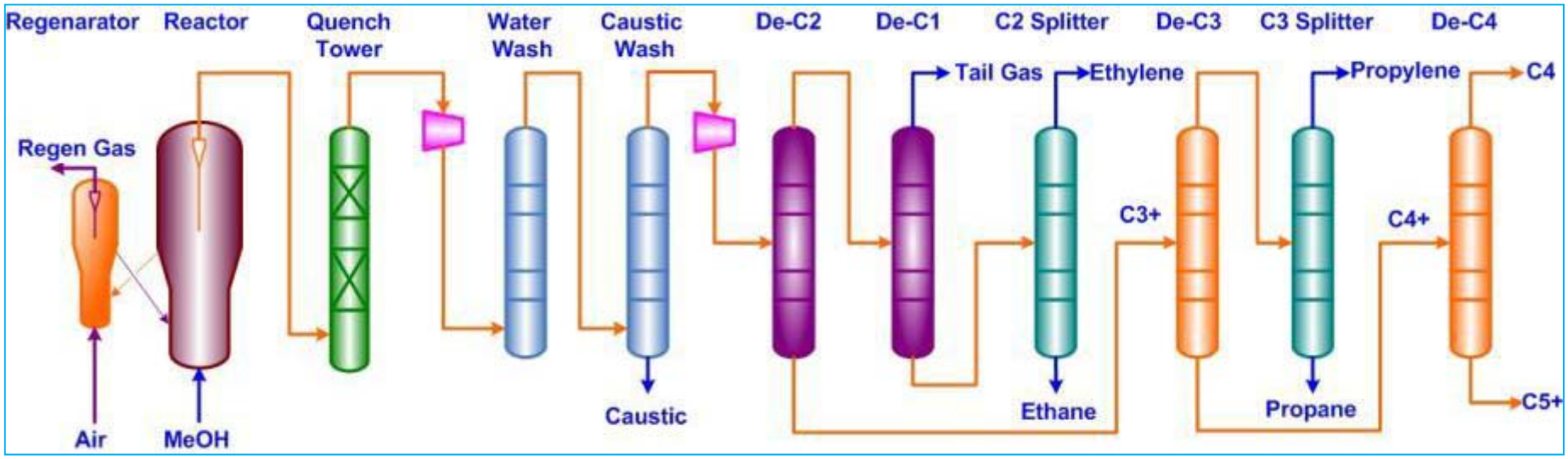
Zhongyuan 600kt/a S-MTO commercial plant



Complete process integration

- MTO R-R system
- Quench & separator
- Oxygenates recovery and recycle
- Full light olefins recovery
- Polymer grade products
- Olefins catalytic cracking unit

- Efficient catalyst with stable performance and less loss
- Efficient R-R system
- Front-end de-ethane recovery process
- Products quality control
- Steady operation for more than 30 months without unplanned shut-down.

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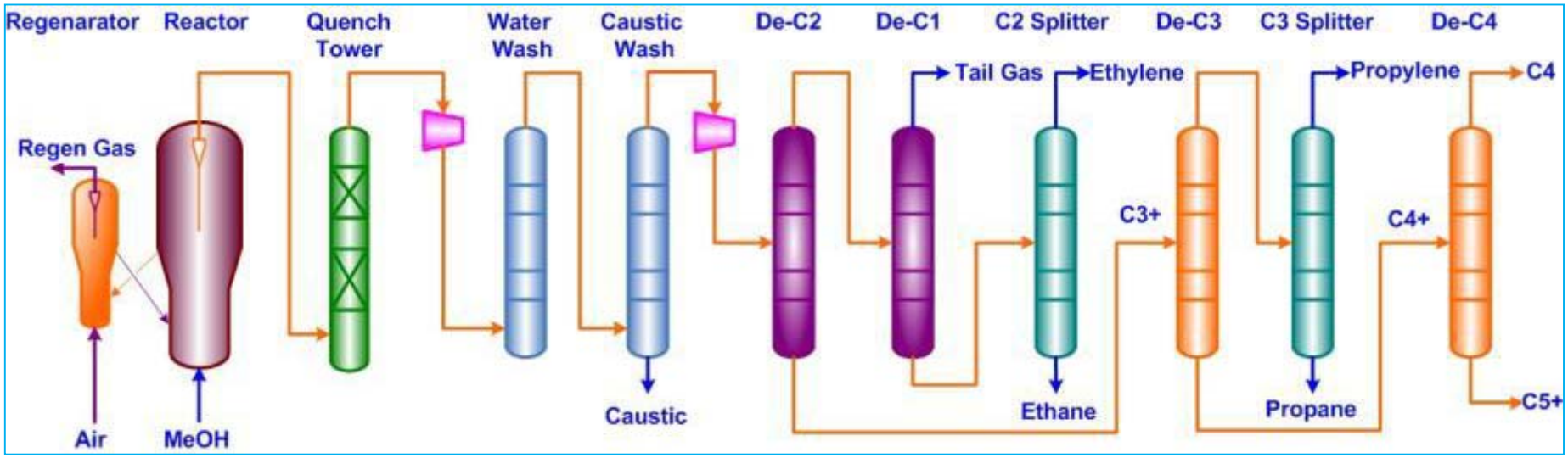
Zhongyuan 600kt/a S-MTO commercial plant



- The transformation of methanol to products over a specially designed SMTO catalyst in a fluidized bed reactor. The deactivated catalyst is regenerated in a regenerator and recycled for re-use.
- Reactor effluent is then washed and cooled to remove catalyst fines and recover the heat in the quenching unit. After compression, the product gas enters washing column to remove oxygenates and acidic constituents. After drying, product gas enters a front-end de-ethane recovery process to get polymer grade ethylene and propylene.

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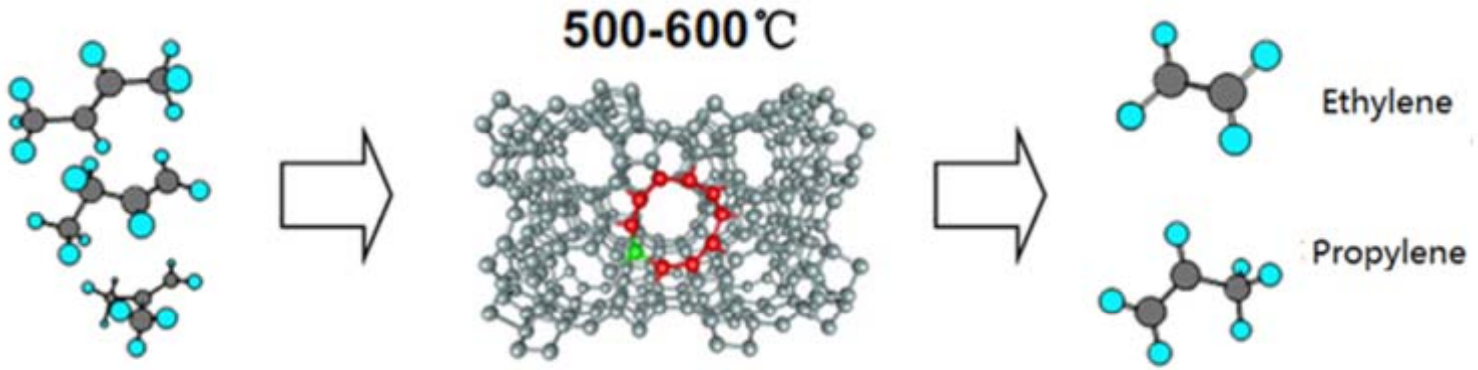
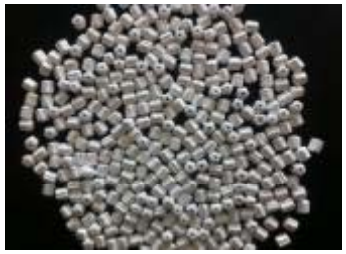
Olefins catalytic cracking (OCC) process



OCC Pilot Plant



OCC Catalyst

- Started OCC research in 2000
- Pilot test completed in 2005
- OCC commercialization in 2009

60kt /a OCC Plant

Feedstock for OCC process

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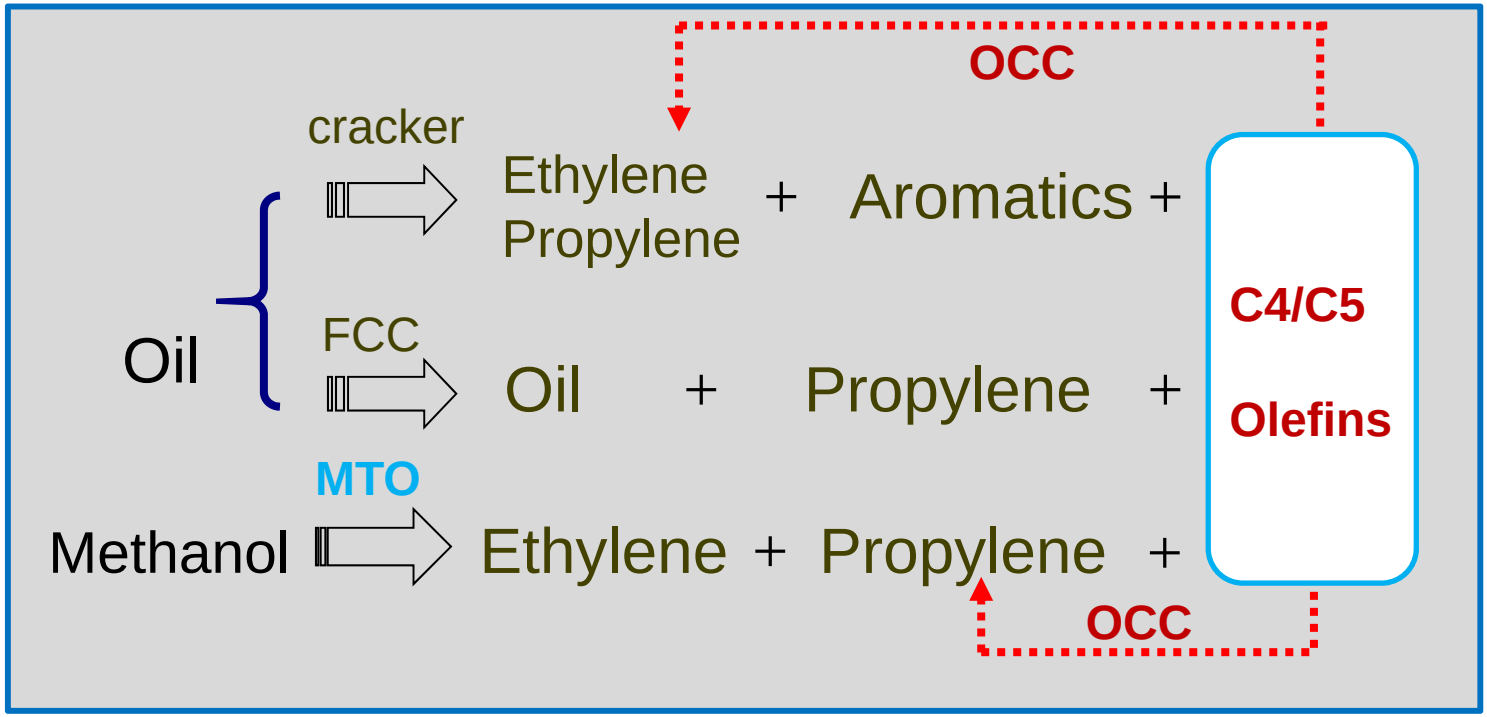

- Good feedstock flexibility, C4/C5 olefins from steam crackers, refineries or MTO plants are all favorable feedstock for the OCC process. The OCC catalyst has strong tolerance to feedstock impurities such as diolefins, sulfides and nitrogenous compounds.

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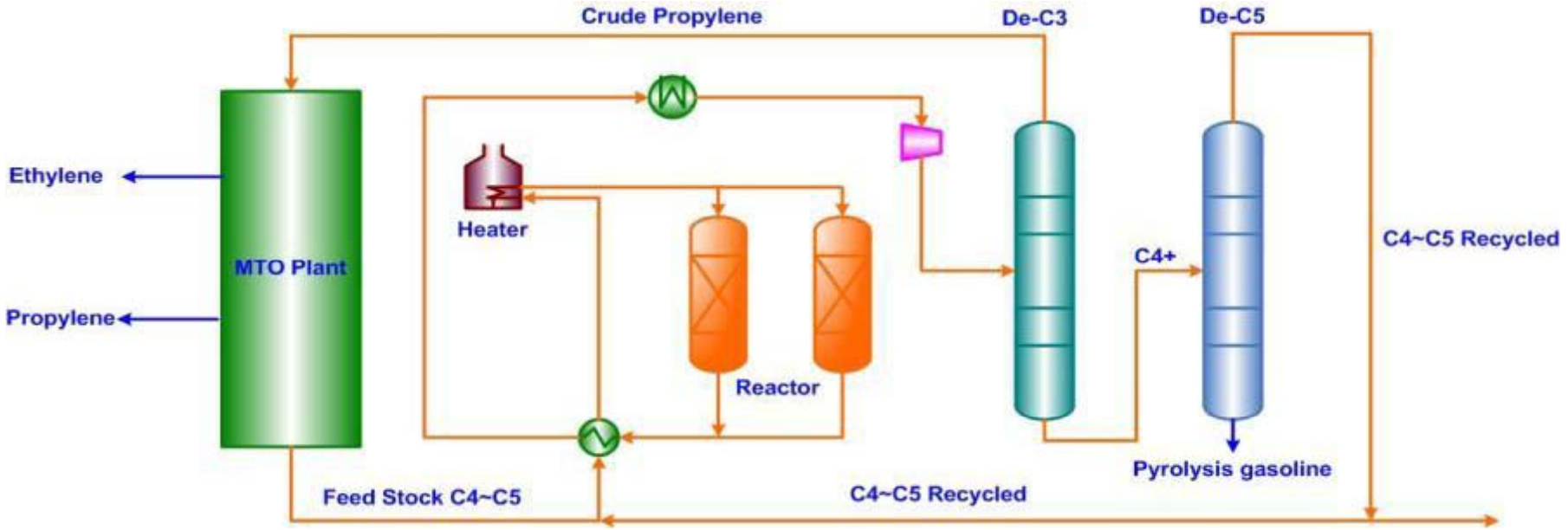
Olefins catalytic cracking (OCC) process



- Heated C4/C5 olefins are fed into the reactor for catalytic cracking. The reactor is a fixed bed reactor. The effluent from the reactor enters into the compressor after being cooled. The separation unit includes de-propanizer and de-pentanizer. The de-propanizer overhead is sent to the olefin recovery unit in the MTO plant. C4+ fractions are sent to the de-pentanizer and produce gasoline from the bottom of the de-pentanizer and stream from the de-pentanizer overhead is recycled to the reactor.

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The world's first S-MTO/OCC configuration

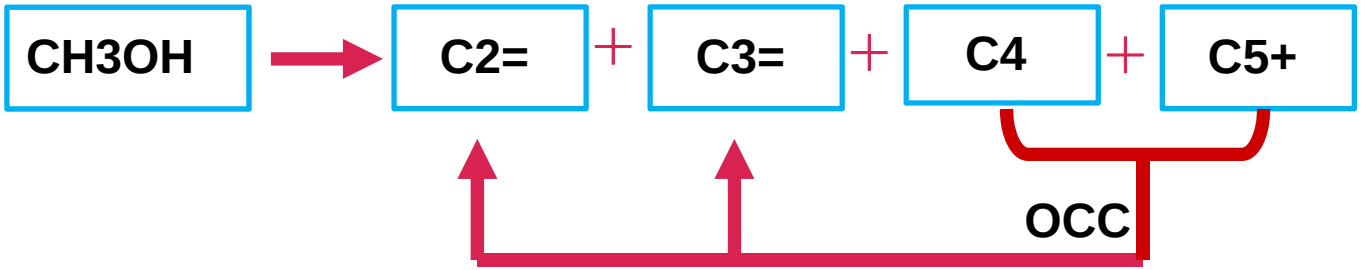
MTO unit in Puyang

C4+

2011.11

OCC unit in Puyang

OCC integration increases the selectivities of C2-C3 olefins by >10%



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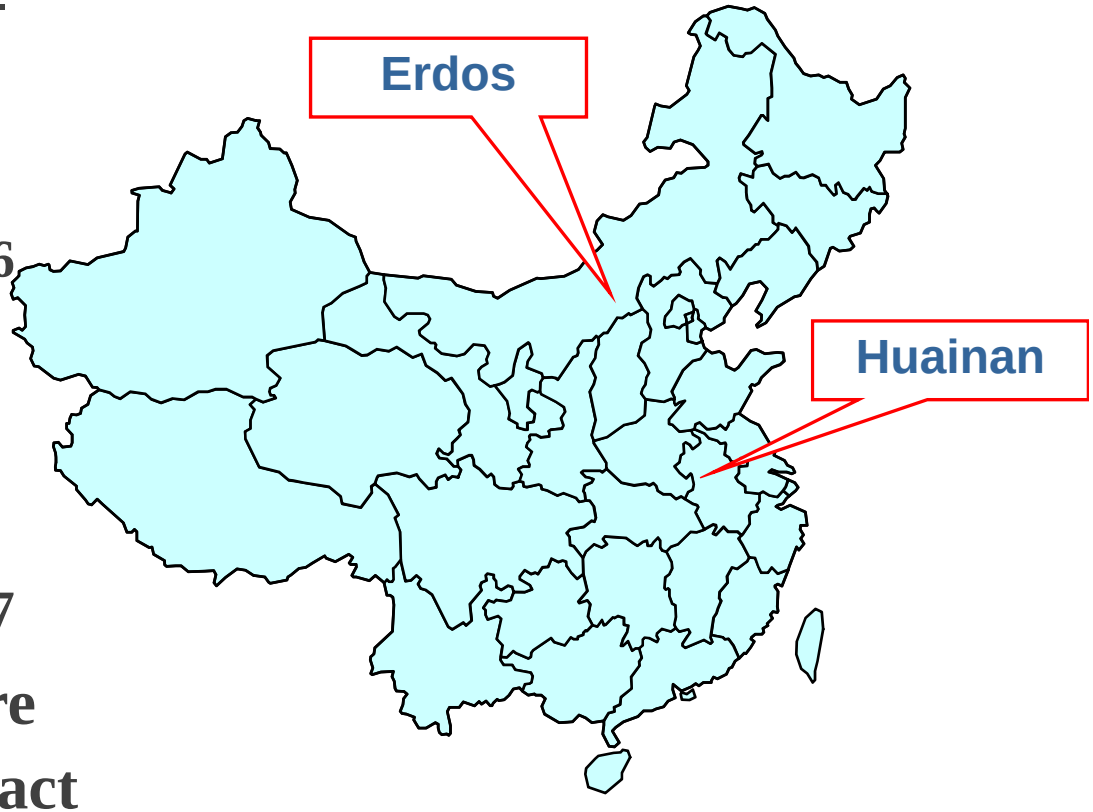
Prospective of S-MTO/OCC commercial plants

- ZhongTianHeChuang S-MTO commercial plant
  - 2*1800kt/a methanol
  - Expected start-up in 2016
- Zhongan S-MTO commercial plant
  - 1800kt/a methanol
  - Expected start-up in 2017
- Several other projects are in promotion or in contract



Strong global interest---additional license expected in next few years

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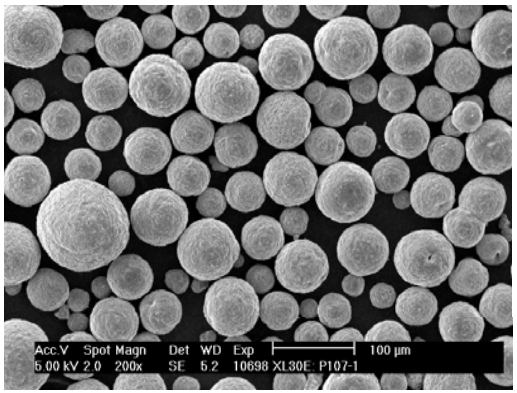
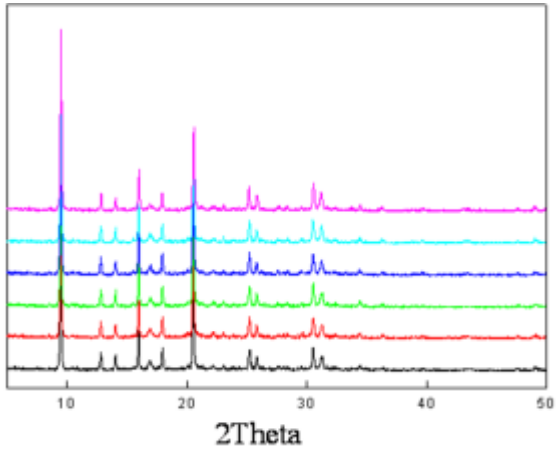
Characteristics of S-MTO/OCC Technology

- With a high performance SMTO catalyst and a fluidized-bed reactor, The methanol conversion is more than 99.98 %. The selectivity of ethylene and propylene can reach 81 wt%, and the consumption of methanol is about 2.98 t/t (ethylene +propylene).





- The ratio of ethylene to propylene can be adjusted from 0.9 to 1.1 with high yield and high productivity output.

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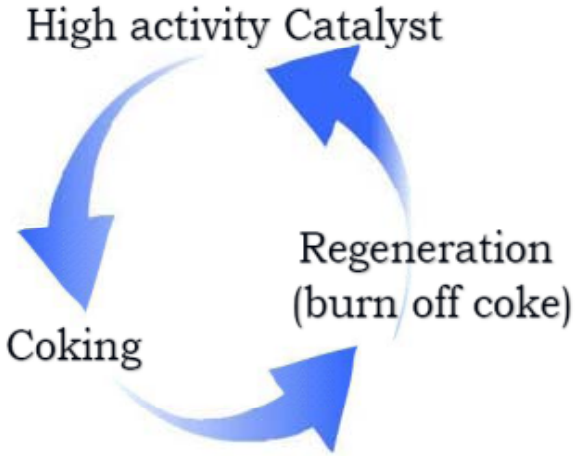
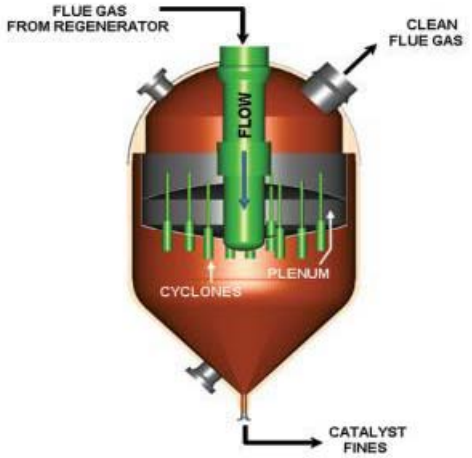
Characteristics of S-MTO/OCC Technology

- Efficient fluidized bed reactor and two-stage regenerator





- SMTO catalyst with good attrition resistance and high efficient cyclones adopted for reactor and regenerator respectively keep the catalyst loss level lower to less than 0.25 kg/t methanol.

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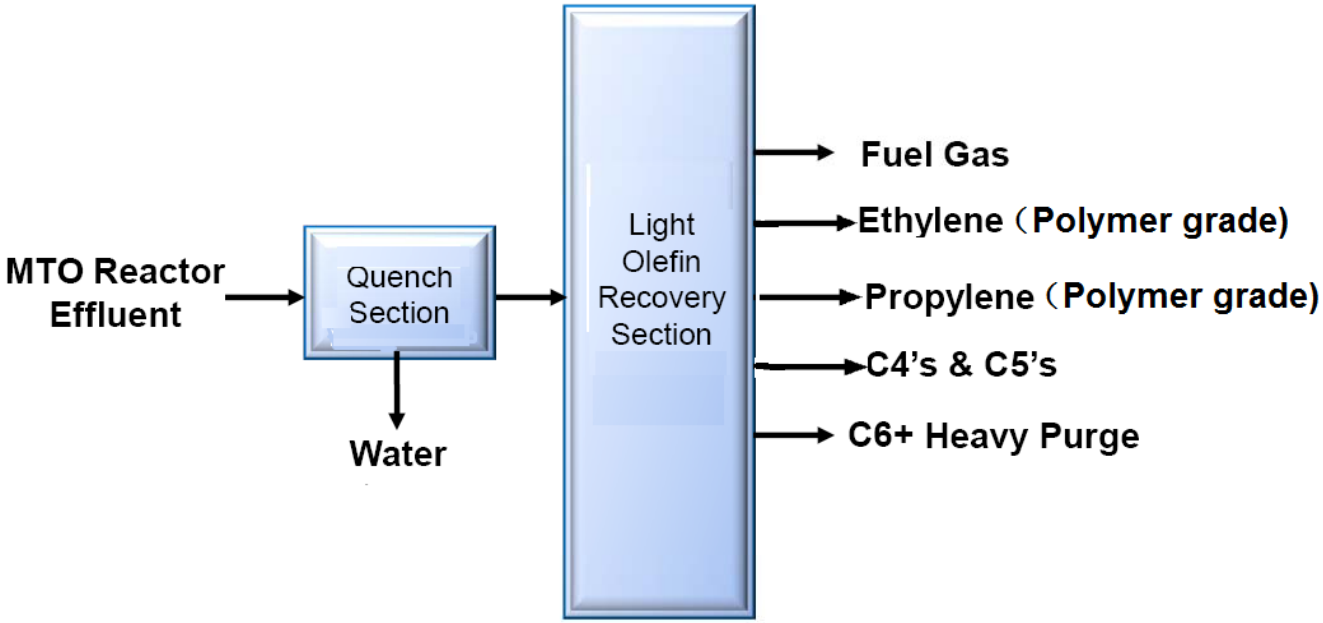
Characteristics of S-MTO/OCC Technology

- Crude methanol is also applicable, which can reduce the cost of methanol purification unit.
- Guaranteed quality of products , such as PE, PP.



Front-end de-ethane recovery process

- The world's longest running plant in stable operation without unplanned shut-down.

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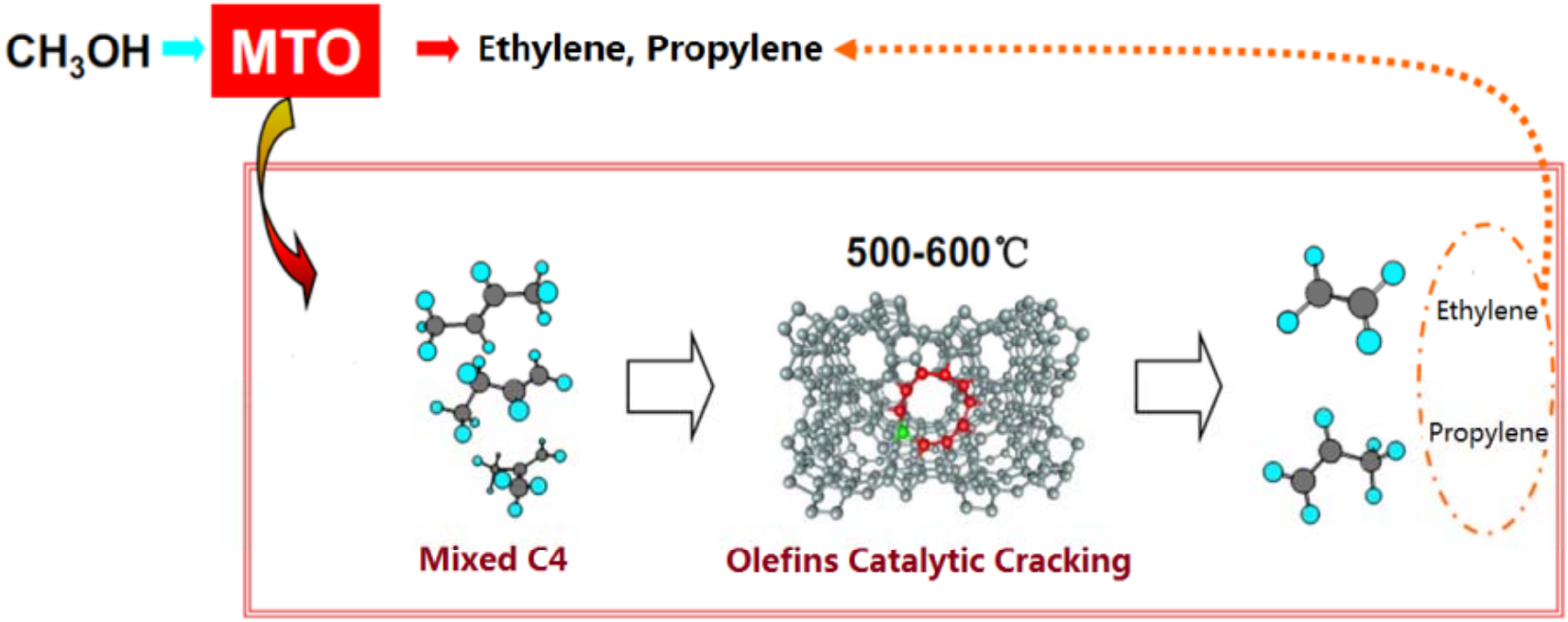
Characteristics of S-MTO/OCC Technology

- When S-MTO integrated with OCC process.
  - The consumption of methanol is about 2.65t/t (ethylene +propylene)
  - The ratio of ethylene to propylene can be adjusted from 0.8 to 1.2.



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S-MTO/OCC Technology

- Total added production value of 7 billion RMB for enterprises.
- Achieve new profit and tax 1.5 billion RMB for enterprises.
- SINOPEC Scientific and Technological Progress Award
  - the Special Contribution Prize
- Shanghai Technology Invention Award
  - the First Prize


应用证明

项目名称	60万吨/年甲醇制低碳烯烃技术工业应用			
应用单位	中国石化中原石油化工有限责任公司			
通讯地址	河南省濮阳市范利西路		邮编	457000
联系人	邵卫增	手机	13513913792	电话及传真	05934471002
应用成果起止时间	2011年10月-至今			

经济效益（万元）

年度	2012	2013	2014
新增产值	164596	237467	227281
新增利润	10580	39906	48058
新增税收	2645	9976	12015
创收外汇（万美元）			

使用情况：

1. 中国石化中原石化公司甲醇进料规模为60万吨/年甲醇制低碳烃工业装置，采用中国石化自主研发的S-MTO成套技术。由甲醇转化单元和烯烃回收单元组成。2010年8月开工建设，2011年10月投料，开车7小时即生产出合格的产品，实现装置安全、环保、全面投料开车一次成功，至2012年至2014年装置运行统计，累计生产聚合级乙烯32.8万吨，聚合级丙烯30.7万吨，达满负荷运行，实现新增利润98544万元，新增税收24036万元。
2. 2012年7月，对该成套技术进行了72小时标定。标定结果为：甲醇转化率大于99.9%，烃烯平均选择性为81.06%，甲醇单耗为2.981/t（乙烯+丙烯），装置能耗为393.58kg标油/吨（乙烯+丙烯），能后通过有针对性的技术改造和能效优化，目前装置能耗降至340 kg标油/吨（乙烯+丙烯）。
3. 该成套技术以甲醇为原料生产聚合级乙烯和丙烯，工业装置运行结果表明，SMTO催化剂具有优异的反应活性、选择性、再生性能、耐磨性能与稳定性能，S-MTO装置工艺流程合理，工程设计可靠，设备选型、材料选择合理，控制稳定，可满足长期安全稳定生产的要求。
4. 作为替代石油资源生产乙烯、丙烯的新技术，S-MTO成套技术的开发成功，有力促进我国烯烃工业原料多元化的发展，对于保障我国能源安全，促进我国经济和社会可持续发展均具有重要的意义。

2015年4月30日


中国石化集团科学技术进步奖

证 书

为表彰中国石化集团科学技术进步奖获得者，特颁发此证书。

项目名称：高性能甲醇制烯烃催化剂及S-MTO成套技术开发

奖励等级：特等奖

获 奖 者：中国石油化工股份有限公司
上海石油化工研究院

证书号：2013-J-T-01-D1


荣誉证书

授予：上海石油化工研究院甲醇制烯烃（MTO）创新团队

中国石化优秀创新团队

二〇一三年三月


荣誉证书

授予上海石油化工研究院MTO创新团队：

“中国石化先进集体”荣誉称号。

中国石油化工集团公司
二〇一三年六月

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S-MTO/OCC Technology

- S-MTO patent applications : over 300 patents (authorized over 160 patents), including 7 foreign patents.
- S-MTO has independent intellectual property rights and SINOPEC is willing to cooperate with potential partners for technology licensing.

Thanks for your attention!

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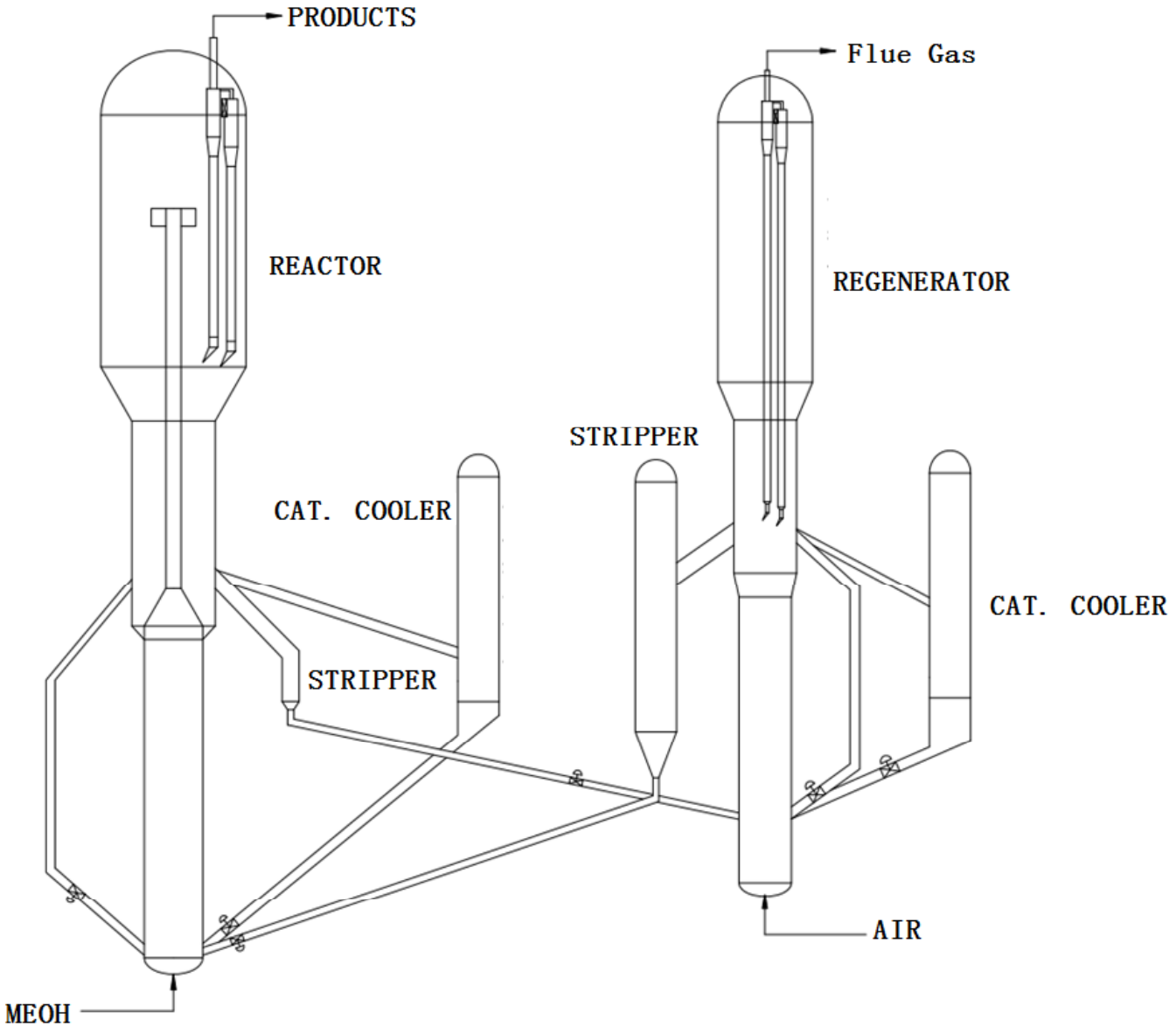
中国石化
SINOPEC

Confidential

S-MTO REACTOR –REGENERATOR SYSTEM



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