

Chapter 5

CATALYTIC PROCESSES FOR LIGHT OLEFIN PRODUCTION

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1. INTRODUCTION

Consumption of petroleum in the transportation fuel sector is expected to show only a modest rate of growth in the near future. Fuel specifications are becoming increasingly stringent due to new environmental regulations, and energy sources such as biofuel and especially fuel cells for vehicles are becoming increasingly attractive as environmentally friendly alternatives. In the petrochemical sector however, consumption of hydrocarbon raw materials is expected to grow more rapidly. The building blocks for the petrochemical industry are mainly light olefins, principally ethylene and propylene, and aromatics including benzene, toluene and xylenes (BTX). Steam cracking has been the major source of light olefins and aromatics for more than half a century. The proportions of different steam cracking feedstocks used worldwide are shown in Figure 1. Naphtha is currently the dominant feedstock, accounting for 50~55% of the total. It is expected that ethane, associate gas and condensates will gradually replace naphtha as the major feedstock because the former are easier to obtain, at a lower price, in the most productive oilfields. In North America and the Middle East, ethane and associate gas already make up 25~40% of the feedstock for steam cracking. This threatens to induce an imbalance in the ethylene to propylene ratio in the overall output from steam cracking because typical ethane pyrolysis gives 79% selectivity to ethylene and less than 1% selectivity to propylene at 70% conversion, whereas steam cracking of naphtha gives approximately 30% ethylene and 15% propylene. It is predicted that by 2010, the annual demand for ethylene and propylene will be 120 Mt and 82 Mt respectively (a propylene to ethylene ratio of 0.68). The propylene stream from refineries

currently accounts for one third of the total supply, and it is clearly necessary to develop new ways of increasing propylene production. A variety of new processes for modifying the propylene to ethylene ratio are emerging, such as transformation or product shift by isomerization, hydroisomerization, metathesis, interconversion, skeletal isomerization and catalytic cracking.

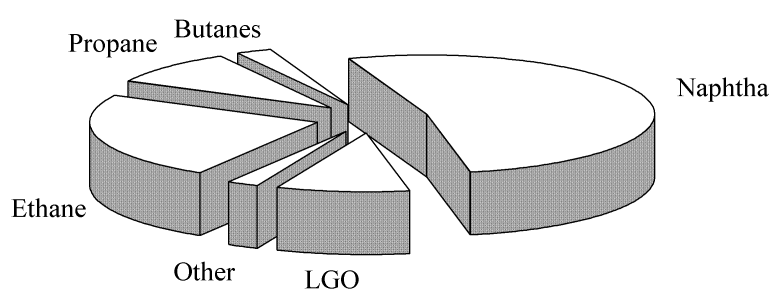


Figure 1. Proportions of different feedstocks used in steam cracking

Increasing integration of petroleum refining with petrochemicals is an inevitable tendency not only for economic and environmental reasons but also because of an increasing reliance on deep upgrading of crude oil. Statistics show that reserves of heavy crude are much larger than those of conventional crude and deep upgrading of heavy crude, for both refining and petrochemicals, is attracting more and more attention from scientists and engineers. Integration will also lead to a rational development of both refinery product slates and petrochemical building blocks.

In the manufacture of the key building blocks for petrochemicals, i.e. ethylene, propylene and other olefins as monomers for polymerization, and BTX as the basic raw material for various synthetic pathways, thermal steam crackers currently still predominate. Catalytic processes such as FCC, alkylation, isomerization, catalytic reforming and hydroprocessing play a decisive role in the production of clean fuels and lubricants in refineries. The integration of refining with petrochemicals leads to optimization of all the processes involved, and development of processes with an adjustable ratio of ethylene to propylene production is now becoming possible. It can be expected that catalytic processes will play an increasingly significant role in the production of light olefins, especially when heavy or low-grade oil is used as the feedstock. This Chapter introduces the latest progress towards the aim of increasing propylene production in FCC and related processes for light olefins.

2. FUNDAMENTALS OF THE CRACKING MECHANISM FOR LIGHT OLEFIN PRODUCTION

There are two routes for production of light olefins by catalytic cracking, which differ according to whether heavy or light hydrocarbons are employed as feedstock. When heavy hydrocarbons are used, they undergo primary cracking to form light naphtha olefins followed by secondary cracking to produce light olefins. Light hydrocarbon feedstocks are by-products from refining and petrochemical plants, i.e. C₄ and C₅ fractions of relatively low added value, which are suitable for further cracking to ethylene and propylene. The reaction pathways involved for the two types of feedstock differ to some extent.

The complex composition of heavy feedstocks means that a large number of reactions can take place, both in parallel and consecutively, on the catalyst. The relative rates of the various reactions, taken together with the relative ease of formation of various carbocations from the parent molecules, lead to a bewildering array of possible reaction pathways. The matter is complicated by the presence of a variety of active sites on the heterogeneous catalysts. These sites not only differ in their acid strength but also in their nature. A variety of reactions of carbocations can take place on these acid sites, including cracking, isomerization, hydrogen transfer, alkyl transfer and C-C bond formation as well as coke formation. Cracking reactions of large molecules tend to predominate however.

In the FCC process using heavy feedstocks, light olefins are probably produced by secondary cracking of primary olefins in the FCC naphtha fraction. The reaction proceeds readily over ZSM-5 zeolite-containing catalysts. It is widely accepted that olefin cracking over catalysts with Brønsted acidity involves initial protonation of the double bond to form a tricoordinate carbenium ion, with subsequently scission of a carbon-carbon bond in the beta position, to form a free olefin and a smaller carbenium ion.

Anderson et al.¹ recently attempted to predict the optimum zeolite-based catalyst for selective cracking of naphtha range hydrocarbons by the pathway proposed by Haag and Dessau in 1984. According to this mechanism, light olefins are produced from alkanes via “protolytic cracking”, in which alkanes are protonated to form carbonium ion transition states that can undergo either C-C bond cleavage yielding alkanes (including methane and ethane) or C-H bond cleavage yielding dihydrogen and carbenium ions. These carbenium ions subsequently form alkenes via back-donation of a proton to the zeolite. Formation of ethylene is probably via this pathway.

Weitkamp et al.² introduced a classification of carbenium ion beta scission processes. The process where the carbenium ions before and after scission are both tertiary, is denoted as Type A. Type B1 scission refers to reaction of a secondary ion to give a tertiary ion, while type B2 involves a change from a tertiary to a secondary ion. Type C involves conversion of a secondary ion to

another secondary ion, and type D involves transformation of a secondary ion to a primary ion. Buchanan³ added an additional category of primary to tertiary ion transformation, designated as type E. Although the beta scission of primary carbenium ions can produce ethylene, formation of other types of carbenium ion, which mostly produce propylene by terminating the reaction pathway, is more likely.

Cracking of the second category of feedstock - light hydrocarbons such as C₄ olefins - is likely to involve a bimolecular process and probably proceeds via initial oligomerization to form C₈ species, which then undergo further cracking to form light olefins. Our study of C₄ saturates and that of Wakui et al.⁴ both showed that butanes are difficult to crack directly. They must first be dehydrogenated to form butenes, which are then consecutively cracked following the usual olefin reaction pathways.

It should be noted that in addition to Brønsted acid sites, Lewis acid sites also play a very important role in olefin production, although in fact these two types of acid sites can be interconverted at high temperatures. In general, heating the zeolite catalyst to a high temperature results in a loss of Brønsted acidity with a corresponding increase in Lewis acidity. This alters the activity and selectivity of the zeolite in favor of a high light olefin yield. We have found it is of great importance to maintain an optimum L/B ratio in order to maximize ethylene yield under severe operating conditions.

Table 1 shows that when ZSM-5 zeolite is modified by treatment with silver (samples AGZ-1 and AGZ-2) the number of Brønsted and Lewis acid sites both increase, but the increase in the number of Lewis sites is much more marked. By using these zeolites as catalysts for cracking of heavy oil at 650 °C, substantially higher yields of ethylene and propylene can be obtained compared with the reaction over quartz as a representative inert solid. Furthermore, increasing the number of acid sites, especially Lewis sites, leads to an enhanced ethylene yield. Our experimental data are summarized in Table 2.

Table 1. Acid sites in modified ZSM-5 zeolites (Aging conditions: 800 °C for 4 hrs under 100% steam)

Sample	Acid amount, mmol.g ⁻¹		L/B	L+B
	B-acid	L-acid		
ZSM-5	20.34	5.95	0.29	26.29
AGZ-1	32.20	48.81	1.51	81.01
AGZ-2	44.07	64.09	1.45	108.16

Corma et al.⁵ postulated that in highly dealuminated zeolites the cracking reactions take place on extra-framework aluminum sites following a radical-type pathway, which will give more C₁ and C₂ hydrocarbons, mostly ethylene. The mechanism for the cracking reactions we observe at 650 °C (results shown in Table 2) may involve either carbenium ion or radical ion intermediates but this still has to be determined.

Table 2. Ethylene and propylene yields (in wt%) from heavy oil cracked over different catalytic materials

Zeolite	H ₂	Methane	Ethylene	Propylene	C ₂ ⁼ /C ₃ ⁼	C ₂ ⁼ +C ₃ ⁼
Quartz (inert)	0.08	2.12	4.74	4.01	1.18	8.75
ZSM-5	0.09	2.17	5.08	8.70	0.58	13.78
AGZ-1	0.27	2.61	8.23	11.78	0.70	20.01
AGZ-2	0.27	2.80	8.99	12.77	0.70	21.76

3. CATALYSTS

In the FCC process, it is generally accepted that after vaporization the large molecules of heavy hydrocarbons undergo cracking on both the surface of the Y-zeolite and on the surrounding silica-alumina matrix as a primary reaction. The smaller molecules thus formed permeate into the pores of the Y-zeolite and reach the active sites of the catalyst where the desired catalytic cracking reactions take place. Great efforts have been made to redesign the catalyst formulation as well as improve the process of catalyst manufacture in order to optimize the yield of light olefins.

As far as improvement of catalyst formulation is concerned, there are two approaches to the goal of enhanced light olefin yields in the FCC process: incorporation of ZSM-5 containing additives into conventional FCC host catalysts or reformulation of the catalysts especially for olefin production.

Both of these methods have their advantages and disadvantages. Mixing the conventional FCC catalyst with ZSM-5 containing additives gives the advantage of flexibility in FCCU operation according to changes in the market demand for gasoline or olefins. The disadvantage is the difficulty in providing the pore size distribution gradient in the mixed zeolite catalyst which gives the desired ratio of light olefins as products of primary and secondary cracking. Furthermore, according to the accepted reaction mechanism, the intermediates from primary cracking should first be desorbed from the acid sites of the main catalyst and then enter the pores of the ZSM-5 containing additive. In the course of this migration, the intermediate species can undergo some undesired reactions. As a result, the yield of light olefins may be adversely affected. From the viewpoint of the physical properties of a mixed catalyst in an FCCU, the two kinds of solids should be closely matched in density and attrition index in order to keep their relative proportions constant over time. This necessitates a careful choice by the user of both host catalysts and additives.

A specially formulated catalyst for maximizing the yield of light olefins can be tailored in the light of the feed properties and target products by optimizing the composition of a mixture of different natural zeolites. The pore size distribution of the matrix should be such as to allow access to the large molecules of the feedstock, whilst incorporation of large pore Y zeolite favors intermediate molecule formation and mesoporous ZSM-5 favors production

of light olefins. The gradient in pore size distribution allows ready access to a series of reactants of different molecular sizes. Furthermore, the acidity of natural catalytic materials, as well as their strength and density can be adjusted to give predominantly light olefins.

Modification of ZSM-5 is crucial if olefins are to be produced under much more severe operating conditions than those employed for conventional FCC. In the Research Institute of Petroleum Processing (RIPP) of SINOPEC, there has been a long-term program aimed at enhancing the hydrothermal stability and selectivity of ZSM-5.

It is well known that incorporation of rare earth cations can greatly improve the hydrothermal stability of Y zeolite. Shu et al.⁶ have reported the incorporation of rare earth ions into the ZSM-5 structure by a seeding method in which an REY zeolite is dispersed in a gel containing Si-, Al-, Na- sources and water and the mixture converted into an MFI type zeolite. The resulting ZSM-5 zeolite containing rare earth ions was further modified under hydrothermal conditions and the final catalyst, denoted ZRP-1, has outstanding hydrothermal stability as shown in Table 3.

Table 3. Activity retention of ZRP-1 based catalyst in n-C₁₄ cracking⁷

Conditions	Conversion, wt%
780 °C, 100% H ₂ O, 4 h	77.1
800 °C, 100% H ₂ O, 4 h	74.2
820 °C, 100% H ₂ O, 4 h	74.0

It was found that introduction of phosphorus into the ZRP series of zeolites further stabilized the crystal structure and was successful in reducing dealumination at high reaction temperatures allowing a large fraction of the acidity, and hence activity, to be maintained. Based on this experience, a modified MFI type catalyst CEP-1⁶ was developed by RIPP especially for the Catalytic Pyrolysis Process (CPP) with the aim of giving high activity and selectivity for light olefins under severe operating conditions. The hydrothermal stability of the catalyst is shown in Table 4.

Table 4. Hydrothermal stability of the CEP-1 catalyst*

Aging time, h	4	8	12	16	20	24	28
Activity Index	65	62	55	55	54	54	52

*At 820 °C, 100% steam

The stability of carbenium ions decreases in the order tertiary>secondary>primary, meaning that the yield of ethylene is generally much less than that of propylene. Zhang et al.⁸ found that by adjusting the acid type, acid strength and acid distribution, the ratio of ethylene to propylene can be altered in favor of ethylene. A modified MFI type zeolite PMZ was formed by treatment of ZRP-1 with alkaline earth metal ions. When PMZ is used as the catalyst for middle distillate cracking at 520 °C, the ratio

of ethylene to propylene is increased compared with that obtained over the ZRP-1 precursor, as indicated in Table 5.

Table 5. Comparison of ethylene yields obtained with modified MFI type zeolites

MFI Zeolite	Conversion, %	Ethylene, wt%	Ethylene/Propylene
ZSM-5	44.06	0.82	0.13
ZRP-1	63.06	2.63	0.31
PMZ	63.01	3.30	0.49

It should be noted that in addition to the catalytic carbenium ion pathways for light olefin production, thermal reactions involving free radicals are also a significant source of ethylene and indeed predominate at higher temperatures. Table 6 gives a comparison of the impact of such thermal reactions on the yields of ethylene and propylene at different temperatures.

Table 6. MAT results with PMZ as catalytically active material and quartz as inert carrier

Reaction temp., °C	650		680	
	Quartz	PMZ	Quartz	PMZ
Product yields, wt%				
Cracked gas	17.05	37.94	30.68	45.08
in which, Ethylene	5.19	8.48	9.31	11.20
Propylene	4.39	15.95	8.07	17.95
Butylenes	2.35	6.80	4.59	7.56
C ₅ +Naphtha	23.21	18.22	25.10	18.33
LCO	49.02	37.40	34.92	26.31
HCO	7.66	5.20	5.33	3.41
Coke	0.12	0.98	0.49	1.80
Loss	2.94	0.26	3.48	4.35
Conversion, wt%	43.32	57.40	59.75	70.28
C ₂ ⁼ +C ₃ ⁼ +C ₄ ⁼ , wt%	11.93	31.23	21.79	36.71
Olefin selectivity, wt/wt				
C ₂ ⁼	0.12	0.15	0.16	0.16
C ₃ ⁼	0.10	0.28	0.14	0.25
C ₄ ⁼	0.05	0.12	0.08	0.11

4. NEW TECHNOLOGY

In the last few decades, great efforts have been made to produce light olefins by catalytic processes in order to achieve a rational utilization of heavy feedstocks or petrochemical by-products. Some papers in this area presented at the 17th WPC attracted considerable attention from both academic and industrial researchers. A variety of very promising processes have been developed, and some have already been commercialized. All of the new catalytic processes aim to tackle the problem of low propylene to ethylene ratio caused by the recent feedstock change for steam crackers.

4.1 Deep Catalytic Cracking (DCC) ⁷

Deep Catalytic Cracking (DCC) is a new fluidized catalytic cracking process using a proprietary catalyst for selective cracking of a wide variety of heavy feedstocks to give light olefins. The process, developed by RIPP of SINOPEC, has been commercially proven with seven units built since 1990, six in China and one in Thailand. The DCC-I process is similar to that of conventional FCC with a modified reactor consisting of a riser plus fluidized dense bed. The dense bed at the end of the riser results in a longer residence time at a high catalyst/oil ratios favoring secondary cracking of primary intermediates, which is thought to enhance propylene production at the cost of gasoline yield. In the DCC-II system, the dense bed is removed in order to allow flexibility in propylene and gasoline yield according to market demand. Table 7 shows a comparison of the key features of DCC with those of conventional FCC.

Table 7. Comparison between DCC and FCC processes

Process	FCC	DCC
Feedstock	A wide range of heavy oils	A wide range of heavy oils preferably paraffinics
Catalyst	Various types of Y zeolite	A modified pentasil structure zeolite
Hardware		
Reactor	Riser	Riser and bed
Regenerator	Base	Similar
Main fractionator	Base	Higher vapor/liquid ratio
Stabilizer/absorber	Base	Bigger
Compressor	Base	Larger capacity
Operating conditions		
Reaction temp.	Base	+30~50°C
Regeneration temp.	Base	Similar
Catalyst/oil ratio	Base	1.5~2 times
Residence time	Base	More
Oil partial pressure	Base	Lower
Dilution steam	Base	More

The experience accumulated over eight years in four refineries and one petrochemical complex has shown that light olefin yields are greatly dependent on the feedstock properties as detailed in Table 8. Daqing paraffinic feedstock gives the highest propylene and isobutylene yields, with 23.0 wt% and 6.9 wt% respectively. For intermediate base feeds, propylene yield is more than 18 wt% for DCC-I and 14.4 wt% for DCC-II operation with an FCC naphtha yield near 40 wt%.

Table 8. DCC light olefin yields

Refinery	Daqing	Anqing	TPI	Jinan	Jinan
Operation mode	DCC-I	DCC-I	DCC-I	DCC-I	DCC-II
Feedstock	Paraffinic VGO+ATB	Intermediate base VGO	Arabian HVGO+ DAO+WAX	Intermediate base VGO+DAO	
Reaction temp., °C	545	550	565	564	530
Olefin yields, wt%					
Ethylene	3.7	3.5	5.3	5.3	1.8
Propylene	23.0	18.6	18.5	19.2	14.4
Butylenes	17.3	13.8	13.3	13.2	11.4
In which					
Isobutylene	6.9	5.7	5.9	5.2	4.8

The DCC gasoline fraction is rich in BTX especially xylenes. Table 9 lists the BTX content in the DCC gasoline fraction and DCC 75°C~150 °C light gasoline range. Recovery of BTX from the narrow cut for petrochemical applications is economically viable.

Table 9. BTX content in DCC gasoline fraction

	DCC naphtha	75~150°C cut
BTX content, vol%	25.90	57.56
In which		
Benzene	2.41	5.36
Toluene	9.84	21.87
Xylenes	13.65	30.33

It has been clearly demonstrated that increasing propylene production, even at the expense of gasoline yield, is a commercial proposition in an integrated refining-petrochemical complex.

4.2 Catalytic Pyrolysis Process (CPP) ⁹

The Catalytic Pyrolysis Process (CPP), also developed by RIPP of SINOPEC, is an extension of DCC which gives an increased ethylene yield while keeping propylene production at a reasonable rate. The key features of this process are as follows:

- A new catalytic material has been developed which reduces the activation energy required, thus allowing the reaction to be carried out at a significantly lower temperature compared with that required for steam cracking, and also favors the production of light olefins.
- The catalyst possesses excellent hydrothermal stability and attrition resistance.
- The operating conditions for CPP are more severe than for Resid FCC (RFCC) to an extent that it is allowed to be operated in existing idle RFCC units without the risk of damage to the fabric of the plant.
- The heat required for the cracking reaction can be provided by burning

coke and HCO in the regenerator, making the reaction fully self-supporting.

- A specially designed stripper located between the regenerator and reactor removes the flue gas carried over from the regenerator.
- Since the reaction temperature is higher than for conventional RFCC, a post-riser quench has been introduced for heat recovery as well as termination of secondary reactions in order to prevent further thermal degradation of the target products.

Commercial trial runs were successfully completed in early 2001 at the PetroChina Daqing Refining & Chemical Co. using a revamped DCC unit with a capacity of 80,000 t/a. Three sets of conditions were employed: Mode 1 – for maximum propylene yield; Mode 3 – for maximum ethylene yield; Mode 2 - intermediate between the two. Feedstock properties, major operating parameters and product distribution can be seen in Tables 10, 11 and 12. Across the three modes, the combined yield of ethylene and propylene ranges between 34 and 38 wt% and the total yield of $C_2 = \sim C_4 =$ olefins is around 45 wt% in each case. The ethylene to propylene ratio can be adjusted by variation of the operating conditions.

Table 10. Feedstock properties

Operating mode	Mode 1	Mode 2	Mode 3
Density (20 °C), g/cm ³	0.9002	0.9015	0.9012
CCR, wt%	4.7	4.9	4.7
Hydrogen, wt%	12.82	12.86	12.84
Sulfur, wt%	0.16	0.16	0.16
Nitrogen, wt%	0.29	0.26	0.25
Nickel, ppm	5.8	6.2	6.3
Composition, wt%			
Saturates	56.3	54.8	55.5
Aromatics	27.2	28.4	28.0
Resin	15.7	16.0	15.7
Asphaltene	0.8	0.8	0.8

Table 11. Main operating parameters

Operating mode	Mode 1	Mode 2	Mode 3
Feed rate, t/h	9.73	8.00	5.90
Reaction temp., °C	576	610	640
Reaction press., MPa(g)	0.08	0.08	0.08
Regeneration temp., °C	720	725	760
WHSV, h ⁻¹	2.5	4.0	Zero level
Catalyst/oil ratio	14.5	16.9	21.1
Steam/oil ratio	0.30	0.37	0.51

Table 12. Product distribution and olefin yields

Operating mode	Mode 1	Mode 2	Mode 3
Product yield, wt%			
C ₂ mines	17.64	26.29	37.13
C ₃ plus C ₄	43.72	36.55	28.46
C ₅ +naphtha	17.84	17.61	14.82
LCO	11.75	8.98	7.93
Coke	8.41	9.67	10.66
Loss	0.64	0.90	1.00
Olefin yield, wt%			
Ethylene	9.77	13.71	20.37
Propylene	24.60	21.45	18.23
Butylenes	13.19	11.34	7.52

We suggest that in order to optimize use of crude oil as a petrochemical feedstock, a combination of steam cracking and CPP may be the best choice, as depicted in the flow scheme in Figure 2.

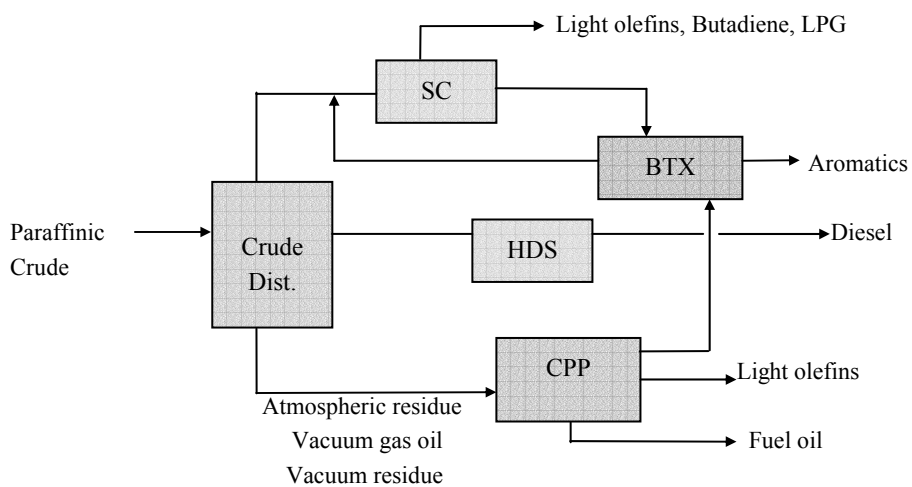


Figure 2. The scheme of crude to petrochemicals

Key economic data for a CPP plant with integrated steam cracker are shown in Table 13. Based on 500 KTA of ethylene produced by CPP and 1000 KTA of ethylene produced by steam cracking, the estimated net product revenue is 450 \$MM/A.

Table 13. Key economic data for a CPP integrated olefins plant *

	CPP/SC \$MM	SC	Δ
TIC			
CPP (50MBPD, 500 KTA C ₂ H ₄)	150		
SC, Recovery (1000 KTA C ₂ H ₄) (SC P/E 0.45)	600	650	
	750	650	100
Operating Cost (including Catalyst)	\$MM/A		
	30	20	10
Net Product Revenue	\$MM/A		
	450	320	130

Δ TIC/Revenue < 1 Year Pay Out

*By courtesy of Mr. Colin P. Bowen of Stone & Webster, A Shaw Group Company

4.3 PetroFCC^{10,11}

The PetroFCC process is licensed by UOP LLC and features RxCAT technology. The process gives high yields of propylene, light olefins and aromatics for petrochemical applications, from feedstocks which can include conventional FCC feeds and higher boiling or residual feeds. The feed comes into contact with the blended catalyst in the riser under very severe processing conditions. The blended catalyst consists of the regenerated catalyst and coked catalyst.

The PetroFCC process employs several measures to improve the yield and selectivity of propylene and lower the yield of dry gas:

- The PetroFCC catalyst has two components. The first component comprises a large pore zeolite, such as a Y-type zeolite. The second component involves medium or small pore zeolites such as ZSM-5 or ST-5, which have high coking resistance.
- The riser inlet temperature is reduced to about 620 °C by cooling the regenerated catalyst with the recycled coked catalyst. The ratio of catalyst to feed can be increased to an extent without any adverse influence on the heat balance in the unit.
- The residence time for the feed in contact with the catalyst in the riser is less than or equal to 2 seconds. The short residence time ensures that the target products are not further converted to undesired products. The diameter and height of the riser should be varied to give the desired residence time.

The expected yield patterns for a typical VGO feedstock in a traditional FCC unit and a PetroFCC unit are compared in Table 14.

Table 14. Yield patterns of traditional FCC and PetroFCC units

Component, wt%	Traditional FCC	PetroFCC
H ₂ S, H ₂ , C ₁ & C ₂	2.0	3.0
Ethylene	1.0	6.0
Propane	1.8	2.0
Propylene	4.7	22.0
Butanes	4.5	5.0
Butenes	6.5	14.0
Naphtha	53.5	28.0
Distillate	14.0	9.5
Fuel oil	7.0	5.0
Coke	5.0	5.5

4.4 Propylur^{12,13}

The Propylur process converts low value light hydrocarbons enriched in olefins into petrochemicals such as propylene and is based on a shape-selective heterogeneous zeolitic catalyst of the ZSM-5 type.

The feedstock for the Propylur process can be C₄ cuts, Raffinate I, Raffinate II or gasoline fraction. Naturally, a feedstock with high olefin content is more favorable. Compounds such as paraffins, cycloalkanes, and aromatics are rarely converted when they pass through the reactor. The diolefin content should be limited to approximately 1.5 % in order to reduce the formation of gum and coke during the reaction.

The Propylur reactor is an adiabatic fixed bed type, similar to that employed in a Claus unit. The operating temperature is approximately 500 °C and pressure is slightly above atmospheric. The hydrocarbon partial pressure is reduced by diluting the feedstock with steam, in order to shift the equilibrium towards the desired product (propylene). This also minimizes coking and gum formation. The reaction is endothermic and requires additional heat.

By cooling the reactor effluent, the steam is condensed and then separated together with some gasoline by-products. The remaining vapor is compressed in order to allow C₃/C₄ separation at reasonable temperatures. Most of C₄+ fraction is recycled to the reactor to increase the ultimate propylene yield. Further separation of the C₃ fraction can be done in the ethylene plant. The single-pass propylene yield is 40% to 45%, and the ethylene yield is 10%. The ultimate yield of propylene is 60% and that of ethylene is 15%, with the butenes recycled.

The catalyst lifetime is predicted to exceed 15 months based on the laboratory pilot-plant experience. The catalyst can be regenerated off-stream in situ by burning the coke deposited on it by controlled combustion with a nitrogen cycle and small air makeup.

When integrated with an ethylene plant, the Propylur plant can give increased propylene to ethylene ratios in a steam cracker. The typical yields of

different products from the Propylur process are shown in Table 15.

Table 15. Typical yields from the Propylur process

	Typical yields, wt%	
	Single pass	C ₄ -recycle
Propylene	40-45	60
Ethylene	10	15
Butylenes	30	

4.5 SUPERFLEX^{14,15}

The SUPERFLEX process is a proprietary technology patented by ARCO Chemical Technology, Inc. (now Lyondell Chemical Co.), and is exclusively offered for license by Kellogg Brown & Root. It uses an FCC system with a proprietary catalyst to convert low-value feedstock with high olefin content to petrochemical products such as propylene and ethylene.

The feedstock can be olefin-rich light hydrocarbons in the carbon range C₄ to C₈, and the ideal feedstocks are C₄ and C₅ streams generated in the steam cracker. Diolefins and acetylenes in the feedstock can be partially hydrogenated to olefins, or the diolefins extracted for other petrochemical applications. Other possible feedstocks are MTBE Raffinate-2, aromatics plant raffinate and refinery streams that are rich in olefins, such as light naphthas from an FCCU, coker or visbreaker. Refinery streams do not require pretreatment or hydrogenation of dienes - there is no limit on feed aromatic or diene content.

The SUPERFLEX FCC system is similar to that of a conventional FCC unit and consists of riser reactor, regenerator vessel and units for air compression, catalyst handling, flue gas handling and feed and effluent heat recovery. The SUPERFLEX system should be integrated into an ethylene plant in order to minimize capital investment, with the feedstock obtained directly from the steam cracker and shared common product recovery. The cooled reactor effluent can be processed in a nearby existing ethylene plant recovery unit. Alternatively, the effluent can be processed in a partial recovery unit to recover recycle streams and olefin-rich streams concentrated for further processing in a nearby ethylene plant.

The conditions involve low hydrocarbon partial pressures, high temperatures and low per pass conversions in order to favor propylene production. The catalyst is very robust, and there is no need to pretreat for typical feed contaminants such as sulfur, water, oxygenate or nitrogen in feeds. The typical ultimate light olefin yields after the recycle operation are listed in Table 16.

Table 16. Ultimate yields from the SUPERFLEX process

Yields, wt%	C ₄ Raffinate	Partially Hydrog. C ₅ S	FCC Lt. Naphtha
Fuel gas	7.2	12.0	13.6
Ethylene	22.5	22.1	20.0
Propylene	48.2	43.8	40.1
Propane	5.3	6.5	6.6
Gasoline	16.8	15.6	19.7

4.6 Mobil Olefin Interconversion (MOI) ¹⁶

MOI was developed by the Mobil Oil Corporation and converts light hydrocarbons containing C₄-C₇ olefins to more valuable light olefins by contacting the feed with a catalyst containing ZSM-5 and/or ZSM-11.

The feedstocks will typically be low value refinery or petrochemical streams, such as steam cracker by-products rich in C₄'s, which have poor propylene selectivity when recycled to the steam cracker. The feedstock can include raffinates, catalytic cracked naphtha, coker naphtha, steam cracker pyrolysis gasoline, as well as synthetic chemical streams containing sufficient amounts of C₄-C₇ olefins. Dienes, sulfur, nitrogen and oxygenates in the feeds are preferably selectively hydrotreated prior to the conversion process. However, feeds with low levels of dienes, sulfur, nitrogen, metal compounds and oxygenates can be processed directly from FCC units, cokers or steam crackers without any pretreatment.

The process uses a dense fluidized bed and the hydrocarbon feed containing the C₄-C₇ olefins is continuously passed through the bed under conversion conditions in the presence of the catalyst. The catalyst is continuously circulated between the fluidized bed and a regenerator. The fluidizable catalyst can transfer heat from the latter to the former thereby helping to supply some of the thermal needs of the conversion reaction, which is endothermic. The operation of the process is similar to that of conventional FCC.

The dense fluidized bed conversion conditions include temperature in the range 540 °C to 650 °C and pressure from 0.10 to 0.45 MPa, catalyst/oil weight ratio of 0.1 to 10, and a weight hourly space velocity (WHSV) of 1 to 10 h⁻¹. Because the catalyst used in the process has lower cracking activity relative to conventional FCC catalysts, a higher temperature compared with that for conventional FCC may be used in order to achieve a higher conversion to the desired light olefins.

The catalyst in MOI contains only ZSM-5 and/or ZSM-11 without any large pore zeolites. The ZSM-5 and/or ZSM-11 preferably have a high initial silica/alumina molar ratio and are modified by phosphorus and metals such as gallium.

The products from MOI include light olefins such as propylene and ethylene. A higher yield of propylene is produced than is usually obtained in conventional catalytic cracking processes utilizing a ZSM-5 additive. The

propylene/ethylene weight ratio is related to the conversion and feed but almost always exceeds 3.0. The combined yield of ethylene plus propylene is about 20 to 30 wt%. Propylene purities of 85 wt% or greater can be achieved. In addition, only relatively small amounts of aromatics such as benzene, toluene and xylenes (BTX) are produced.

4.7 Propylene Catalytic Cracking (PCC)¹⁷

The ExxonMobil PCCSM Process is a new fluid solids naphtha cracking process to convert naphtha olefins to light olefins such as propylene, which employs an optimum catalyst, reactor design, and patented combination of optimum operating conditions to achieve a high degree of reaction selectivity.

The feed can be obtained from cat naphtha, coker naphtha, and steam cracker's C4's and pyrolysis gasoline. The largest source of olefinic feedstock molecules is cat naphtha, which contain 20-60% olefins. Most of linear cat naphtha olefins are converted to light olefins, and at the same time, an increased octane and reduced olefin content naphtha is produced by the concentration of higher octane aromatics, plus isomerization and some additional aromatics formation.

A fluid solids reactor/regenerator configuration is designed for large capacity units. Feed naphtha is preheated and is injected into the reactor of a fluid solids reactor/regenerator system. The hot, regenerated catalyst contacting the preheated feed supplies the necessary sensible heat to complete preheating the feed to reaction temperature, and supplies the heat of reaction. These fluid solids systems can use ZSM-5 containing fluid solids catalysts. In this way, coke make on the catalyst when cracking naphtha is low. Therefore, it requires a means to provide supplemental fuel to burn in the regenerator to supply the necessary sensible heat and heat of reaction. The regeneration of catalyst provides the flexibility to process a variety of feeds, which can contain diolefins, aromatics, or heavy ends to a certain degree.

Reactor effluent is cooled and vapors are compressed for product recovery. Once-through yields of ethylene and propylene typically are in the range of 10-20 wt.% and 30-40 wt.% on feed olefin content, respectively. The propylene's concentration is ranging from 85% to 90% and can be further purified to supply as polypropylene feed. Ethylene can also be recovered in order to achieve maximum economic benefit. Butylenes can be recovered as product, or can be recycled (optionally with unconverted C₅+) for additional propylene production.

4.8 Olefins Conversion Technology (OCT)^{18,19,20}

OCT was originally developed by Phillips Petroleum and was first commercialized in 1965 when it was used to produce ethylene and butenes from propylene, due to the over-supply of the latter at that time. With the

increasing demand for propylene, the OCT process is currently being licensed by ABB Lummus for production of propylene from ethylene and butene-2 by metathesis.

OCT converts normal butene-2 and ethylene to polymer grade propylene via metathesis (Figure 3). The metathesis is essentially equilibrated, with the equilibrium position depending on the temperature and the ratio of reactants. In addition to the main reaction, numerous side reactions between olefins also occur which lower the yield of propylene and cause deactivation of the catalyst.



Figure 3. Metathesis of ethylene and butene-2

The ethylene feed can be polymer grade or lower purity as long as the impurities are below a certain limit. Any saturated hydrocarbons, such as ethane and methane, do not react. A variety of C₄ streams, including mixed C₄'s produced by FCC or steam cracking, or C₄ Raffinate from butadiene extraction or MTBE production, can be used in the process. In order to achieve the full potential propylene production. However, the raw C₄ cut requires pretreatment to maximize its butene-2 content.

The catalysts used in the metathesis process are highly selective and flexible and can operate over a broad range of temperatures and pressures. There are two classes: tungsten-based operating at high (300-400 °C) temperatures, and rhenium-based working at low (20-50 °C) temperatures. Both catalyst types can be deactivated and fouled by heavier organic compounds formed by side reactions. The deactivated catalyst can be regenerated by calcination at 500-600 °C.

A simplified flow process for Lummus OCT can be described as follows. Fresh and recycled C₄'s are mixed with ethylene and recycled ethylene feeds and sent through a guard bed which removes trace impurities from the mixed feed. The feed is heated prior to entering the vapor phase fixed-bed metathesis reactor where the equilibrium reaction takes place. The catalyst is regenerated in situ on a regular basis. The per-pass conversion of butene is greater than 60 wt% with overall selectivity to propylene exceeding 90 wt%. The product from the metathesis reactor contains mainly propylene and unreacted feed.

A standalone OCT unit requires a polymer grade ethylene feed and specific invest. When integrated with an ethylene plant, however, OCT provides the flexibility to economize on feedstock while varying the ratios of light olefins produced. The typical propylene to ethylene ratio of 0.4 to 0.6 in an ethylene plant can be extended to greater than 1. OCT can also be combined with FCC in order to reduce the investment cost per ton of propylene produced.

4.9 Methanol to Olefin (MTO) Process^{21,22}

The UOP/HYDRO MTO process converts methanol to light olefins. The process provides greater selectivity to ethylene and propylene versus C₄+ by-products.

The MTO reaction scheme is shown in Figure 4.

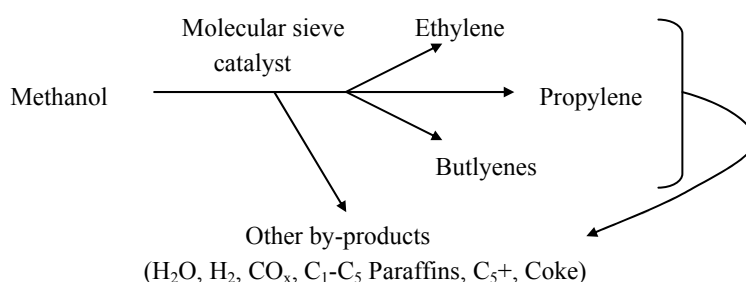


Figure 4. MTO reaction scheme

The ethylene and propylene are produced from a dimethylether (DME) intermediate in the MTO process. Some by-products such as butenes and other higher olefins are also produced. The MTO reaction is exothermic. The coke deposited on the catalyst can be removed by combustion with air in a catalyst regenerator system in order to prolong the active life of the catalyst.

The UOP/Hydro MTO process utilizes the highly selective metalloaluminophosphate molecular sieve catalyst MTO-100, which is based on SAPO-34. The main olefin products are ethylene and propylene, but the catalyst is rapidly deactivated by aromatic coking. An alternative MTO catalyst is the medium-pore zeolite ZSM-5. In this case the main olefin product is propylene, and the deactivation of catalyst caused by aromatic coke is slow, but significant quantities of C₅+aromatic by-products are formed.

In the UOP/Hydro MTO process unit, the methanol and recycled DME come into contact with the catalyst in the reactor and are converted into light olefins. Residence times are very short and the reactor operates in a stable steady-state in the vapor phase at temperatures between 350 and 600 °C, and pressures between 0.1 and 0.3 MPa. In the process, the catalyst is deactivated by coke accumulation, and a part of catalyst is transferred to the fluidized bed regenerator in order to restore its activity.

Oxygenates in the reactor effluent are recovered and recycled. Polymer grade ethylene and propylene can be produced from the reactor effluent by a series of purification steps. The results from an MTO demonstration plant show that the conversion of methanol is 100 %, selectivity to ethylene is above 40 %, and selectivity to propylene is close to 40 %.

5. PROSPECTS

The production of ethylene and propylene is one of the cornerstones of the petrochemical industry and developments in this area are a key to progress in the industry as a whole.

According to reliable forecasts, the world's recoverable conventional oil resources amount to 310 billion tons,²³ while non-conventional oil resources (including extra-heavy oil, oil sands, asphalt and oil shale) total 400-700 billion tons. It is predicted that the output of conventional crude oil will peak in 2030, and by 2060 the production of conventional and non-conventional crude oil will reach 6.54 billion tons. Refineries will face the tough task of upgrading more heavy oils, not only for clean fuels, but also for provision of petrochemical raw materials.

Olefin production technology can be separated into non-catalytic and catalytic processes. Conventional pyrolysis of light hydrocarbons, a non-catalytic process, plays the dominant role in ethylene production and there have been significant advances in reaction selectivity through innovative designs as well as in energy saving. Catalytic processes have been developed in recent decades in an effort to extend the range of possible feedstocks to include heavy hydrocarbons and by-products from refineries and petrochemical streams. Principal issues to consider in the selection of olefin technology for a grass roots plant or a revamped refining-petrochemical complex with expanded capacity are feedstock optimization, by-product slate and markets, capital return, and environmental constraints. Many of these issues are site-specific, especially feedstock supply which varies considerably from region to region. Feedstock preparation for olefin plants mainly involves limited modification of the hydrogen to carbon ratio, either by hydrogen addition or carbon rejection. By virtue of the shortfall in light fraction supply as feedstock, integration of a steam cracker with FCC modified processes such as DCC, CPP or PetroFCC is generally the best choice. Such a combination means making full use of crude by coupling a non-catalytic with a catalytic process.

To comply with current or probable future clean gasoline specifications, the aromatic content as well as the olefin and sulfur content should be strictly limited. In order to increase the isoparaffin content of the gasoline pool, Chen²⁴ has proposed a new clean refinery system with the production and upgrading of light olefins at its heart. He proposed that production of light olefins by catalytic hydrotreating be coupled with high temperature catalytic cracking and upgrading of light olefins based on isomerization, oligomerization and hydration or etherification. All of these processes lead to the manufacture of clean fuels and high quality synthetic lubricants. Catalytic processing for production of light olefins is the key step in the future integration of refining and petrochemicals plants.

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