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Crude oil to chemicals: Light olefins from crude oil

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The possibility to fulfill the increasing market demand and producer's needs processing a cheap and universally available feedstock, such as crude oil, to produce petrochemicals appears to be a very attractive strategy. Indeed, many petrochemicals are produced as side streams during crude oil refining, which primary goal remains transportation fuel production. Availability of some critical feedstocks may then depend on local refining policy. In order to improve flexibility, it has been proposed to directly crack crude oil to produce petrochemicals, in particular light olefins (ethylene, propylene, butenes), using technologies derived from Fluid Catalytic Cracking. This paper attempts to review the main research works done on the topic in the literature in the last five decades, focussing on process as well as catalyst technology, with a special interest for Fluid Catalytic Cracking (FCC) based technology that can be used towards maximizing chemicals from the crude oil, such as : severe cracking conditions, on-purpose additives (from ZSM5 to more exotic, metal doped additives), recycle streams, multiple riser systems.

1. Introduction

Crude oil refineries are generally oriented to the production of transportation fuels (gasoline, diesel and kerosene), with a minor but economically important side production of building blocks for petrochemical industry, mainly light olefins (ethylene, propylene, butenes and butadiene) and BTX. These are the most common petrochemical feedstocks and their markets are expanding.[1] They may be produced as side products of a fuel process (for example benzene from catalytic reforming). Alternatively, they can be produced from a cut with low value as fuel in a dedicated process, for example naphtha in steam crackers.[2] Availability of these petrochemicals is dependent on the refining business. Therefore, it may be sound from the point of view of petrochemical market to produce directly these basic intermediates from a universally available feedstock.

Crude oil makes an ideal candidate, being cheaply available everywhere and compatible with a petrochemical business. While direct steam cracking of crude oil has been attempted, coils coking and limited product flexibility are major issues.[3,4] Still, steam cracking processes with careful oil vaporization have been designed for this purpose[5,6] and ExxonMobil has claimed to build a steam cracker using directly certain crude oils as feed. Several dedicated processes were also developed decades ago to directly crack crude oil using thermal processes with beds of different kind of particles, some of them inspired from fluid catalytic cracking technology, with reactor- regenerator solid circulation.[7,8] Yet they were ethylene oriented, thus working at temperature generally over 700°C, and did not compete well with naphtha steam cracking.

From the point of view of market demand, propylene production is creating new opportunities because:

- Propylene demand is growing faster than ethylene demand.
- Steam crackers have a limited Ethylene to Propylene ratio, usually not greater than 0.6.
- Many steam crackers are switching to cheap ethane, shrinking propylene production.
- On-purpose processes, such as propane dehydrogenation, metathesis, methanol to olefins, have their economics dictated by the feedstock price and availability, therefore limiting their applicability to niche market.

Fluid catalytic cracking (FCC) has been the second major supplier of propylene after steam cracking, and has proven high flexibility in feedstock and product slate. Crude oil cracking in a FCC process may appear as an ideal candidate to fulfill petrochemical producer's needs. Fluid catalytic cracking units usually run on vacuum distillation products namely vacuum gas oil (VGO) and vacuum residue (VR). Also, atmospheric residue (AR) can be used as a feedstock for FCC. In some small refineries it was shown that the FCC could substitute the main distillation unit, separating and converting the heavy part of the crude oil all in once.[9] Problems associated with heavy material or metals in crude oil are readily addressed by Resid FCC (RFCC) technology (which treats, precisely, the heaviest part of the crude). Lighter fractions of the crude, especially the paraffinic naphtha, will crack to a lower extent under traditional FCC conditions.[10] This problem has also been studied by most of the refiners with the aim of increasing propylene (and ethylene) yield in the FCC unit. All the technologies developed to enhance olefin yield in FCC are of high interest for converting crude to petrochemicals. Such a technology may probably be based on a conversion unit which can handle the heavy fractions of the

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crude oil, converting it partially to light olefins and reducing the amount of heavy products to minimum. A modified Fluid Catalytic Cracking process would be an ideal candidate. Others units may also be added to complement the conversion unit, such as steam cracking, to crack cleaner and lighter fractions into light olefins.

This review will then examine, in section 2, the technologies and refining strategies that may be used in a new kind of petrorefinery dedicated to enhance light olefins production from traditional refineries. After considering early thermal cracking intents of cracking crude oil in fluid beds (section 3), we will focus in section 4 on optimized and adapted conventional Fluid Catalytic Cracking technology (process, catalyst, operation) and how it can be used as petrochemicals oriented crude processing unit. Finally, a detailed overview of the commercialized FCC processes dedicated to maximize light olefins is given in section 5.

2. Refining strategy to maximize light olefins from crude oil

Direct processing of crude oil into small olefins was recognized early as an option to decrease costs in the production of ethylene but also, be less dependent from refinery streams (for example naphtha) and general policy towards fuels. The main process to produce petrochemicals is the well-known steam cracking process that may be designed to handle feedstocks from ethane to naphthas or even gas oils. Attempts to process directly crude oil in steam crackers was however not successful due to fouling issues by coke. Thus, a number of processes or strategies have been proposed that suggest conditioning the feed (crude oil) by rejecting the heaviest part and contaminants of crude and upgrading the rest before feeding it to the steam cracker. The rejected part can be used as fuel to bring heat to the process or upgraded in a separate process.

In the process described below in Figure 1-A, a raw separation of the crude oil is performed by partial vaporization at a temperature of 480 to 540°C. The lighter vaporized fraction is then steam cracked under severe conditions (790-840°C, 1450-1550°F), while the heavier part remains liquid in the separation tank. This heavier part, if fed to the steam cracker, would produce significant amounts of coke on the walls of the radiant section (i.e. high temperature coil). A suitable device (distillation, packing, etc) is used to knock out entrained liquid droplets. The liquid droplets are then contacted with steam introduced from the bottom part of the vaporizer at temperatures up to 700°C (1300°F) so that the heavy part of the crude oil can be mildly steam cracked. The coke formed during the process deposits on a packing and can be burned later. Packing may be used to enhance steam / liquid contact and/or distribution of oil across the reactor, and favours vaporization of the heavy crude oil fraction. The liquid falling through the packing finds increasingly hotter steam and increased steam to oil ratio. This favours vaporization, and the heavier parts that are more resistant to vaporization will finally be contacted with vapour at a temperature high enough to (mild) crack the heavier fraction. Lighter products are then vaporized. Steam to oil ratio in the mild cracking section is preferably high. Globally, in the vaporization section, steam to oil ratio is 0.3/1 to 5/1, preferably 1/1. Steam enters the vaporization section at a temperature of 538-704°C (1000-1300°F). Contrary to prior art, where the hydrocarbons are usually passed from preheater to the hotter section as fast as possible, the vaporization reactor can be seen as a trap for the heavier components, which are eliminated through mild cracking, so that only light components with low coking tendency are fed to the radiant, high temperature zone. The non-vaporized material that formed coke on the packing of the vaporization reaction can be burned by conventional steam/air decoking performed during normal furnace decoking cycle. Preheating the crude oil is also performed below 350°C, a temperature notably lower than in traditional steam cracker to avoid fouling, before loading to the vaporization section.

In addition to the packing, a catalyst bed may be disposed at the bottom of the vaporizer to enhance cracking, (Figure 1), helping to remove metals such as Ni, Fe, V and trap non-vaporizable material such as asphaltenes. Materials such as alumina, silica-alumina, molecular sieves, and natural clays may be used. Catalyst may also be supported on random or structured supports (packing). Hydrogen can also be fed to the system in order to reduce coking / fouling.[6] It has been also proposed to assist the mild cracking of the non-vaporized, heavy oil through controlled cavitation of a recycle pump at the bottom of the vaporizer. Implosion of cavitation bubbles provides for additional heat that helps vaporizing the remaining heavy fraction. As the heat is provided locally within the fluid and not trough a hot wall, this minimizes coke formation on the wall. Claims of 97 wt% vaporization of a Sahara blend crude assisted with steam at 704°C were reported.[11] Some yields obtained with an Alaskan crude oil (1.2 CCR, API 39.2, 0.27 wt% Sulphur) are reported in Table 1.[12]

Table 1. Steam cracking yields obtained through assisted crude oil vaporization (Equistar process)[12]

SC temperature	**829°C**	**843°C**
Hydrogen	0.6	0.7
Methane	8.9	9.3
Ethylene	19.3	20.4
Acetylene	0.2	0.3
ethane	2.6	2.4
Propylene	12.2	12.1
Propane	0.7	0.6
Propadiene	0.5	0.5
Butadiene	4.7	4.7
Other C_4	5.7	5.1
C_5^+	44.6	43.9

Some of the non-vaporized heavy liquid may be withdrawn from the process and treated elsewhere.[13] A gas condensate may also be used to dilute the crude oil and facilitate vaporization.[14]

Processing crude oil in steam cracking has been covered in research efforts of many companies.[15] The crude is vaporized in two steps by passing into convection zone of the cracking furnace, then separating vapors from liquids in a flash drum. Liquid droplets in vaporized crude oil, which may contain materials with high coking tendency, have to be carefully removed from the hydrocarbon/steam gas mixture.

Coalescence of these droplets is promoted using an expander or a series of expanders to reduce gas flow and subjecting the gas flow to a centrifugal force.[16] The vaporized fraction is then fed to the steam cracker furnace.

The crude oil then fractionated into naphtha (<220°C AET) then gasoil (220-600°C AET), which are cracked separately under optimized conditions. The non-vaporized residue is withdrawn from the process, avoiding coking issues. Recent announce was made for imminent start of a 1 Mtpy crude oil steam cracking unit at EXXONMOBIL Jurong Island Petrochemical complex in Singapore.

Shell also patented a similar technology.[17] Crude oil steam mixture is preheated to at least 375°C, more preferably 415°C. The preheater wall is maintained wet to inhibit coking. A specially designed vapor/liquid separator that creates a swirl at the upper inlet is used to remove the non-vaporized part from the gas stream. The centrifuge effect created at the upper inlet forces the liquid droplets against the wall of the separator, and liquid further flows downwards in a thin film on the wall. It allows maintaining the gas stream hotter than in conventional flash drum and minimizes coking on the wall.

Saudi Aramco patented a number of configurations to pretreat the crude oil before steam cracking.[18] The crude oil may be hydrotreated and/or solvent-deasphalted in order to produce a highly paraffinic, deasphalted and demetallized stream. Then, the upgraded stream can be further steam-cracked to produce C_2-C_4 olefins and BTX with an acceptable rate of coke formation. Both processes may be carried out under usual operating conditions with known technology, being an advantage of the crude oil to be easier to treat than heavier feeds such as atmospheric resid. Finally, the highly upgraded stream is steam cracked at temperature of 400 to 900°C, 0.3 to 2 steam/oil ratio and 0.05 to 2 seconds residence time.[18c] Depending on crude oil quality, hydroprocessing step may be bypassed.[18a] Deasphalting step may be bypassed too if the heavier part of the crude oil is separated, feeding only the light fraction into hydroprocessing followed by steam cracking.[19] Cut point for the separation can be, for example, 540°C AET, so that the leftover are compatible with residue fuel oil blend. Solvent deasphalting may also be carried out before hydrotreating step.[18b] Heavy Fuel oil from the pyrolysis (steam cracking) step may be blended with the asphalt from DAO.

In the scheme that considers splitting the crude oil at any point before or after pre-treatment, the heavy fraction can then be upgraded in a separate, dedicated process to yield more olefins. This process can be, for example, an FCC.[20] Pyrolytic fuel oil (C_{10}^{+}) from the steam cracker may also be recycled to catalytic cracking. In this particular configuration, catalytic cracker is run in a mode that favour light olefins and aromatics that can be called high severity FCC, as represented in Figure 1-B. Derived from FCC technology, processing temperature is higher, in the 590-620°C range and catalyst circulation in the reactor has been inversed to a downflow, allowing the use of higher catalyst to oil ratio (8 to 20) as well as shorter gas residence time (0.2 to 0.7 second) than conventional risers.[21,22] Different fractions can be fed at different points in the cracking reactor to optimize yields. ZSM-5 (or equivalent) additive amount range is indicated at 30 to 60 wt%, a level far above the traditional blending rate in FCC.

In a similar way, it has been proposed to combine a steam cracking process for the light fraction of a crude oil and a bottoms conversion process, in this case Catalytic Pyrolysis, to maximize the output of petrochemicals, as depicted in Figure 1-C.[23]

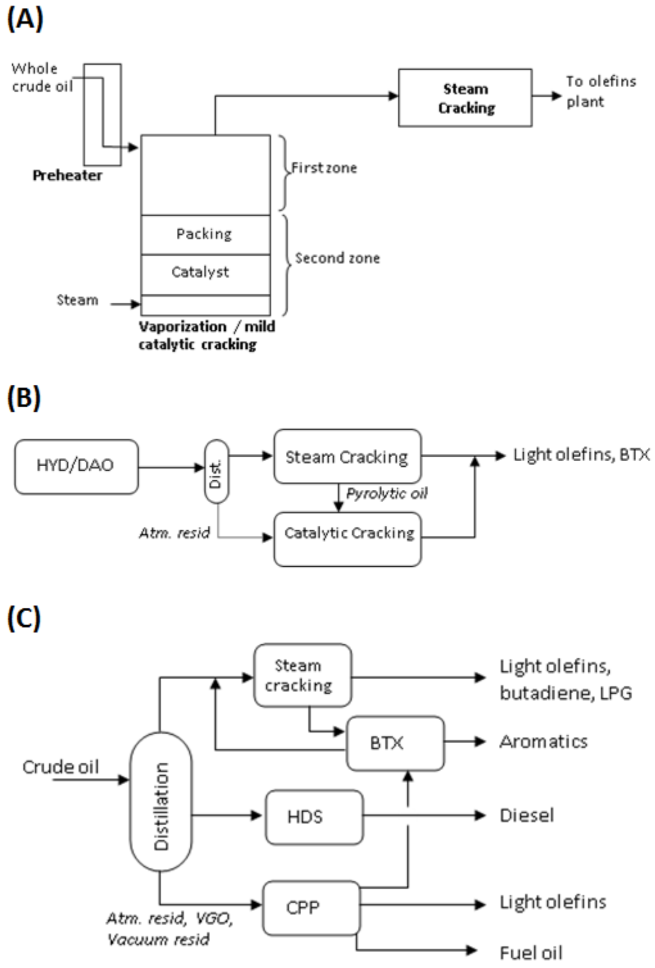

Figure 1. Refining strategies to maximize light olefins from crude oil. (A) Process for steam cracking of crude oil with controlled vaporization.[6] (B) Processing scheme combining pre-treatment of crude, steam cracking and catalytic cracking of the heavy fraction.[21] (C) Steam cracking and bottoms upgrading process combination for petrochemical refinery.[23]

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Table 2: Main processes dedicated to crude oil cracking with circulating solids, operating conditions and ethylene yields. Adapted from Matsunami et Al.[28]

Licensor	**BASF**	**BASF**	**Chiyoda Chemical**	**UBE**	**Lurgi**	**Gulf /S&W**
Process / Bed type	FB, 1 reactor	FB, reactor - regenerator	Fluid bed	Jet flow	Fluid bed	Fluid bed
Crude oil	Minas	Minas	Khafji	Minas	Irak	n/a
Heat supply	Crude Partial combustion	Coke burning	Coke burning	Crude Partial combustion	Coke burning	Coke burning
Particles in bed	Coke	Inorganic oxide	coke	Inorganic oxide	Sand	Coke
Temperature, °C	725	760	850	840	760	750
C_2-C_4 olefins, wt%	41.5	41.5	37.6	47.8	41.6	n/a
Ethylene, wt%	23	25	26.8	28.1	23.1	22.5
Propylene, wt%	12.5	11.2	5.8	11.3	12.8	13.9

Catalytic pyrolysis process will be detailed in the section dedicated to FCC technology. The crude oil may be hydroprocessed upstream to enhance the performance of the complex, as both steam cracker and catalytic converter will perform better towards olefins with more paraffinic feedstocks.

A further development would be processing the whole crude oil directly in a catalytic converter derived from FCC technology, simplifying the processing complex to a single unit. Catalytic cracking offers the possibility to process the crude oil without or with minimal pretreatment (which is a clear advantage of FCC process over steam cracking or hydroprocessing). Indeed, the FCC process has treated for decades the heavier part of the crude oil as main upgrading technology. Conversion of the lighter, paraffinic fraction of the crude oil may nevertheless require substantially different operating conditions than the heavier fraction, so it may be an advantage to split the crude in at least two fractions.[24] This may be combined with the use of specially designed process, for example two downer reactor in parallel with a common regenerator. Radical, one reactor new design was also proposed, taking advantage of the low coking tendency of light crude oils, so that longer catalyst residence time can be afforded as in older, fluid bed FCC units.[25]. A downwards moving bed is used, presenting a large temperature gradient, while oil is injected at the bottom and flows upwards, being cracked at increasing temperatures. Maintaining temperature gradient aims at limited mixing of the catalyst bed, hence the concept of moving bed rather than fluid bed. Separate cracking sections may also be used. Steam is used to carry hydrocarbons through the system and maintain fluidized the catalyst. Temperature profile may be 350-750°C, producing short olefins and C_6-C_8 aromatics in a 2-20 weight ratio.

3. Direct crude processing for olefins in dedicated equipment: an old history

3.1. Former thermal cracking attempts based on fluidized bed of particles.

3.1.1. Overview. Crude oil cannot be directly processed in the steam cracker coils because of coking issues. However, in early 1960's several thermal processes were developed. A number of them use particles (sand or coke) as heat carriers for the process, and presumably as support to remove coke and metals, avoiding fouling. A list of processes with corresponding operating conditions and yields is presented in Table 2. As thermal processes, high temperature were used, generally in the 720-750°C range and up to 850°C in UBE process (still less than in ethane cracker) to produce high amounts of ethylene, from 22 to above 30 wt% together with lower amounts of propylene. This later had a smaller market by then and was less important at that time. A number of other technologies for cracking crude oil with the same purpose using steam as heat carrier or molten salts were also developed and are listed at the end of this section. An excellent review of all these processes was done in early 1980's by Hu.[3] In the sections below a brief description and most relevant details of the processes based on particulate heat carriers are presented.

3.1.2. BASF process.[26] The aim of the process was to produce light olefins and aromatics (BTX) with no residue. The fuel oil and coke generated in the process was eliminated by combustion, providing heat to the process, as in an FCCU. This technology took its roots from the Winkler process for gasification of lignite.

a) Fluidized bed process. In this first implementation, coke particles were used as heat carrier. Heat generation and crude oil cracking were carried out in the same fluidized bed. In the lower part, oxygen was introduced to partially burn the coke. Combustion is a fast reaction, so all oxygen was consumed 1 to 2 meters above the injection grid. In the upper part of the fluid bed, crude oil as well as heavy oil recycled were injected with steam. Some catalytic material may be used in small amounts for controlling emissions, much like in the FCC regenerator. One problem of the process was to maintain the proper amount of coke particles with proper size and shape generated within the process, independently of the crude oil employed. So, careful control of coke combustion was needed. Fluidization ensured good temperature homogeneity in the bed between upper (crude cracking) and lower part (combustion) despite the huge heat requirement. Yields up to 40 wt% of C_2-C_4 olefins were achieved with several crude oils at processing temperatures of 725 to 740°C, with 20-24 wt% of ethylene (Table 3-A). If necessary, coke excess could be recovered, as well as a naphthalene fraction from the light pyrolysis oil. A commercial unit producing 40,000 tpy of ethylene was run for several years in Germany.

b) Fluid Flow process. A second process was developed with a design similar to that of FCC. Instead of coke particles, an inorganic oxide material is used as heat carrier, and this one is in constant circulation between reactor and regenerator vessels. Riser technology was still to be developed, and the necessity of maintaining short gas residence time to avoid recracking led to original reactor design. High gas velocity and a coarse heat carrier (0.3-2mm) were used in a reactor with an unusual height to diameter ratio of less than one. Free space above the bed was minimized. An upper disengaging zone was placed above reactor to minimize particle entrainment and rapidly quench the cracked gas. The coke and soot formed in the cracking process were then burnt in the regenerator, together with the recycled heavy oils, at temperatures above 900°C. Solid recycle rate to crude oil input of 10-15 were reported. Yields were similar to the fluid bed process, with slightly higher ethylene yields due to a higher operating temperature (Table 3-B). While the fluidized bed process was simpler in design (one reactor, no catalyst transfer), it required a larger reactor than fluid flow process. The gaseous products were contaminated with CO and CO_2 from the coke combustion. Also, it yielded more by-products, which may have been used to produce syngas to feed an ammonia plant. By the contrary, the Fluid Flow process could be run at higher temperature, maximizing ethylene yield.

Table 3. Operating conditions and main yields of several crude oils from the BASF Fluid bed process and BASF Fluid Flow Process.[26]

(A) BASF FLUID BED PROCESS

Feedstock	Crude Oil			Heavy Fuel Oil
	Minas	Bahia	Lybian	
Cracking temperature, °C	725	740	740	740
Product yields (wt-%)				
Ethylene	23.0	23.5	20.6	15.3
Propylene	12.5	11.8	11.6	9.3
Butenes + Butadiene	6.0	5.4	4.5	3.8
Ethane	4.5	4.6	4.6	4.7
Pyrolysis light oil	14	14.5	16.6	14.2

(B) BASF FLUID FLOW PROCESS

Feedstock	Crude Oil		Heavy Fuel Oil
	Minas	Lybian	
Cracking temperature, °C	760	760	790
Product yields (wt-%)			
Ethylene	25.0	22.0	30.0
Propylene	11.2	10.5	9.8
Butenes + Butadiene	5.3	5.8	5.1
Ethane	4.3	3.7	2.8
Pyrolysis light oil	17.5	22.5	23.0

Table 4. Yield pattern in KK process with a Kuwait crude, residence time 0.5s and steam/oil ratio of 1.[28]

Feedstock	**Cracking temperature**		
	750ºC	800ºC	850ºC
Product yields (wt-%)			
Methane	11.0	12.8	15.0
Ethane	3.3	2.7	2.0
Ethylene	19.7	24.7	26.8
Propylene	15.2	11.2	5.8
Butenes	4.8	2.7	1.8
Butadiene	5.8	4.9	3.2
Aromatics	15.7	13.0	21.8
Other liquids	12.5	13.3	11.4
Coke	7.4	7.7	8.9

3.1.3. KK process. Research began in 1964 at Tokyo University with a 3cm i.d. reactor, and a system with a fluid bed of coke particles circulating between a reactor and a regenerator was selected.[8] Special feed nozzle was designed to avoid coke deposition, similar in their concept to spray nozzles. Crude oil was preheated at 400ºC, and contact coke particles in a fluid bed reactor maintained at 750-800ºC. The coke particles were regenerated at temperatures close to 1000ºC. The residual oil from the process can be recycled to the regenerator to provide additional heat or burned separately to maintain heat balance. A series of articles details results with several crudes as well as several crude fractions in an attempt to give a guide for process optimization depending on crude oil.[27] Five Japanese companies (Chiyoda, Toyo Soda, Maruzen, Mitsui, Mitsubishi) partnering with Japanese Agency of Industrial Science & Technology developed further the process.[28] Ethylene yields from 22 to 32 wt% were obtained at 800ºC and 1 to 1 steam to oil ratio depending on the crude. More paraffinic crudes tend to give more light olefins. Propylene yields of 7-13 wt% are obtained with crudes at 800ºC, maximum yields are obtained at shortest gas residence time. Yield pattern with a Kuwait crude are summarized in Table 4.

3.1.4. Ube process. Ube also developed at the end of the 1960's a process based on a fluid bed of inorganic oxide (mullite) particles.[29] Previous studies showed that residence time of 0.2-0.3 second and temperatures of 830 to 880ºC were optimal for ethylene production, so a spouted bed design was undertaken. Crude oil was injected from the bottom in the bed of solid, forcing gas circulation through the bed. Gas velocities of 25-35 m/s in the gas jet stream were achieved, while superficial gas velocity within the bed was maintained around 6-7 m/s through fluidization gas (steam plus oxygen) fed through a funnel-shaped gas distributor that supported the solid. Coarse particles were used, 1.5 to 4 mm. Heat for the process was supplied by partial combustion of the crude by oxygen fed from below the solid bed.

Table 5. Yield pattern example, UBE process, at a cracking temperature of 840ºC.[29]

Product yields (wt-%)	
Ethylene	28.1
Propylene	11.3
Butenes + Butadiene	8.4
Pyrolysis gasoline	12.2
Heavy oil	4.4

Cracked gas from the reactor was quenched with water or gasoline. The quencher was a fluid bed of particles above the jet flow reactor, maintained at 350-400ºC. Coke formed on the solid particles in this section was burned in a regenerator at 800-900ºC, cooled down and returned to the quencher. Olefin production cost was estimated 25-30 % cheaper than with naphtha steam cracker. Operating at very high temperatures, ethylene yields and total light olefins close to 30 wt% and 50 wt% respectively, could be obtained (Table 5).

3.1.5. Lurgi Sand cracker. Lurgi designed this process originally for crude oil, although for economic reasons feed was shifted to gasoline (at the time where gasoline was produced in excess by refineries). The sand was used as a heat carrier with a configuration similar to catalytic cracking process. A number of patents are related to the process.[30-32]

After heating at 350-400ºC and mixing with waste heat steam, hydrocarbons were contacted with sand at a temperature of 700-850ºC depending on the feedstock and the desired propylene to ethylene ratio. The fluidized bed was maintained at a narrow range temperature, and gas residence time was set at 0.3-0.5 seconds. Cracked gas was then separated from sand by cyclones, and then cooled to 150ºC. Using feeds heavier than naphtha required some improvements: oil washes were performed in the heat recovery system to minimize fouling, while reactor effluent was quenched with gasoline to minimize secondary reactions that yields more aromatics at the expense of olefins. Sand was fed at a temperature 100-150ºC higher than reactor temperature. The coke from the operation deposited on the sand as a film. Coke, together with recycled heavy fuel from the process was burned in a lift reactor acting as a regenerator. Sand was then stored in a hopper above the main reactor. Due to the very high temperature, all equipment was provided with refractory lining.

Circulation rate of the sand was approximately 20 times the amount of feed in the reactor. Other heat carriers than sand were tested such as corundum, which reduced by one order of magnitude the solid losses, but did not compensate for higher cost of the material. Some tests were carried out with undisclosed catalytic materials. While olefin yields remained nearly unchanged, this stimulated the production of hydrogen and CO. Operation at lower temperature was also conducted to boost propylene production, or dehydrogenate propane to reach high selectivity (80% at 50% conversion per pass). Typical yield pattern with light gasoline (ibp-160ºC) and a crude oil are reported in Table 6.

Table 6. Cracking yields for naphtha and crude oil in Lurgi Sand Cracker.[30]

Feed	Gasoline (40-160)		Iraqui crude	
Trx	750	800	730	760
Product yield, wt%				
Ethylene	25.9	31.6	19.6	23.1
Propylene	15.6	12.5	12.6	12.8
Butenes	6.4	2.6	4.7	2.0
butadiene	3.8	3.7	3.4	3.7
Total olefins	*51.7*	*50.4*	*40.3*	*41.6*
Methane	14.1	15.7	9.6	10.8
Ethane	3.0	2.9	3.1	3.1
Propane	0.4	0.4	0.6	0.3
Butanes	0.5	0.4	0.5	0.2
Total paraffins	*18.0*	*19.4*	*13.8*	*14.4*
$CO_2 + H_2S$	0.3	0.2	0.9	0.4
H_2	0.8	1.0	0.6	0.8
CO	0.2	0.3	0.4	0.3
Acetylene	0.4	0.9	1.3	0.7
Nitrogen	0.2	0.2	0.2	0.2
Total other gases	*1.9*	*2.6*	*3.4*	*2.4*
Gasoline (ibp-200)	20.5	17.6	17.0	16.5
Distillate (>200ºC)	6.9	9.0	20.5	22.1
Coke	1.0	1.0	5.0	3.0

3.1.6. Thermal Regenerative Cracking (Stone & Webster). Gulf and Stone & Webster designed a process with an inert solid similar in size to FCC catalysts circulating between a reactor and a regenerator. It was designed for heavy oils, but may also handle crude oils. In order to maintain very short residence time, that is to say in the order of 0.25 second, a downer design was developed.[33] The solid-gas mixing zone is carefully designed to ensure good mixing, and the design served as a basis for short contact time downer process for catalytic cracking of VGO. The mixture has a velocity of 5-25 m/s, and the reactor length is typically less than 5 times the diameter. Steam to oil ratio of 0.2 to 0.4 is used. Cracking temperatures are above 700°C, and may be as high as 900°C. The stripped, coked solid particles are contacted with a fuel gas from a combustor at 1260°C, raising solid temperature to 950°C in an ascending tube. At that temperature, there is enough heat to initiate the reaction between coke and steam.

Using a paraffinic feed, yields of ethylene of 22.5 wt%, propylene of 13.9 wt% and liquids of 18.6 wt% were reported. While research was discontinued in the 1980's, further development using a catalytic material was carried out in the 90's, and the process was renamed as Quick Contact. Claims of Ethylene and propylene yields of 18-19 wt% were reported.

3.2. Other processes not using particulate materials. A number of other processes were also designed for the processing of crude oil or heavy oils to yield olefins, mainly ethylene, all having special features to tackle coking problem. Some used superheated steam (above 1500°C) for heat transfer or used molten salts to prevent coil walls coking. The following processes can be mentioned:

- Advanced Cracking Reactor, developed by Union Carbide and Kureha Chemical Industry Co. It uses steam heated in a burner at 2000°C as heat transfer medium, cracking temperatures of 910-960°C, very short contact time of 0.02 second and quenching with oil.
- Dow process, using superheated steam generated in a combustor.
- Cracking Oil by Steam and Molten Salts (COSMOS), where the crude oil or heavy oil is cracked in a tubular furnace at temperatures of 800°C or above. Wall coking is prevented by spraying a mixture of $LiCO_2$, Na_2CO_3 and K_2CO_3 in the furnace, forming a wet coating on the wall. This coating acts as a catalyst for coke and pitch steam reforming.
- Paccal cyclic thermal cracking, where atomized oil is sprayed downwards on checker bricks at 1200°C in refractory lined tubular reactors, operating in pairs in a cyclic reaction/regeneration pattern.

3.3. Lessons from early technology. Fluid bed technology allowed obtaining yield patterns similar to that obtained through steam cracking, with a strong ability to cope efficiently with the contaminants present in a crude oil that impedes to feed it directly into a steam cracker. Yet due to the thermal nature of the process, propylene to ethylene ratio was bound to remain low and relatively inflexible, while propylene demand increases faster than ethylene. Also, opportunity (cheap) crude oil tends to be significantly heavier than several decades ago, which implies that the process has to deal properly with a large fraction of heavy material. Introducing a catalyst is the obvious step to take forwards, leaving directly towards fluid catalytic cracking technology.

4. FCC and FCC-related technology for enhancing propylene yields

4.1 Introduction

In the last few decades, a huge attention have been paid by refiners, researchers and catalysts manufacturers to optimize and redesign FCC unit processes and catalyst formulations in order to enhance the yield of light olefins produced via catalytic cracking of heavy hydrocarbons. The two major levers that can be used in this operation, used independently or complementary, are the optimization of the operating conditions of the unit, and the second one to the optimization of the FCC catalyst formulation.

FCC process hardware and operation optimization will be reviewed in section 4.2, with focus on its impact on the yield of light olefins. The different sections will cover: reactor technology (i.e. riser vs. downer reactor), reaction temperature, feed atomization (i.e. pre-vaporization option), contact time, catalyst-to-oil ratio, hydrocarbons partial pressure, naphtha recycle, and the nature of the feed.

The two catalyst options that are concerned when it comes to enhancing light olefin yields in the FCC process are the addition of shape-selective ZSM-5 and the reformulation of the base cracking catalyst composed of Y zeolite and often an active matrix. Both of these methods have their advantages and drawbacks, and may be used synergetically to maximize light olefins yields. The catalytic system may also be tailored according to the process hardware and processed feedstock properties by optimizing the composition of a mixture of different zeolites and/or optimizing the properties of the Y zeolite. When processing heavy feedstocks, the pore size distribution of the matrix plays a crucial role. At short contact time, diffusion of large molecules may be a limit, requiring the use of high accessibility materials. This last also help in product diffusion, limiting hydrogen transfer reactions that otherwise reduces light olefins yield. Finally, the acidity of catalytic materials, as well as their strength and density can be adjusted to maximize light olefins in the product stream. All these issues will be discussed in section 4.3.

4.2. FCC process hardware and operation optimizations for maximum light olefins production

4.2.1. Reactor technology. In conventional FCCU the catalyst particles move in an up-flow reactor or riser, against gravity. Back mixing of solids inside riser reactors results in a wide variation in residence times for the solids, as well as clustering and radial solids segregation. On the contrary, in a down-flow reactor the catalyst and the feed flow downward along with gravity to minimize back-mixing in the reactor and to obtain a narrower distribution of residence time.[22,34]

Because the FCC process involves successive reactions, the desired products such as olefins and gasoline are considered intermediate products. Suppression of back-mixing is the key to achieving maximum yield of these intermediates. A simplified reaction scheme about the competing reactions involved in light olefins production is shown in Figure 2.[35] Mainly the higher (linear) olefins are the reactants, which can be converted to light olefins. However, besides cracking and isomerization, these higher linear olefins can also undergo other reactions, such as hydrogen transfer and aromatization. Therefore, it can be concluded that the maximization of light olefins in the FCC is consistent with the objective of reducing the quantity of aromatics being produced and that the selection of an optimum and relatively short residence time allows the maximization of intermediate products such as gasoline and light olefins. A down-flow reactor would be then the optimal option to maximizing olefins yields.[34]

It has to be taken into account that in a down-flow reactor, there is relatively little conversion in the entrance region since the solids are not held up there as much as they are in a riser.[36] Thus, higher catalyst-to-oil ratio, reaction temperature, and/or catalyst activity will be necessary compensate for lower catalyst holdup and lower catalyst residence time, thus maintaining an adequate conversion level. Fortunately, developments in highly accessible catalyst technologies make it possible to run down-flow systems under conventional FCC conditions without penalty in conversion.[36,37]

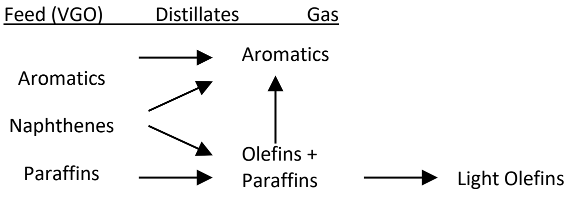

Figure 2. FCC Reaction model: Production of aromatics vs. light olefins.[35]

Table 7. FCC Down-Flow vs Riser comparison at 8.8 % Coke yield.[36]

FCC process	C/O	Propylene	LPG	Bottoms
Riser	7.8	4.8	18.0	11.4
Downflow	8.7	6.6	20.3	13.0

Characteristic improvements in LPG and light olefins yield by FCC down-flow operation compared to up-flow operation are given in Table 7. In addition, down-flow reactors allow working with higher catalyst-to-oil ratios because lifting of the catalyst by vaporized feeds and steam is no longer a limiting issued.[38,39]

4.2.2. Reaction temperature. Higher reaction temperature than in a typical FCC unit would be preferred in order to increase olefins yields. Conventional FCC is typically operated at low to moderate severity (510ºC–530ºC riser outlet temperatures) with flexibility to swing between maximum gasoline and maximum distillate mode. Attempts to operate the FCC unit at higher temperature to produce more light olefins should be economically evaluated as incremental light olefins will come at the expense of secondary cracking of gasoline and in excessive dry gas (C_2 and lighters) yields. In addition, under higher reaction temperatures, thermal cracking of hydrocarbons will begin to compete with catalytic cracking, resulting in increased undesirable products such as dry gas and coke. It is important to have in mind that, in a determined industrial unit, the amount of coke and dry gas that can be handled has a maximum fixed by due to compressor and blower capacity, as well as regenerator mechanical limits. Therefore, for each FCCU and specific market, an optimum reaction temperature will exist that maximizes the economical advantage of shifting production towards olefins at the expense of gasoline yield and increasing coke and dry gas selectivities.[39] Buchanan et al. reported that a temperature increase from 500 to 650ºC only gave light olefins increase equivalent to about 5 wt% of ZSM-5 additive (Table 8).[40] The increase of the reaction temperature to improve light olefins yield in a conventional FCCU is therefore quite limited as a single tool, and should be accompanied by other measures such as controlled short contact time reactor (for instance down-flow reactor) in order to avoid as much as possible thermal cracking and unwanted dry gas formation.[38]

It has been observed that the synergy with the addition of ZSM-5 for boosting light olefins yield was limited. This is apparently due to the depletion of the precursor gasoline-range olefins, on which ZSM5 mainly acts.[40]

Table 8. FCC Operation at higher reactor temperatures.[40]

Process / Yields (wt%)	Dry gas	Gasoline	Propylene
Base case	2.6	45.0	4.2
Higher temperature	3.3	44.2	6.3
ZSM-5 addition	2.6	42.7	5.2

Both methods increase the cracking rate of gasoline olefins relative to the rate of hydrogen transfer, yielding short olefins rather than gasoline-range paraffins.

4.2.3 Proper feed vaporization. In the FCC process, heat transfer occurs when the colder feed contacts the regenerated hot catalyst and is vaporized. The initial contact of the catalyst with the feed has a decisive influence on the conversion and selectivity to desirable products. If vaporization and catalyst contacting are not fast enough, thermal cracking may happen, leading to the formation of by-products, such as coke and fuel gas. Contacting unvaporized feed with the catalyst may also raise coke yield. This is especially true with residue-containing feeds. The positive effect of feed dispersion on conversion is widely recognized.[41] Improvements in the contact between catalyst and feed always aim at promoting a quick vaporization of the feed and an intimate contact with the catalyst in the mixing area, on a timescale of milliseconds.

Almost all the conventional FCC industrial units use some type of device (atomizer) that combines the hydrocarbon feedstock with steam before being injected into the riser reactor. By means of especially designed nozzles, the potential energy of the feed and steam, along with the geometry of the nozzles, cause the feed to disperse into mist size droplets which allow a very fast feed vaporization when contacting with the hot catalyst. In order to improve further the initial contact between feed and catalyst, dedicated feedstock pre-vaporization systems, such as the PREVAP process designed by Petrobras S.A., were developed.[42] In this system, feed is to a large extent vaporized before it makes contact with the hot cracking catalyst from the regenerator vessel. Heat exchange with the catalyst is then no longer necessary to vaporize the feed. As a result, coke deposits on the catalyst surface are reduced, gasoline and light olefins yields are improved, and the unit is allowed to operate under very short contact times (less than 0.5 second). One may visualize the PREVAP concept as follows: the feed is introduced into the riser in a "supercritical" state and instantaneously flashes over the feed nozzle, which acts as a "relief or restriction valve". It is argued that PREVAP will be an important design innovation for maximum light olefins FCC technology aiming at extremely reduced contact times between catalyst and hydrocarbons, thus improving yield slate (Table 9).

Table 9. Yields at 9.0 wt% coke, Pilot riser testing of PREVAP concept.[42]

FCC process	Propylene	LPG	Gasoline	Bottoms
Base case	4.5	16.3	40.3	15.7
with PREVAP	5.2	16.2	43.3	13.8

4.2.4. Residence time. It is well accepted that for the conventional FCCU an optimum operating window of residence time exists in order to maintain at the same time a satisfactory conversion and minimize thermal cracking, undesirable secondary reactions and coke formation. Indeed, if the residence time is too low, the bottoms cracking are negatively affected, whereas long residence time promotes dry gas production. Nevertheless, short residence time of feed and product hydrocarbons should be favourable to minimize secondary reactions and, in particular, bimolecular reactions such as hydrogen transfer which consume olefins and therefore to increase the olefinity of the products and in particular of the LPG and gasoline fractions.[34] As reaction temperature is often increased to boost light olefins yield, residence time tends to be shortened to avoid excessive thermal cracking.

Downer reactors are ideally suited for this, while it may result difficult to lower residence time to sub-second range in riser reactors, as the catalyst has to be pushed upwards. Catalyst backmixing do not help either. Proper downer design of downer reactors needs to ensure adequate mixing of the catalyst and feedstock at the reactor inlet and the fast separation of the catalyst and products at the reactor outlet.[39] Downer reactors also allow working at higher catalyst-to-oil ratios, mitigating at the same time the lower conversion and bottom cracking implied by the use of relatively short residence times. Table 10 gives an example of the impact of the residence time on the dry gas and light olefins production in a conventional FCCU and illustrates the fact that it exists an optimum residence time which is dependent on the feedstock nature and the catalytic system used.[43]

4.2.5. Catalyst-to-oil ratio. Through the heat balance of the unit this value is bound to the reaction temperature, being higher when temperature increases. This factor will then amplify reactor temperature effect in increasing the conversion and maximizing light olefins production.

Working at low residence time as depicted in the former section usually results in lower conversion due to a decrease in bottom cracking. Raising the catalyst to oil ratio will then compensate the lower conversion due to short contact time increasing directly the catalytic cracking contribution.[39] Circulating increased amounts of catalyst in a riser type unit may result problematic as larger amounts of steam may be used, reducing partial pressure and catalyst concentration. By the contrary, downer reactors are much less limited in these aspects.

Table 10. Influence of the FCCU residence time on the yields of dry gas and light olefins.[43]

Residence time (s)	2.5	1.5	0.7
Dry gas (wt%)	4.11	2.78	2.29
Ethylene (wt%)	6.02	6.88	5.96
Propylene (wt%)	19.36	22.30	21.64
Butylene (wt%)	12.56	13.41	14.12

Table 11. Ethylene and propylene yields (in wt%) from heavy oil cracked over different catalytic materials.[34]

	Ethylene	Propylene	C2=/C3=
Quartz (Thermal cracking)	4.74	4.01	1.18
Zeolite catalyst (mainly catalytic cracking)	5.08	8.70	0.58

An additional advantage for the production of light olefins is that the use of high catalyst-to-oil ratios decreases the temperature drop observed during the endothermic cracking reactions and facilitates the proper feed vaporization of the injected feedstock at the inlet of the FCCU reactor.

Finally, the use of high catalyst-to-oil ratios enhances the contribution of catalytic cracking over thermal cracking. Knowing that the thermal cracking favours ethylene production, the use of high catalyst-to-oil ratios favours catalytic cracking reactions and allows to decrease the Ethylene-To-Propylene ratio and to give the flexibility to adjust the light olefins production in function of the market, as shown in Table 11.[34]

4.2.6. Hydrocarbon partial pressure and steam. Lowering the hydrocarbon partial pressure decreases the cracking reaction rate.[44,45] For commercial units working at pressure from 2 to 4 bars, however, conversion may appear little affected by pressure change.[46] This non-linear behaviour reaction was explained by the fact that coking reactions that rely on bimolecular reactions such as hydrogen transfer are more affected by pressure than cracking reactions. As a result, higher pressure results in higher coke-on-catalyst, hence more deactivated catalysts and lower catalyst circulation rate, offsetting the increase of reaction rate. At high conversion of the VGO feed (>90%) it was also observed that the partial pressure had little effect on the conversion as the remaining material is refractory to cracking. Working with high catalyst-to-oil ratio will then appears as offsetting the effect of the lower partial pressure, as the amount of catalytic sites will be always enough to drive the conversion up to the point that only refractory material remains in spite of lower reaction rate of the feed VGO.[44]

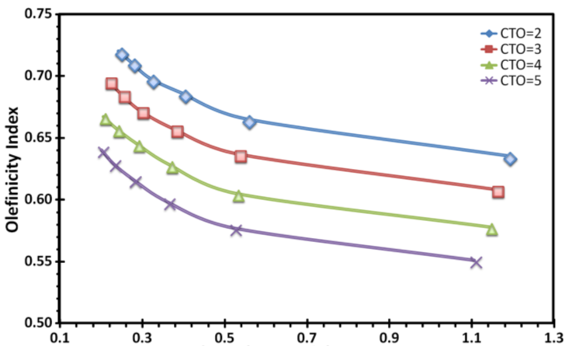

Figure 3. Olefinicity index versus hydrocarbon partial pressure.

Regarding selectivity, it has been observed that the decrease of the hydrocarbon partial pressure in a FCCU favours LPG and in particular light olefins such as propylene and butylenes, whereas propane and butanes selectivity is lowered. This is illustrated in Figure 3, where LPG olefinicity index (defined as the ratio of the total yield of LPG olefins to the total yield of LPG) is found to increase with the decrease of the hydrocarbon partial pressure, whatever the cracking severity represented here by different Catalyst-To-Oil ratios. Increased olefinicity is a direct consequence of hydrogen transfer reactions, which by being bimolecular, are more strongly affected by the change of the hydrocarbon partial pressure than unimolecular cracking reactions that mainly drives conversion.[44,47]

For the same level of conversion, less olefins are converted to paraffins when lowering the partial pressure.

Low hydrocarbon partial pressure may also directly affect residence time in the unit. As a consequence, thermal cracking may be proportionally lowered and dry gas yield decreased, improving selectivity towards more valuable products.

Steam is usually employed in the FCCU for carrying over the catalysts and dispersing the feed. At usual FCC temperature (520ºC) it was found acting essentially as a physical diluent with no noticeable influence on the chemistry of the cracking.[48] In the case of processes such as Steam Catalytic Cracking, working at substantially higher temperature, say above 600ºC, and in the presence of large amounts of steam, a noticeable (and reversible) effect on the reaction rate of small paraffins was found besides the evident hydrothermal deactivation. It was attributed to adsorption competition on the active site of the hydrocarbon with the water, which takes more importance as main cracking mechanism shifts from beta-scission to protolytic cracking at higher temperature.[49]

4.2.7. FCC naphtha recycling. As proposed by many researchers, one possibility to increase light olefins yield in the FCCU would be to reprocess high olefinic FCC naphtha. Using this option, it would be possible to transform the naphtha-range olefins into LPG-range olefins, while at the same time, olefins content of FCC naphtha may be reduced, facilitating downstream upgrading.[10,50,51] The simplest and logical first option for FCC naphtha reprocessing in the FCCU would be to blend it directly to gas oil feed.

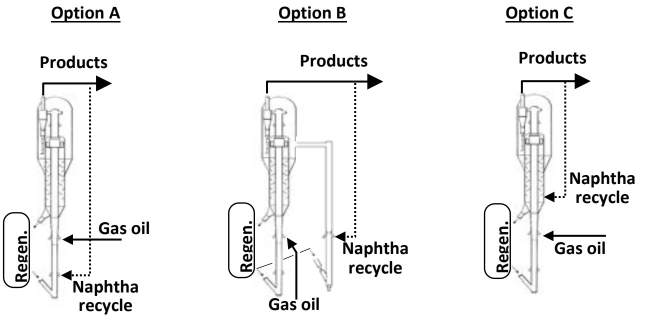

Figure 4. Different schemes for naphtha recycling in the FCC.[52]

Table 12. Impact of the FCC naphtha recycling option on FCC products yields.[52] Projected results at 77wt% conversion. LCN recycle is 21 wt% of gasoil feed rate.

LCN recycle	none	Bottom of the riser	Parallel riser	separator
Yields, wt%				
Dry gas	2.4	4.4	2.8	2.5
LPG	23.6	30.8	28.2	27.3
Propylene	*8.6*	*12.5*	*10.6*	*10.0*
Butenes	*10.6*	*12.9*	*12.2*	*12.5*
Gasoline	47.3	37.7	41.9	43.1
Coke	3.9	4.2	4.4	4.3
Selectivity of LCN cracking				
Olefins LPG		65	67	79
Propylene		40	37	33
Gasoline composition				
Paraffins	33	35	41	40
Olefins	25	12	11	14
Naphthenes	10	9	10	10
Aromatics	32	44	39	37

Nevertheless, it appeared that using this scheme, and even using shape selective catalyst such as ZSM-5 zeolite, only a low conversion is achieved despite the high olefins content of the processed feedstock blend.[10]

This particular behaviour has been attributed to the competitive adsorption of gas oil molecules and particularly polynuclear aromatic products on the catalyst, hindering naphtha conversion. Therefore, other options to effectively crack and recycle FCC naphtha in the FCCU were explored as depicted in Figure 4. Naphtha can be injected at several locations in the riser and stripper of the FCCU, offering a wide range of severity.[53]

FCC naphtha can be fed at the bottom of the riser before the gas oil injection zone (option A) where it may be cracked under higher severity conditions than in classical gas oil cracking; processed in a parallel riser or downer reactor sharing the same stripper and regenerator system than the main riser reactor and where it is possible to optimize the cracking conditions for maximum light olefins production from FCC naphtha (option B); or recycled at the end of the riser reactor or in the catalyst stripper, where it contacts a coked catalyst under mild temperature (option C).

As shown in Table 12, FCC naphtha reprocessing allows increasing light olefins and in particular propylene yields far beyond the values obtained when operating FCCU in a conventional way. Nevertheless, even if it is possible to achieve higher light olefins production through all the different proposed recycling schemes without disturbing to a large extent the coke selectivity and therefore the FCCU heat balance, the maximum light olefins is obtained when feeding the olefinic FCC naphtha at the bottom of the riser reactor (option A). Nevertheless, this option implies at the same time a much higher dry gas yield which can be a problem for the majority of the commercial FCCUs which are limited by compressor capacity.

On the contrary, reprocessing the FCC naphtha in the stripper zone (option C), even if less efficient, significantly increases the LPG olefins yields with the huge advantage to produce only small quantities of additional dry gas and coke yields and to lower in a large extent the olefin content of the cracked naphtha. In addition, the great advantage of option C is that the implementation of this strategy does not require major modifications of the FCCU and therefore a low capital investment compared to options A and B which implies respectively a much higher compressor capability and the revamping of the FCCU to integrate the naphtha dedicated riser or downer reactor.

4.2.8. Feedstock. A major variable for the yield of small olefins is of course the composition of the oil fed to the unit. Hydrogen content is closely related to the maximum achievable yield of olefins in the unit.[53] This value is closely related to the amount of paraffins in the feed, that are mainly the precursors of the distillate range olefins that may further be cracked into small olefins as in Figure 2. Of course maximizing propylene also requires to adequate the process and catalyst system to avoid hydrogen transfer reactions that reduces small olefins yields, otherwise benefits of using highly paraffinic feed are lost. The difference in propylene yield between low hydrogen (more aromatic) and high hydrogen (more paraffinic) feeds tends to widens as propylene yield increases. In order to achieve maximum small olefins yields, it may be of consideration by the refiner to severely hydrotreat the feed to be cracked.

During the past three decades the FCC feed quality tended to be heavier, with an increasing tendency to incorporate resid. Also these feeds tended to be more aromatic, which difficult conversion towards light olefins. It was shown however that the use of resid is not always detrimental to olefins production, if the proper catalytic system is used, with high resistance to deactivation by coke and metals. While resid may contain large aromatic cores, yielding aromatics, it may also contain long aliphatic chains connecting these cores, which can be converted into olefins. Also, higher coke-on-catalyst tends to decrease hydrogen transfer reaction rate.[54] Recently, tight oils also have entered the market and may be very interesting feedstocks for olefins production due to their paraffinic nature.[55]

Beyond traditional, oil based stocks, others stocks may also been interesting. Fischer-Tropsh waxes, produced either from ethane reforming or biomass gasification, would be ideal candidates, being highly paraffinic.[56] There is no impediment in chemistry that ethanol be co-processed with other feeds, yielding ethylene by dehydration. Indeed, that would help reducing hydrocarbon partial pressure of the co-processed oil, but would put pressure on gas compressor if not designed upfront. Hydrotreated pyrolysis oils were found processable in FCC, with limited selectivity to small olefins.[57] Vegetable oils were also proposed as feedstocks, as they possess long (linear) hydrocarbon chain to be cracked towards small olefins. Yet it seemed that propylene yield increase was very limited, being these chains more prone to intra cyclization, yielding gasoline components instead of small paraffins.[58]

4.3. FCC catalyst systems optimizations for maximum light olefins production

4.3.1. About HY zeolite and modified Y zeolites. It is well known and accepted that LPG and gasoline olefins production in a conventional FCC unit is favoured by the use of low hydrogen-transfer activity Y zeolite based catalysts.[59] According to Corma et al., bimolecular hydrogen transfer mechanism implies that an adsorbed carbenium ion takes an hydride ion from a nearby donor molecule to desorb as saturated molecule, while the donor hydrocarbon is further adsorbed as a carbenium ion and may either desorb as a dehydrogenated product, or suffer a β-cracking process to yield an unsaturated molecule and a smaller carbenium ion.[60] The extent of the hydrogen transfer activity of an FCC catalyst is then directly governed by the density of paired acid sites and the affinity for olefin adsorption.[47,61] Therefore, catalyst parameters of the Y zeolite based catalysts, such as for example, rare earth content, unit cell size, zeolitic compound content, matrix content and activity, etc…, which have an influence on the overall acidity and olefin adsorption affinity of the commercial FCC catalyst will have a direct impact on the ability of the catalyst to produce light olefins during FCC operations. It is also important to notice that the extent of the light olefins production during FCC operation is, in all cases, very dependent of the nature of the processed feedstocks, being easier, for instance, to produce C_2-C_4 olefins from gasoline pool range olefins.

The introduction of rare earth (RE) in Y zeolite minimizes the framework dealumination under hydrothermal conditions and, as consequence, increases activity per weight of zeolite and enhances the rate of hydrogen transfer.[62] This improves both the activity and the hydrothermal stability of the catalyst. The degree of dealumination of the zeolitic component in the FCC catalysts has an important impact on the hydrogen transfer: the more dealuminated the zeolite, the less extended the reaction. On average, active sites of rare earth exchanged HY zeolites are weaker and in closer proximity to each other than those found in a more highly dealuminated catalyst characterized by lower unit cell size. As a result of the greater number of active sites, both the primary cracking and primary hydrogen transfer reactions that occur within the zeolite are enhanced. Primary cracking reactions involve the initial scission of the carbon-carbon bond to form higher valued liquid products in the gasoline pool range. Primary hydrogen transfer reactions are those that occur between cracked products to terminate the cracking reactions in the gasoline range, thus, reducing the overcracking of gasoline to C_3's and C_4's (Table 13).[35]

The hydrogen transfer reactions are thus greatly increased with the addition of rare earth to the USY zeolite, stabilizing at the same time the gasoline fraction selectivity. In addition, this reaction also promotes the hydrogenation of olefins, reducing gasoline octane number. Besides that, hydrogen transfer can also promote the formation of carbonaceous deposits on the catalyst and a correlation between coke formation and rare earth exchange was found.

Table 13. Loss in light olefins due to rare earth incorporation.[35]

vol%	Conversion	Gasoline	Propylene
Silica-alumina gel	75.5	47.5	8.5
REHY	85.5	61.0	5.9

Hence, an optimum content of rare earth element in Y zeolite based FCC catalyst should be searched according to the FCC unit production targets and the processed feedstock.[63] The historical trend was towards the use of REUSY catalysts with high rare-earth levels as illustrated in Figure 5, that accompanies the increasing trend in feed contaminants, especially metals.

The recent surge in Rare Earth price led to the development of RE-free catalysts with improved stability and gasoline selectivity, which may be of interest for the production of light olefins in combination with ZSM5. In addition, it has been observed that depending on the type of rare earth cations introduced in the zeolite, different degrees of framework dealumination take place.[64]

Furthermore, a correlation between the decrease in the unit-cell size and the rare earth ionic radius and its coordination to the oxygen framework was observed (Figure 6). According to the Fichtner-Schmittler equation, the smaller the incorporated rare earth cations, the higher will be the dealumination and the smaller the unit-cell size parameter.[65]

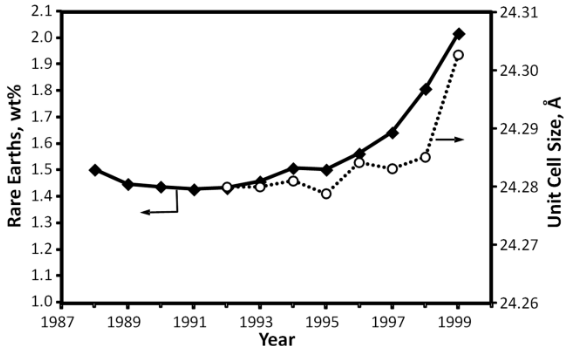

Figure 5. Rare earth content and unit-cell size of equilibrium FCC catalysts.[59]

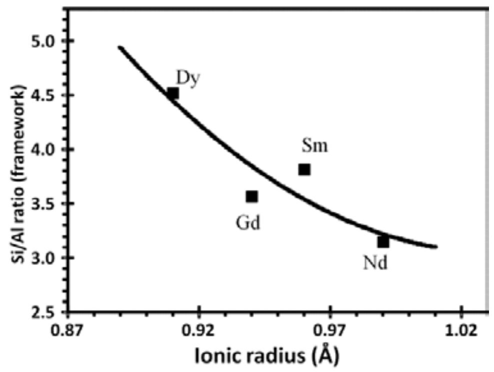

Figure 6. Relationship between the Si/Al ratio (UCS) of the REHY zeolite and the ionic radius of the incorporated rare earth cation.[63]

Therefore, knowing that the higher the FCC catalyst unit-cell size, the more intense the hydrogen transfer, it is clear that the use of low radius rare earth cations to stabilize the HY zeolite is beneficial for the production of light olefins during FCC operations even if the activity and stability of the FCC catalyst will be negatively affected. Y zeolite used in FCC catalyst presents acid sites of Lewis and Brönsted types. The first one is mostly associated to non-framework aluminium species while the last one is related to acidic hydroxyl groups attached to the framework. It is universally recognized that the concentration, strength and distribution of acid sites play a key role in determining the overall activity and selectivity of the Y zeolite during FCC operation.[64] While cracking reactions require the presence of strong acid sites, other reactions such as isomerization, cyclization and hydrogen transfer take place over weaker acid sites. Knowing that the incorporation of rare earth elements in the Y zeolite limits the degree of framework dealumination, the SiO_2/Al_2O_3 ratio is lower and therefore the unit-cell size of REHY is higher than the one of an HY zeolite. It is quite interesting to notice that rare earth exchanged HSY zeolites equilibrate at a unit cell size of about 24.30 to 24.35 Å, while it is generally observed that HSY zeolites equilibrate at a unit cell size of about 24.25 ±0.02 Å.[66] The increase in the number of framework Al atoms in the rare earth exchanged zeolitic compound of the FCC catalyst increases the probability to find paired acid sites which have a lower acidic strength than isolated acid sites (Figure 7) but which are suitable for carrying out isomerization, cyclization and/or hydrogen transfer reactions.

Cyclohexene cracking was used by Suarez et al. to characterize the ratio between isomerization (that requires only one site) and hydrogen transfer (that requires paired acid sites), and found good correlation between this ratio and the ratio of total acid sites over paired acid sites.[67] Below 24.30Å where most aluminium atoms are found isolated, isomerization to hydrogen transfer ratio increased sharply.

In summary, at lower unit cell sizes (below 24.30Å) the activity of the zeolite is low due to the low concentration of active sites and at higher unit cell sizes hydrogen transfer reactions are favoured due to the rapid increase in the number of paired Al atoms. This explain the lower content of light olefins, olefinic compounds in the gasoline pool and the higher coke selectivity when processing gas oil over rare earth exchanged zeolites.[66] In addition to the increasing activity, the incorporation of rare earth elements improve the olefins adsorption capacity of the Y zeolite based catalyst, thus further increasing the rate of hydrogen transfer reactions of rare earth exchanged FCC catalysts.[61]

In addition, it appears that the ionic radius of the rare earth element used to stabilize the Y zeolite has an influence on the impact of the rare earth incorporation over the acidity of the zeolite, being higher the density of the Brönsted acid sites with larger ionic radius of the rare earth atom (Figure 8).[68] Two possibilities are commonly presented: (i) the acidity related of the acid sites is increased due to a polarization carried on by the rare-earth cations and/or (ii) these new acid sites are stronger than those eliminated by ion exchange.

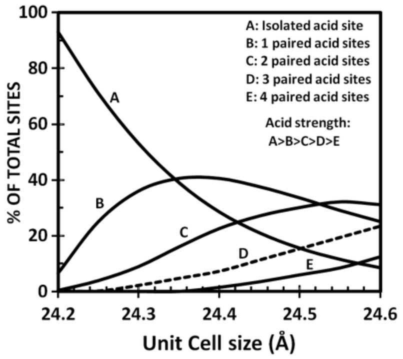

Figure 7. Acid site distribution in Y zeolites as a function of unit cell size.[66]

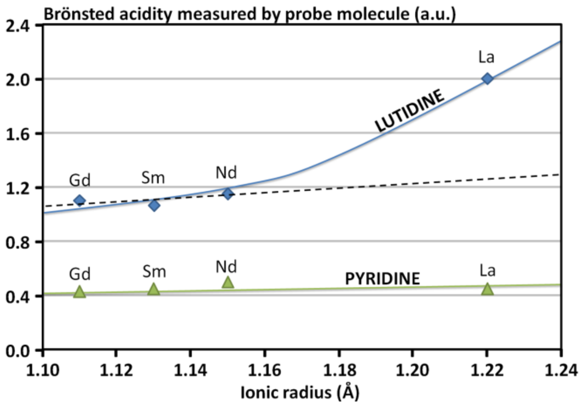

Figure 8. Influence of the ionic radius of the rare earth cation on the Brönsted acidity of the Y zeolite.[68]

As an example, it was found that the Brönsted acid sites of CeHY zeolites are stronger than those of HY and the total number of acid sites decreases with the increasing cerium content.[69]

Finally, another important parameter which can help to tune the Y zeolite based FCC catalyst selectivity through light olefins is the nature of the matrix (i.e. amorphous or active) and the zeolite-to-matrix ratio. Silica and/or alumina based materials are commonly used as binders (or matrices) and provide the dilution of active zeolite crystals, resistance to attrition and large pores for the access of feed molecules to active cracking sites. The binders may be designed to be acidic or non-acidic according to the different requirements. If coke reduction is required, a non-acidic binder like silica gel can be used. On the other hand, an acidic binder is recommended if the FCC catalyst is used for residual feed cracking, since in this case large molecules in the residual feed must be cracked at the surface of matrix to smaller sizes that can diffuse into the pores of the zeolite to be further selectively cracked.[70] It has been repeatedly reported that the use of active matrix allows to increase the gasoline yield and its octane number, the LPG yield and its olefinicity, together with the LCO yield due to the enhance of the bottoms conversions (Table 14). However, the gasoline yield can increase and the coke make can increase due to some non-selective cracking reactions when using active matrices.[71] Other materials were also studied as potential active matrix components: sepiolite (magnesium silicate), amorphous silico-alumino-phosphate (ASAPO) or other mixed oxides such as SiO_2-ZrO_2, or SiO_2-Al_2O_3-MgO of a FCC catalyst and have shown that it is possible to change the overall FCC catalyst selectivity and in particular to increase even more the olefinicity of the LPG pool using new materials as matrices compared to commercial SiO_2–Al_2O_3 based matrices.[72]

In commercial FCC catalysts having active matrices, the overall activity and selectivity is therefore determined by both zeolite and matrix and it is possible to adjust the catalyst activity and selectivity changing the zeolite-to-matrix ratio. The optimum ratio generally depends on feedstock composition, process operating conditions and desired product slate, but the following general trends can be drawn. At high zeolite-to-matrix ratio, the selectivity pattern approaches that of pure zeolite cracking, while at low zeolite-to-matrix ratio the selectivity pattern is dominated by the matrix.

At constant catalyst activity, it is observed that a decrease in zeolite-to-matrix results in an increase of LCO, coke, dry gas yields, and a decrease in bottoms yields. The gasoline octane and olefin/paraffin ratio in LPG also increase under these conditions (Table 15).[64]

Table 14. Typical effect of matrix added to REY zeolite on FCC product selectivity, at 65 wt% conversion.[61]

	active matrix	**Low SA inactive matrix**
Matrix SA (m^2/g)	130	30
Propane	1.4	1.3
Propylene	3.2	2.8
Butanes	6.0	5.7
Butenes	3.5	2.9
$C_3^=$ in C_3 cut	0.70	0.68
$C_4^=$ in C_4 cut	0.37	0.34
Gasoline	43.5	46.5
Coke	6.2	4.5

Table 15. Cracking selectivity trends of different Y zeolites and of active matrix.[64]

	USY	REUSY	REHY	REY	ACTIVE MATRIX
Unit Cell Size	←		Decrease		
Framework Si/Al	←				
RE content	←		Increase		
Dry yield	Low	Low	Low	Low	High
C3/C4 yield	High	Moder.	Moder.	Low	High
C3/C4 olefins	High	Moder.	Moder.	Low	High
Coke/conversion	V. Low	V. Low	Low	Moder.	High
Gasoline selectivity	Moder.	High	High	High	Low
Octane potential	High	Moder.	Low	Low	High
LCO selectivity	Moder.	Moder.	Low	Low	High
DO selectivity	Moder.	Moder.	High	High	Low

Special attention should also be paid on diffusion issues with heavier feeds. Highly accessible catalysts will enhance bottoms cracking as well as diffusion of reaction products outside the catalyst, limiting hydrogen transfer reactions that reduce olefins yields.[73] A catalyst with a high bottoms cracking ability will be a necessity in a short residence time process.[74] The increase in mesopores surface area has been shown to increase resid cracking activity and lower coke yield.

In conclusion, the Y zeolite to be incorporated into a process dedicated to maximize light olefins should minimize as much as possible hydrogen transfer reactions while maintaining a good level of conversion. Rare Earth levels should be kept as low as possible while maintaining a good hydrothermal stability. USY type catalysts will be preferred, with reasonable amount of active matrix to maintain bottoms upgrading capacity. The right amount will depend on the targeted operating conditions, taking into account this will be some kind of high temperature, high catalyst-to-oil ratio operation. Thus, optimum composition may slightly differ than normal FCC operation, and catalysts with lower activity may be preferred as high temperature and CTO will boost catalytic activity.

This poses the problem of proper catalyst testing at the laboratory scale. Fixed bed, Micro Activity Test, in spite of its well documented drawbacks, is still much used due to its simplicity, allowing a fast generation of preliminary performance data.[47,75] It is well known that the long residence time of the catalyst, and the continuous deactivation during the test, tends to magnify hydrogen transfer reactions, yielding more aromatics and less olefins in the products, as well as more coke. This tendency is generally exacerbated with resids. A number of modifications of the original, ASTM-3907 protocol aimed at reducing these drawbacks, and usually features shorter reaction time, higher temperature, dilution of catalyst and feed.[76,77] Catalytic fixed fluid bed (ACE) has emerged in the last years as the competitor of MAT test as standard catalytic cracking test. The main difference is that the catalyst bed is fluidized, which eliminates the formation of temperature and coke profiles along the bed.[78] Nevertheless, the same time averaging effect occurs as with fixed bed. Y catalyst ranking have shown systematic deviations between the two protocols a swell as with pilot plants.[79,80] A number of equipments were designed to offer a more realistic simulation of riser cracking. The Riser Simulator is a fluid bed with gas recirculation working with a gas/catalyst contact time of 2-10 seconds.[81] Micro-riser features a transported bed reactor where very good piston flow was achieved.[82] Residence time could be regulated from very short (50 milliseconds) to several seconds by changing the numbers of coils of the reactor. Microdowner features a downer type transported bed reactor and is also capable to work at very short catalyst residence time (below 0.5s).[83] Injector and stripper design received special attention to ensure good feed dispersion and fast product separation, minimizing secondary reactions. Resids can also be handled. Its downer design allows working with very high catalyst to oil ratio and high reactor temperature, being a very good match for high severity processes simulation.

4.3.2. ZSM-5 zeolite and modified ZSM-5 zeolites. ZSM-5 zeolite ($Na_n{\bullet}Al_nSi_{96n}{\bullet}O_{192}{\bullet}16H_2O$ with $0 < n < 27$) belongs to the high silica pentasil zeolite family and gives, thanks to its intermediate pore size distribution, a preferential cracking selectivity to light olefins (C_2–C_5) in general and to propylene in particular at the expenses mainly of linear and low octane compounds of the gasoline pool. While it was thought initially that these compounds in the gasoline were directly cracked, it appeared rapidly that under the FCC operating conditions, ZSM5 cracked essentially gasoline olefins, converting them into light olefins instead of gasoline-range paraffins through hydrogen transfer reactions on the main cracking catalyst. As a result, the gasoline contained less paraffins and proportionally more aromatics by concentration effect, improving octane number.[84,85] A side consequence is that the amount of small olefins will be limited by the size of the gasoline olefins pools. Thus, as the amount of ZSM5 in the FCCU inventory rises, propylene and small olefins yields rises until a plateau is reached. A few percent of zeolite is generally enough to obtain maximum effect. ZSM-5 based catalysts are generally used in commercial FCCUs as separate particles additive of the Y zeolite FCC base catalyst, adjusting the crystal content of pentasil zeolite in the overall catalytic system according to the feedstock composition, process operating conditions and desired product slate. Optimum additive content was claimed to be around 25 wt% of the inventory, with a ZSM5 content of 10% in additive based on Area measurement data.[86] Above optimum value, no further improvement in olefins yields is obtained and the dilution effect of the base cracking catalyst becomes noticeable, decreasing conversion. The optimal content of additive will depend on ZSM5 content, but also operating conditions. It is expected that a process designed for small olefins will run at high CTO and temperature, thus optimal ZSM5 content may be lower than normal FCC operation. Note that the use of ZSM-5 in units running in distillate mode (low conversion to favour middle distillates), while effective in producing light olefins, may also be prejudicial to middle distillate yields as some paraffins from this fraction may be cracked on the additive, reducing yield and decreasing diesel quality.[87]

As in the case of Y zeolite, an improvement in accessibility of the catalyst will lower the occurrence of secondary reactions such as hydrogen transfer. ZSM5 with nanosized crystals (<100 nm) have shown improved activity, stability and slightly more selectivity to propylene.[88]. Mesoporosity can be introduced by alkaline treatment or secondary templating, improving selectivity to propylene.[89]

ZSM-5 based additives were firstly commercially introduced into the FCC process in the 1980's to improve gasoline octane numbers. Nevertheless, today the additive is principally used with the purpose of increasing C_3–C_5 olefins yields. The efficiency of the ZSM-5 based additives to increase gasoline octane and light olefins selectivity have been repeatedly proved since then.[85,90,91]

The addition of ZSM-5 additive is one of the efficient methods for improving the yield of light olefins because it provides refiners with a high degree of flexibility to optimize the production output. Catalyst producers have developed methods to increase the concentration of the ZSM-5 in their additives in order to avoid dilution effects at high levels of additive. The breakthrough technologies in this area involve the stabilization of the ZSM-5 to hydrothermal deactivation at higher concentrations in the additive.[91] It is generally well accepted in the literature that the light olefins increase which occurs when using hydrothermally deactivated ZSM-5 combined with USY catalysts, is mainly due to the selective monomolecular cracking of gasoline pool olefins previously produced by the USY catalyst.[44,86,92,93]

Skeletal isomerization is energetically favoured with respect to cracking for lower carbon number carbenium ions, while higher carbon number carbenium ions are preferably cracked to C_2–C_5 olefins. Pentenes are simultaneously formed and consumed by ZSM-5 additives. Table 16 and Figure 9 show some examples of changes of product selectivity and in particular of light olefins production which can be expected when adding 10 wt% of ZSM-5 additive to a FCC catalyst and processing different feedstocks.[94]

A complete and detailed review of ZSM-5 based catalyst modifications has been published by Rahimi et Al.[95]

Figure 9. Effect of the incorporation of 10wt% ZSM-5 additive (2.5 wt% of pentasil crystal) to a USY FCC Ecat on light gases yield and olefinicity at a conversion level of 60wt%.[94].

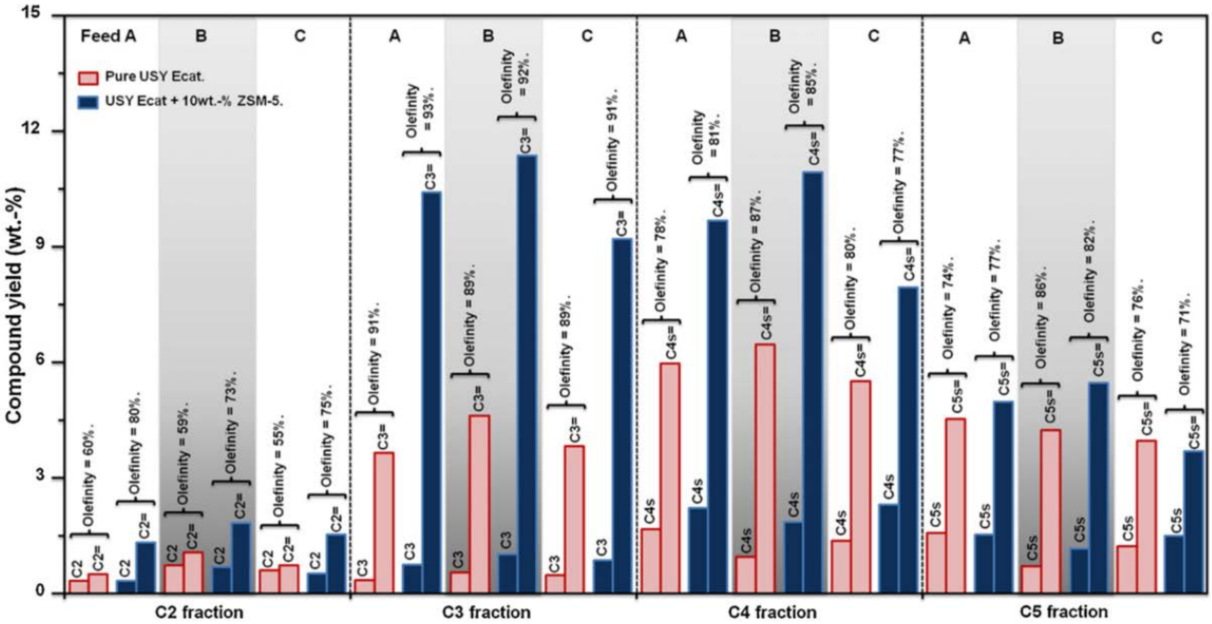

Table 16. Effect of the addition of 10wt% ZSM-5 based additive (2.5 wt% of pentasil crystal) to an equilibrium USY catalyst on product yields at a conversion level of 60wt%.[94]

	Feedstock A		Feedstock B		Feedstock C	
	Base USY	**USY + 10 wt% ZSM-5***	**Base USY**	**USY + 10 wt% ZSM-5***	**Base USY**	**USY + 10 wt% ZSM-5***
Conversion (wt.-%)	60.0	60.0	60.0	60.0	60.0	60.0
Gases yield (wt.-%)	13.0	+12.2	15.2	+13.4	13.4	+9.9
Dry gases (wt.-%)	1.4	+0.7	2.5	+0.8	2.1	+0.6
LPG (wt.-%)	11.6	+11.5	12.7	+12.6	11.3	+9.3
Hydrogen yield (wt.-%)	0.079	-0.015	0.056	-0.012	0.103	-0.024
Hydrogen transfer Index	1.63	+0.56	2.90	+0.88	2.01	+0.09
Propylene/i-butene ratio	1.6	+1.1	1.7	+0.8	1.7	+1.1
i-C4/n-C4 ratio	5.6	-1.3	2.9	-0.7	3.9	+0.4
i-C5/n-C5 ratio	8.4	-1.9	3.9	-1.0	6.0	+0.8
Gasoline yield (wt.-%)	43.8	-12.5	37.9	-11.4	39.1	-10.6
Light gasoline yield (wt.-%)	29.9	-8.7	27.9	-6.9	27.1	-7.8
Heavy gasoline yield (wt.-%)	13.9	-3.8	10.0	-4.5	12.0	-2.8
LCO (wt.-%)	18.0	+5.8	11.1	-2.7	19.3	-2.2
HCO (wt.-%)	22.0	-5.8	28.9	+2.7	20.7	+2.2
Coke yield (wt.-%)	3.2	+0.3	6.9	+1.4	7.5	+0.8

Table 17. Amount of Brönsted (B) and Lewis acid (L) sites for P/HZSM-5 and HZSM-5 zeolite samples at different desorption temperatures.[97]

Zeolite sample	Amount of acid sites (µmol.g^{-1}) (200ºC)				Amount of acid sites (µmol.g^{-1}) (350ºC)			
	B	L	B+L	L/B	B	L	B+L	L/B
HZSM-5	524.4	49.4	574.8	0.09	477.8	28.7	506.5	0.06
0.1P/HZSM-5	501.6	89.7	591.3	0.18	506.3	25.3	531.5	0.05
0.5P/HZSM-5	534.9	52.9	587.8	0.10	477.8	27.6	505.4	0.06
1P/HZSM-5	296.8	43.7	340.5	0.15	255.6	19.5	275.1	0.08

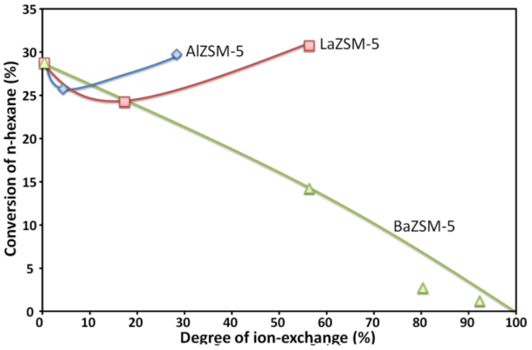

Figure 10. Activity of La, Al and Ba ion-exchanged ZSM-5 zeolites in the n-hexane cracking reaction. [103]

The optimization of the design of the H-ZSM-5 based catalyst for maximization of light alkenes should take into account the balance between the number/strength of acid sites and type/amount of metals incorporated in the modified catalyst and the necessary low coke ability and stability of the modified catalyst. Concerning acidity, it is well accepted that the global acidity of a given zeolite depend to a huge extent on the density and strength distribution of the Brönsted acid sites. The density of the Brönsted acid sites depends of the ion exchange capacity and is therefore directly proportional to the Al^{3+} content of the zeolite and is greatly affected by the Si/Al ratio and the dealumination stability of the material. On the other hand, as shown before, the strength of the Brönsted sites depends on the interaction between the proton and the zeolitic framework. For instance, a completely isolated Al tetrahedron will create the strongest type of Brönsted acid site. Therefore, the two main parameters governing the acid strength of the Brönsted sites are the structural characteristics of the zeolite and its chemical composition. The structural characteristic of the zeolite is related to the proton lability that depends on the angle formed between the two adjacent tetrahedral T at the oxygen carrying the proton.

Regarding the chemical composition factor, the acid strength depends on the number of Al atoms (aluminate tetrahedral) that are adjacent to a silanol (silicate tetrahedron) group.[96] The strength of the Brönsted acid sites can also be affected by isomorphic substitution. For instance, it has been shown that gallium or iron zeolites exhibit dehydrogenation properties and are much less acidic than aluminum zeolites.[97] Moreover Boron-substituted for Si in pentasil ZSM-5 zeolites yield very weak acidity strength.[98,99]

The first usual and most widely used modification method applied for improving HZSM-5 zeolites performance is the incorporation of phosphorus in the zeolite framework.[100] It is thought that phosphorus stabilizes the lattice aluminum ions by retarding aluminum from leaving the zeolite framework and hinders structural changes of zeolite that significantly results in enhancing the hydrothermal stability of the catalyst.[101-105] Therefore, even if the incorporation of phosphorus has a negative impact on the initial acidity of the zeolite, phosphorus modified ZSM-5 zeolite retain a larger fraction of the acidity compared to H-ZSM-5 zeolite when the catalyst undergoes severe hydrothermal conditions.[90] It has been reported that the incorporated phosphorous species are responsible for both the enhanced acid stability and the significantly improved catalytic performance in the cracking of C4 olefin and naphtha light olefin (i.e., ethylene and propylene).[103,104] An increasing propylene and butenes selectivity is also claimed when using phosphorus modified HZSM-5 in the catalytic cracking of n-decane.[105]

Altogether, the modification of HZSM-5 zeolite with phosphorus decreases Brönsted acidity; and/or converts strong Brönsted acid sites of HZSM-5 into weak Brönsted acid sites that increases the density of the weak Brönsted acid sites without changing the overall acid–base properties. Reducing the Brönsted acidity of phosphorous modified HZSM-5 provides a pathway for reaction to occur with enhanced light olefin production.[103,105] Table 17 gives an example of acidity modification when incorporating phosphorus to a HZSM-5 zeolite.

On the other hand, it appears that the incorporation of low electronegative charge-balancing cations such as alkali metals and/or alkali earth metals allows modifying the ZSM-5 acid character by weakening acid strength or reducing acid sites and is even able to make the zeolite basic. It is observed that the quantity of the stronger acid sites reduces with the alkaline earth modification by increasing the ionic radius. Barium as the strongest Lewis base in alkaline earths series resulted in the highest yield of light olefins.[106] Moreover, the base strength of the ZSM-5 catalyst rises with increasing the aluminium content of the framework and reduces with decreasing the ionic radius of the exchanged cation (e.g. Li <Na<K<Rb<Cs). It is also influenced by the exchange of Al and/or Si ions in the zeolite framework for Ga and/or Ge, respectively. It is thought that the modification of ZSM-5 zeolite based catalysts with the elements enhancing the surface basicity decreases the readsorption of the basic compounds of the cracking products, such as ethylene, propylene, and butenes, and this is apparently the major cause

of the lower aromatics and higher light olefins formation. In addition, the alkaline earth metal treatment of HZSM-5 zeolite is able to limit hydrogen transfer reactions and stimulate the dehydrogenative cracking by controlling the HZSM-5 acid character and dehydrogenation activity leading to an improve of light olefins yield.[101,107,108]

Nevertheless, it has been reported that the thermal and hydrothermal stabilities of the alkali-treated ZSM-5 zeolites are slightly deteriorated because of the introduction of mesopores caused by the desilication. Weak alkali solutions dissolve a small amount of silica and alumina, so create mesopores by enlarging the micropores of zeolites, while strong alkali solutions destroy their crystal structure; therefore, convert them to amorphous materials with macropores and extremely small acid sites.[109,110] Figure 10 gives an example of the decrease of the ZSM-5 zeolite activity when incorporating alkali metals and/or alkali earth metals to a HZSM-5 zeolite.

The possibility to incorporate transition metal elements to a HZSM-5 zeolite has been also studied by various authors. Metals are generally associated to detrimental effects in the FCCU (primarily Ni, V, Fe) as they tend to promote dehydrogenation reactions leading to coke, making their use unlikely in heavy feed cracking. Yet it may be of high interest in the case of very low coking feeds such as naphtha, cracked in dedicated processes as described in section 5.2.

Due to their electron configuration, transition metals are able to form chemical bonds with neutral molecules and it has been observed that the incorporation of transition metals creates new Lewis acid sites in HZSM-5 zeolites, leading to an increase of the acid activity of zeolites and influencing directly the selectivity of the catalytic cracking products.

Therefore, the incorporation of transition metal ions into zeolites leads to interesting bifunctional catalysts in which metal and acid centers can act simultaneously.[111] The transition metals, such as Ni, Co, Zn, Cu, Cr, and Mn, introduced into pentasil type zeolites are generally used as active components for hydrogenation or dehydrogenation,[112,113] or aromatization reactions.[114,115] The reported results depict that Co, Cu, Zn, and Ag loaded sites on HZSM-5 zeolites accelerate the dehydrogenation cracking and cyclo-dehydrogenation reactions.[101,107,108]

Altogether, the combination of Lewis sites for the dehydrogenation of the paraffinic feedstock with Brönsted acid sites for the cracking of subsequent higher olefins to light olefins, could enhance the yield of light olefins.[116]

It has been reported that the iron or chrome incorporation in HZSM-5 leads to increasing the selectivity to aromatic hydrocarbon and decreasing the total olefins, because of improving further oligomerization and cyclization reactions.[117,118]

In addition, the use of Cu-exchanged HZSM-5 with an optimum balance between dehydrogenation activity of the metal and acid function of the shape selective HZSM-5 zeolite seems promising to improve the yield of light olefins. Indeed, it has been observed that small amount of copper ions hinders framework dealumination during hydrothermal treatment compared to HZSM-5 or the Ga- and Cr-modified samples. The total number of acid sites of the Cu/HZSM-5 sample seems, at the same time, to be higher than the rest of the metal transition modified ZSM-5 zeolites.[119] Meanwhile, addition of Zn by Chemical Vapor Deposition (CVD) seems to cause a decrease of the Brönsted acidity intensity of ZSM-5 zeolite, without increasing the density of Lewis acid sites, unlike Ga/HZSM-5 catalysts.[120]

Finally, the influence of rare earth modification on the catalytic performance of the ZSM-5 zeolite has not been completely elucidated and is still controversial. Nevertheless, it has been reported that the introduction of a rare earth metal ion into HZSM-5 zeolites could have a great impact on its acidic properties, modifying the density of acid sites and at the same time changing the acid nature (i.e., the Lewis/Brönsted ratio).[121,122] However, if some researchers have observed that the incorporation of lanthanum in HZSM-5 zeolite lowers the number of strong acid sites and increases the number of weak acid sites,[121] other authors claim that the total amount of acid sites of rare earth-modified HZSM-5 zeolites increases and estimate that the amount of weak, strong, and total acid is respectively impacted as follows:[122]

- Sm >Nd>Pr>Eu> Ce > La > HZSM-5 >Gd for weak acidity
- Nd>Eu> La > Sm > Ce >Pr>Gd> HZSM-5; for strong acidity
- Nd> Sm>Eu>Pr> Ce > La > HZSM-5 >Gd for total acidity

On the other hand, the introduction of rare earth elements also modifies the basicity of ZSM-5 zeolites as rare earth oxides usually possess some basic characters. Indeed, considerable changes of the basicity have been observed when loading an increasing amount of La to a HZSM-5 zeolite. It has been therefore suggested that the La-loading of the HZSM-5 zeolite implies a generation of basic sites on the surface of the latter.[101] In addition, as the amount of La loading increases, the olefin adsorption over La/HZSM-5 zeolites decreases.[107] Therefore, the main reason for the higher yield of ethylene and propylene is due to the decrease of the rate of the bimolecular reactions which is negatively affected by the decrease of readsorption of the basic compounds of the cracking products, such as ethylene, propylene, and butenes. Yields of ethylene plus propylene close to 60 wt% at 650°C were reported.[101]

4.3.3. Other additives. Besides Y and ZSM-5, other zeolites present interest in cracking and light olefins production. Stability problems and/or synthesis costs have so far prevented their commercial application. It is long known that zeolite beta improves butenes yields.[123]. Hierarchization through alkaline treatment allowed increasing both diesel and propylene selectivity.[124] ITQ-7, a large pore tridimentional zeolite, also exhibited high gasoline and small olefins selectivity.[125] Zeolite MCM-22, used as an additive, exhibited high selectivity to propylene, but low cracking activity and stability problems.[126] ITQ-21, which has a structure similar to that of zeolite Y, presented excellent cracking activity, yielding more propylene and a gasoline with lower olefinicity.[127]

For the cracking of naphtha rich in small paraffins, which are difficult to crack under typical FCC conditions, specialty catalysts beyond Y and ZSM5 may be used. Petrobras developed special additives based on a mixture of ZSM-5 and ferrierite, which are said to increase propylene yield over traditional ZSM-5 addition.[128] Ferrierite, a small pore zeolite (4-5.5Å pore size) was found to suppress hydrogen transfer and cyclization reactions that lead to higher small paraffins and aromatic yield in products.[129,130] Propane yield was found stable while increasing propylene yield upon ferrierite addition to the catalytic system, while a substantial increase is observed upon addition of ZSM-5. Yet ferrierite has a lower activity than ZSM-5, thus a mixture of the two additives was found optimal. Optimal mixture is claimed as at least 0.5:1 FER:MFI weight ratio. High silica to alumina ratio is preferred, and ratios as high as 200-400 for FER and 600 to 1600 for MFI has been claimed.[131] Traditional stabilization by Phosphorus of pentasil-type catalyst was also claimed.[132]

In processes using very high temperature as well as high amount of steam such as the proposed Steam Catalytic cracking, it was proposed to replace ZSM5 by IM5, which presented a higher activity. As with ZSM5, IM5 hydrothermal resistance could be largely improved by incorporating Phosphorus, leading to a catalyst with improved overall activity, and improved selectivity towards ethylene and aromatics while preserving propylene selectivity.[133]

Table 18. FCC related processes for petrochemicals and related technology.

Process name	Developer/licensor	Trx (°C) (1st riser) (2nd riser if applicable)	C2= yield	C3= yield	Status / Remarks
VGO/resid cracking + Naphtha recycle					
Maxofin	ExxonMobil / KBR	510-540 VGO 550-600 Naphtha	4	18	Naphtha recycle. commercial
Indmax	Indian Oil Co./ABB Lummus	530-600	3-7	17-25	Commercial (1 unit), naphtha recycle optional
Selective Component Cracking (SCC)	ABB Lummus	500-600	n/a	24	Naphtha recycle
PetroFCC	UOP LLC	510-620	6	22	RxCat, naphtha recycle
High Olefins Catalytic Cracking	Petrobras	n/a	3-9	8-14	Downer, naphtha recycle Industrial scale test
Petroriser	Total / Axens	510-540 resid 550-600 Naphtha	>3	>12	R2R implementation 127,000 bpd unit commissioned
TMP (propylene / middle distillate)	China Petrochemical University / Petrochina	500-520 520-540	<4	20	Multiple recycles, Dual risers, 40,000 bpd unit revamp
Middle Distillate and light Olefins selective process (MILOS)	SHELL	500-540 565-620	2-3	10-17	Naphtha recycle in dense bed. Pilot plant studies
High severity VGO / resid cracking					
Deep Catalytic Cracking (I & II)	RIPP-SINOPEC / Stone &Webster	510-575	2-6	14-21	commercial
Catalytic Pyrolysis Process (CPP)	RIPP-SINOPEC / Stone &Webster	560-700	8-19	17-23	Commercial trials
High Severity FCC (HS-FCC)	KFUPM/JCCP/Saudi Aramco / Axens	580-630	2-3	17-25	Downer. 3,000 bpd semi-commercial unit (Japan)
NeXCC	Neste Oy / Fortum	520-650	n/a	16	Multi port cyclones compact design. Pilot studies
Naphtha cracking dedicated process					
Superflex	ExxonMobil / KBR	600-650	20	40	C_4-C_{10} Olefinic feeds, 1 com. operation (SASOL 2006)
Propylene Catalytic Cracking	ExxonMobil	510-630	2-7	6-17	1.5bpd Pilot plant unit Cracked naphtha feed
Advanced Cracking Olefins	ExxonMobil / KBR	650-750	25-30	30-35	Small paraffins feed

Table 19. Benefits and drawbacks of processing options. Adapted from Soni et Al.[134]

PROCESS CHANGE	PROS	CONS
Temperature increase (contact time)	Low-cost route to increased olefins	Excess dry gas/coke make
Cracked Naphtha reprocessing	Product selectivity optimization	Increased dry gas, large loss of gasoline
Spent catalyst recycle	Increased catalyst-to-oil ratio	High circulation rate, poor selectivity

5. Commercial FCC and FCC-related processes designed for maximizing light olefins

Increasing the yield of the valuable light olefins, especially propylene, remains a major challenge for many integrated refineries, not only for economic and environmental reasons but also because an increasing reliance on deep upgrading of crude oil. In this landscape, deep catalytic conversion process, such as FCC, will play an increasing role.

This section reviews the different catalytic cracking technologies that have been significantly investigated and/or commercialized aimed at maximizing petrochemicals (C_2-C_4 olefins and BTX). A list of the processes described below can be found in Table 18. We have segregated processes depending on the philosophy applied for boosting olefins.

First, traditional FCC process is boosted raising reactor temperature and adding (more) ZSM5 to the catalyst inventory, within certain limits as the process flow remains very close to a traditional FCC. Catalyst circulation rate and compressor capacity may be limited, which in turn limit the increase of temperature, usually in the 530-560ºC range. In addition, an additional riser is often added to crack recycled naphtha stream in optimized conditions. This approach requires the minimum investment.

In order to increase further olefins production, dedicated, high temperature high catalyst to oil ratio were developed. They often rely on downer design to reach short time on stream so that extreme temperature (above 600ºC) can be reach while dry gas and coke yields remain under control. Reactor temperature implies Catalyst to Oil ratio in the 15-40 range, significantly above traditional riser designs.

The main problem for optimal naphtha recracking is the need to use the same catalyst than VGO cracking, which implies a higher rate of hydrogen transfer than desirable due to the presence of some form of Y zeolite and matrix as base cracking catalyst for heavy fraction. Hence, some processes were developed based on FCC technology but fed with a range of naphtha instead. Special catalyst formulations are then allowed, such as all ZSM5 or metal-containing materials, allowing higher selectivity to olefins or improved cracking activity for difficult materials such as small paraffins.

5.1. Boosting olefins yields from heavy feeds cracking.

5.1.1. Common features. The heavy feed processes based on VGO/resid cracking aimed at increasing light olefins share a number of features that are reviewed more in details below. Besides feed selection, the most used process modifications implies running the unit at higher severity, re-processing a part of the cracked naphtha and/or partial recycle of coked catalyst. Table 19 summarizes the benefits and drawbacks of such options.[134]

High severity operation relies mainly on higher cracking temperature, which also entails higher catalyst-to-oil ratio. The goal is to over-crack distillates (beyond maximum gasoline mode), producing increased quantities of light olefins. This “brute force” method is the simplest way of increasing light olefins production, but comes with major drawbacks such as an increased production of dry gas that may overload the gas plant (compressor and separator) and higher coke make, especially at higher residence time. Careful control of residence time will help controlling the formation of undesired products. While downers are ideally suited to work at low residence time, enabling high temperature and catalyst to oil ratios, this implies a major revamping of the unit, with uncertain economics in spite of better product slate. Grassroots downers units are more likely to be built.

Re-processing of the olefin-rich cracked naphtha can yield incremental light olefins. Visbreaker or coker naphthas may also be reprocessed. This operation can be carried out in the same or a separated reactor, or even a separate process if a custom catalyst is used. Recycling cracked naphtha will nevertheless entail an increase in dry gas yield and maximal gasoline product loss.

In the partial-catalyst-recycle approach, part of the spent catalyst is recycled back to the reaction section to increase the catalyst to oil ratio, achieving lower mixing temperature (less thermal cracking), and lower hydrogen transfer because of partial catalyst deactivation. Nevertheless, catalyst circulation needs to be increased largely, and selectivity is not always optimal.

Besides these modifications, nearly all design also feature highly efficient atomizing nozzles to improve feed vaporization, as well as riser termination devices and efficient strippers to reduce recraking, minimizing dry gas and coke yield.

In conjunction with appropriate process modifications, optimized catalysts will be used, featuring low hydrogen transfer and high accessibility. The basic catalyst formulation relies on Y zeolite with low Rare Earth, highly accessible matrix to boost bottoms cracking when short contact time are used, together with large amounts of shape-selective ZSM5 catalyst. Beyond basics, proportions of the different components will be adapted to each design.

5.1.2. Cracked naphtha recycles in a parallel riser. Most of the operating companies or licensors that have developed technologies for propylene boosting in FCC have extended their technology into cracked naphtha recycling on the same unit. Most of the processes have converged to the same technological solution, that is cracking the recycled naphtha in a parallel riser to the main VGO cracking riser, in order to be able to crack the recycled naphtha under controlled, usually more severe conditions than VGO cracking. Stripper and regenerator vessels as well as the catalyst are common to the different risers. In some cases, this technology has been applied for simultaneous diesel cut and small olefin yield optimization. Some examples are:

- High Olefins Catalytic cracking developed by Petrobras.
- Maxofin process by UOP.
- Petroriser from Axens.
- TMP from Sinopec.
- MILOS from SHELL.

Parallel risers have been arranged in different ways depending on the base FCC proprietary technology, featuring all the advances already applied by each licensor for cracking VGO at high severity. The fraction most commonly recycled is the light cracked naphtha, in particular the C_5 to C_7 fraction which has the highest content of olefins.

Several papers cite a Petrobras High Olefins FCC process running on naphtha recycle. A downer technology was also developed, with at least a pilot plant in use.[135] A special additive formulation is used, comprising a mixture of ZSM5 and ferrierite zeolites, detailed in section 4.3.3.

An example of Maxofin process operation and yields is compared with FCC in Table 20.[136] While VGO cracking operation is maintained at the same temperature than the traditional process (538ºC), ZSM-5 is added to the catalysts inventory and naphtha is recycled and cracked at 593ºC, catalyst to oil ratio of 25 (riser outlet temperature).

Compared with the base case with ZSM-5, propylene yield is boosted 4 wt%, ethylene and butenes adds another 3 wt%, with gasoline decreasing 17 wt%. The naphtha resulting from this operation is very rich in aromatics, with BTX making up to 60 wt% of C_5-C_{10} naphtha fraction. The Maxofin technology is simply derived from the robust, well known Orthoflow® technology and adapted with dual riser technology. The dual riser operation, sharing a common catalyst, ensures that enough coke will be produced in the process to maintain heat balance.

Besides recycling naphtha from the primary cracking, it has also been proposed to incorporate other streams to the second riser, for example other olefinic streams, such as coker naphtha or C_4 raffinate, increasing further the amount of light olefins produced.

Table 20. Maxofin yield pattern, compared with traditional process. 85-87 wt% conversion.[136]

Operating mode	Max $C_3^=$	Interm.	Max. fuels
Recycle	Yes	No	No
ZSM-5	Yes	Yes	No
Riser Temperature, ºC	538/593	538	538
C_2 minus	7.6	2.3	2.2
Ethylene	4.3	2.0	0.9
Propylene	18.4	14.4	6.2
Butenes	12.9	12.3	7.3
Gasoline	18.8	35.5	49.8
Coke	8.3	6.4	5.9

Paraffinic naphtha may also be fed to Maxofin unit, but will convert to a lesser extend into small olefins due to the low reactivity of small paraffins at temperatures below 650ºC and relatively short contact time.

Petroriser is an adaptation of R2R technology from IFP/S&W with a second riser dedicated to recycling light naphtha.[137] Besides increasing propylene (and ethylene) as well as reducing naphtha, there is a synergy between naphtha recycle and resid cracking, the first acting as a ”chemical” cooler due to the very low coke make during naphtha cracking. Thus, it helps maintaining the heat balance, compensating the high coke from the resid operation. Axens announced that Petroriser™ technology had been licensed in Abu Dhabi (Ruwais refinery) for a very large RFCC unit (127000 bpd), using an atmospheric resid (API 21º, 4-6 CCR). Propylene yields above 12 wt% are expected. TMP process developed by State Key of Heavy Oil processing/Petrochina is another variant of the dual riser operation, aimed at optimizing propylene yield as well as maintaining reasonable distillate quality and reducing olefins in gasoline.[138,139] It builds on a series of previous studies on dual riser/multiple injection points technology for example.[140-142]

Atmospheric resid (AR) is cracked in a first riser, with riser outlet temperature in the range of 500-520ºC. A C_4 fraction may be injected upstream the AR to be cracked at very high temperature and cool down the catalyst before contacting the resid. In a second riser, naphtha is recycled to be cracked and increase olefins yields. Heavy cracked oil may be injected upstream naphtha, in order to crack this recycled feed under more severe conditions and reduce it as much as possible. Second riser outlet temperature is 520-540ºC. Some yields obtained by processing a Daqing AR (d_{20}=900 kg/m^3, CCR 4.5 wt%) are summarized in Table 21. Residence times in both risers are reported to be below 2 seconds.

A naphtha recycle process was also investigated by Shell: Middle Distillate and light olefins Selective process (MILOS). Besides improving light olefins yields, its second objective was also to preserve or improve diesel cut, which is important for European market. The second reactor is not a riser but a dense bed run at 565-620ºC, a temperature high enough to achieve reasonable naphtha conversion.[143-145] The dense bed is fed with fresh catalyst from the regenerator.

Table 21. Product yields obtained in TMP process, industrial test results, MMC-2 catalyst (test 1) and LTB-2/LCC-2 (test 2).[138]

Yield*, wt%	Test 1	Test2
Dry gas	4.6	5.4
LPG	34.5	36.8
of which propylene	19.6	21.3
Gasoline	33.7	28.6
Diesel	13.4	17.4
HCO	3.4	2.7
Coke	9.9	8.7

*0.5 wt% loss

Table 22. Yield comparison between DCC and MILOS process at similar propylene yield.

Yield, wt%	DCC	MILOS
Dry gas	10.3	5.4
C2 minus (excl C2=)	4.9	2.3
Ethylene	5.4	3.1
LPG	36.3	37.6
Propane	3.0	2.1
Propylene	17.0	17.1
Butanes	4.9	5.8
Butylenes	11.4	12.6
Gasoline	29.5	28.2
LCO	10.4	15.8
HCO	5.8	8.0
Coke	6.6	5.0

Spent catalyst from this dense bed is mixed with regenerated catalyst and fed to the primary riser were the main cracking reaction takes place. Heavy oil/unconverted oil may be recycled to the reactor to maximize conversion. Catalyst used for maximum middle distillate mode may have moderate activity and a zeolite/matrix ratio between 1 and 2. ZSM-5 up to 10 wt% may be used to increase propylene yield.

With the appropriate feed and increasing VGO cracking severity, propylene yields of 23 wt% are claimed. Running in middle distillate mode may allow propylene yield as high as 17 wt% as compared with DCC process in Table 22. In both examples the feed has around 12.4 wt% hydrogen.

5.1.3. Naphtha reprocessing in the same riser.

5.1.3.1. Indmax (I-FCC, I-Max). This process was developed by Indian Oil Corporation and licensed by ABB Lummus Technology Inc.[146,147] The range of operating conditions proposed for the process is the typical for maximizing olefins production: a reactor temperature in the 530-600ºC range, allowing a CTO between 12 and 20, a dilution steam of 3 to 50wt% and a regeneration temperature of 650 to 750ºC. Feedstocks are the same as VGO, including residue, to be cracked in a riser type reactor.

In order to boost further the light olefins production, part of the products is recycled to the riser and injected above (downstream) the VGO inlet. Recycle stream can include up to 40 wt-% of the naphtha, the diesel and the unconverted liquid products. In this configuration, LPG olefins yields of 20 to 40% were obtained, with a selectivity up to 80% of olefins in LPG fraction.

The catalyst employed in the Indmax process is claimed to be composed of 1-6 wt% of ultra stable Y-zeolite, 8-25 wt% of pentasil zeolite, 0-8 wt% of bottom selective active material, 0-1 wt% of rear earth's components and 91-60 wt% of non acidic component and binder. A catalyst composition is adapted depending on the nature of the processed feedstock. The Indmax catalyst formulation is also highly tolerant of metals and can operate with high vanadium concentration on the equilibrium catalyst. This ability to accept feeds with high metals level is very important for residue operations.[109]

Table 23. Indmax commercial plant performance data.[134]

Feed	
Feed Composition	Atm. Residue + Delayed Coker Liquids
Feed Density (ATB+CCHGO)	0.9456
Coker Naphtha	0.7164
CCR (ATB+CHGO)	3.75 wt-%
Yield, wt-% (Fresh feed basis)	
Dry gas / Ethylene	7.4 / 3.3
LPG / Propylene	36.3 / 17.2
Gasoline (C_5 – 200ºC)	34.7
Conversion, wt-% (up to 200ºC D86)	86
Gasoline Octane (RON)	99

The first commercial unit to utilize the Indmax process was commissioned in 2003 at the Guwahati Refinery (Assam, India). The plant performance test run data is presented in Table 23. The unit operates on a heavy feed with CCR of 3.75 wt%.

5.1.3.2. Selective Component Cracking, SCC (ABB Lummus).[148,149] The cracked products to be recycled to the process covers a range of materials such as higher carbon number olefins or straight run products from other conversion units. These components are injected separately, downstream from the fresh feed injection point through a set of injectors in the riser reactor system situated at a point where the conditions are ideal for cracking these components due to the high activity as well as the high temperature that the catalyst presents at this point. A unique feature applied in this invention that helps to preserve the yield of light olefins formed in the riser reaction zone is the fact that the cyclone situated at the reactor outlet are operated at a lower pressure than the interior of the vessel in the separation zone. This provides for a complete separation of the reacting hydrocarbons from the catalyst so as to quickly terminate secondary chain reactions. With an adequate paraffinic feed, yields of 24 % propylene were reported (Table 24).[149]

Table 24.FCC Unit Operated in SCC mode : Product Yields[148]

Feed API	**25.9**
Riser Outlet, ºC	**570**
Yields, wt%	Base
Dry gas	7.2
Propane	2.8
Propylene	23.8
Butane+ butenes	20.4
Gasoline	25.5
LCO	9.6
Bottoms	3.2
Coke	7.5

5.1.4. RxCat technology and Petro FCC (UOP). Another innovation by UOP combines the former short time process with the use of RxCat technology. RxCat recycles spent catalyst from the stripper directly to the reactor and mixes with regenerated catalyst. The catalyst mixture is then contacted with hydrocarbons. The catalyst mixture is cooler than regenerated catalyst, so that thermal cracking is lowered when contacting with hydrocarbons. Also, coke on the catalyst will affect primarily the most acidic sites that are more prone to give dry gas products, thus lowering dry gas yield.

The combination with short contact time cracking allowed designing a reactor with two different contact time zones in the same riser reactor: the first one with higher temperature and very short contact time, followed by a second one with cooler reaction temperature and longer contact time.[150-152] Reactions products are extracted between first and second zone. This allows treating two feeds under significantly different reaction conditions: for example a lighter feed with lower reactivity (for example naphtha) in the first zone under more severe conditions, and a second, heavier feed in the second zone under milder conditions.

Two versions were proposed: in the first one, the feed is injected together with regenerated catalyst into a disengaging vessel, where it mixes with recycled spent catalyst. Hydrocarbons products are evacuated from the disengaging vessel through cyclone, while the catalyst mixture is fed to the second, riser-type reaction zone.[151] In the second version, regenerated catalyst and spent catalyst are readily mixed in the bottom Y section of the riser, and the mixture is fed to a riser reactor.[152] In a first injection point a first feed is injected. At a short distance, a separation device allows separating 60-90% of the vapor from this first section as well as part of the catalyst, while the rest of the catalyst and vapor flow their path to the riser reactor. Downstream the separation device, a second feed is injected as shown in Figure 11-A.

This concept then allows producing higher yields of olefins processing for example low boiling range feedstocks fractions (i.e. naphtha for example) in the first zone and heavy boiling hydrocarbons in the riser zone. One limitation is the need to use the same catalyst compositions for each cracking zone.

The composition of the catalyst used in this invention includes amorphous clay type catalysts with a 30% or more ZSM-5 zeolite dispersed in a porous inorganic carrier such as silica, alumina or zirconia. Circulating of a certain amount of inert material may present an advantage, decreasing the average coke-on-solid ratio of the solid entering the regenerator without affecting the solid to oil ratio on the reactor side of the process. Suitable inert solids are any refractory material with low coke production such as alpha alumina, fused alumina and low surface area clays.

The combination of RxCat technology and severe cracking operation conditions in the riser are the basis of the PetroFCC process licensed by UOP.[153] A scheme of the unit is presented in Figure 11-B, where the RxCat mixing vessel is clearly visible. This process gives high yields of propylene, light olefins and aromatics from feedstocks which can include conventional FCC feeds as well as higher boiling or residual feeds.

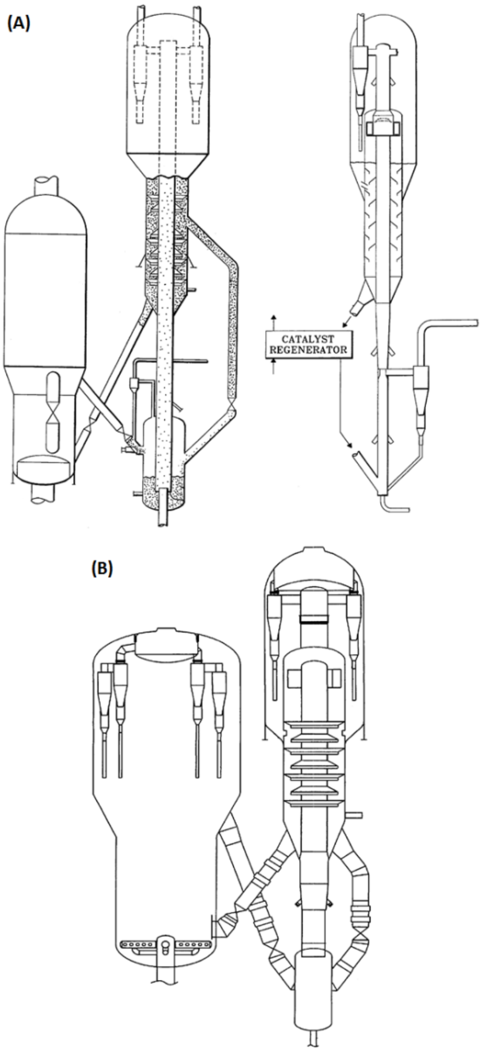

Figure 11. (A) RxCat reactor configurations. Reprinted from Lomas et al.[151,152]. (B) PetroFCC process schematics.[153]

The catalyst used in the petroFCC process has two components: A first component comprising a large pore molecular sieve (X zeolite or Y zeolite) with a limited content of rear-earth elements (≤ 1wt%) and a second component comprising at least 1 wt% of a zeolite with no greater than medium pore size (for instance ZSM-5 or ST-5) (RxCat technology). The high concentration of medium or smaller pore zeolite in the second component of the catalyst composition improves selectivity to light olefins by further cracking the lighter naphtha range molecules.

But at the same time, the resulting smaller concentration of the first catalyst composition still exhibits sufficient activity to maintain conversion of the heavier feed molecules to a reasonably high level. Regenerated catalyst is blended with coked catalyst, with a ratio of the coked to the regenerated catalyst in a range of 0.3 to 3.0 weight bases, to make the blended catalyst which is introduced in the riser reactor. The blended catalyst composition will contain at least 0.1 wt% coke before contacting the feed.

Table 25. Yield patterns of traditional FCC and PetroFCC units. Adapted fron Xiequing et Al.[23]

Component, wt%	FCC	PetroRiser
H_2S, 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
Gasoline	53.5	28.0
LCO	14.0	9.5
Bottoms	7.0	5.0
Coke	5.0	5.5

The recycling of the coked catalyst along with regenerated catalyst allows increasing the catalyst to feed ratio within the riser, avoiding the heat balance limitations of a conventional FCCU. UOP claims that blends of coked and regenerated catalyst (up to 50 wt%) have comparable activity to that of regenerated catalyst.[152]

Moreover, authors argue that recycling coked catalyst including large pore zeolite and/or an active amorphous material and a zeolite with no greater than medium average pore size and blending it with regenerated catalyst improve the yield of light olefins and the overall conversion. Additionally, according to them, the lower temperature of the catalyst resulting from blending hot regenerated catalyst on cooler recycled catalyst improves olefins selectivity.

Operation conditions of 510-620°C of temperature reaction, catalyst to oil ratios of at least 10 weight bases and preferably between 15 to 25 g/g, steam diluents rate between 10 to 55 wt% minimizing the hydrocarbon partial pressure and contact times no greater than 2 seconds in a riser type reactor are typically used to carry out reactions in the PetroFCC process and maximizing the olefins yield and selectivity. Yields patterns from traditional FCC unit and a PetroFCC unit are compared in Table 25.

5.2. High severity, dedicated process for light olefins from heavy feeds

5.2.1. Deep Catalytic Cracking, DCC. The Deep Catalytic Cracking process appeared in the 1990’s and is licensed by Sinopec, Research Institute of Petroleum Processing and Stone &Webster. It uses a design very close to a standard FCC unit but is run at more severe operating conditions in order to optimize light olefins production.[154,155] Still, operating conditions remains far less severe than those found in steam cracking (SC). DCC can handle the same feeds as an FCC, but paraffinic feeds are preferred as it improves olefins yields. It features higher temperature (30 to 50°C), higher catalyst to oil ratio (1.5 to 2 times), lower hydrocarbon partial pressure (higher steam to oil ratio) and longer contact time to enhance olefins yields and bottoms cracking. A riser followed by a fluid bed is used to obtain longer residence time. As a result, dry gas yield and coke are largely increased, leading to adjustments in stabilizer, main fractionator and compressor capacity.

Yields of up to 15 wt% propylene and 15 wt% butylenes were claimed using reactor temperature in the 500-650°C range, catalyst to oil ratio in the 2-12 w/w range, steam to feedstock ratio of 0.01-2 by weight, WHSV in the range of 0.2 to $20h^{-1}$ and a reaction pressure from 1.5 to 3 bar in a fluidized or dense phase transfer reactor. Further patents were taken on optimized conditions to enhance further the production of light olefins, as well as high octane gasoline.[156,157]

Two types of DCC operating modes are usually presented in the literature depending on the product slate desired. DCC Type I is focused on propylene maximization and is carried out at higher severity reaction conditions while DCC Type II works at lower severity operation conditions with the aim of increasing iso-olefins yields. Process yields for each DCC type are compared in Table 26 with conventional FCC yields and typical steam cracking yields obtained with a light gasoil.[35,158,2] Reactor temperatures in DCC modes are substantially higher than in FCC, but remain largely below that of Steam Cracking (SC). Steam usage is also higher than for FCC, but, again, remains considerably lower than for SC. DCC catalyst circulation rates are higher than FCC operations.

While paraffinic VGO feedstocks gives the highest propylene and isobutylene yields, naphthenic and aromatic feeds can also be processed, albeit a lower olefins yield due to the lower hydrogen content of the feed.[110]

The optimal conditions for olefins production imply an increase in dry gases yield meanwhile gasoline yield is reduced. This new yield product distribution will be economically affordable depending on the marked demand.

First patents claimed the use of acidic solid catalyst, formed by USY zeolite, a pentasil zeolite or a mixture of them supported on Kaolinite.[159] Pentasil-type materials are abundantly used to promote propylene yield, while Y zeolite content was lowered as high temperature and residence time increases activity.

Table 26. DCC types I and II, FCC and SC operating conditions comparison and typical DCC vs FCC product slate and yield structure.[158,2].

	Type I	Type II	FCC	SC[a]
T (ºC)	530-575	505-555	500-550	750-870
Cat/oil (w/w)	8-15	7-12	5-10	-
Steam (feed wt%)	20-30	10-15	1-6	30-80
Type of cracking	Riser & bed	Riser	Riser	Batch
Typical Yields, wt%				
Dry gases	11.9	5.6	3.5	28.8
LPG	42.2	34.5	17.6	27.3
Ethylene	*6.1*	*2.3*	*0.8*	*19.4*
Propylene	*21.0*	*14.3*	*4.9*	*13.9*
Butylenes	*14.3*	*14.7*	*8.1*	*7.0*
Gasoline	26.6	39.0	54.8	18.9
Diesel	6.6	9.8	10.2	25
HCO	6.1	5.8	9.3	
Coke	6.0	4.3	4.3	-

[a]typical yields from a Vacuum Distillate, low severity Steam Cracking

Each mode of operation may use an optimized catalyst. Formulation may contain varying amounts of high silica zeolite having pentasil type structure and Y zeolite. The catalyst named CRP-1 was developed for use in the DCC maximum propylene operation and presents a relatively low activity to ensure high olefin selectivity, while CS-1 and CZ-1 were developed to produce high isobutylene and isoamylene selectivity as well as propylene selectivity.[154] All these catalysts can be modified/stabilized using well known FCC techniques such as adding Rare Earth and/or phosphorus, incorporate a high matrix activity for the primary cracking of the heavy hydrocarbons, a modified mesoporous pentasil zeolite to enhance the secondary cracking of gasoline.[160,161] These modifications are aimed at improving skeletal isomerization activity, lowering hydrogen transfer, maintaining coke selectivity and hydrothermal stability as well as high metal tolerance.

In order to increase further the yield of light olefins, a segregated feed pattern was implemented.[162] A first cracking reaction is operated at relatively high weight hourly space velocity (higher than 50 h^{-1}), to convert approximately 35 to 60 wt% of the hydrocarbons feedstock at a temperature between 500 to 730°C. A second cracking zone is operated at relatively low weight hourly space velocity (less than 30h^{-1}) to complete conversion, at a temperature between 480 to 680°C and a dilution steam of 20 wt% based on the weight of the feedstock. The riser features a first narrower and a second wider reactor section. Regeneration is carried out in two steps. In a first step, 40 to 80 % of the coke deposited on catalyst is burned, while the remaining is burned at temperatures above 700°C, to achieve complete removal of the carbon with excess oxygen. This configuration was claimed to produce more propylene and butenes, and less ethylene.

DCC process can be integrated with other units to improve further olefins yields or change olefins distribution. Steam cracking may be used to crack efficiently small paraffins recycled from DCC output.[23,163] As well, integration with a disproportion unit would allows increasing propylene yield at the expense of ethylene and butenes. With a DCC unit producing 42-48 wt% of C_2-C_4 olefins, it was proposed to flexibilize propylene output from the complex between 17 and 33 wt%.

5.2.2. Catalytic Pyrolysis Process, CPP (Sinopec/RIPP/S&W).

CPP process was thought as an extension of DCC process with the aim of increasing ethylene yield while maintaining reasonable propylene yield.[158] It basically relies on increasing the treatment temperature well above traditional FCC process that is in the range of 560 to 700°C. As a consequence, catalyst to oil ratio will increase since regenerator temperature is usually maintained in a temperature range of 700 to 750°C. For the highest temperature to be achievable, regenerator temperature will tend to drift to the upper end of the temperature range. While a 640°C operation may be carried out with regenerator at 730°C, a 680°C cracking temperature may need regenerator temperature as high as 760°C. It can be implemented by revamping idle RFFC plants or DCC plants. Post-riser quench is implemented to limit the extension of thermal cracking due to a significantly higher reaction temperature than in FCC or RFCC. First commercial implementation was performed in 2001.[23]

An example of operating conditions and resulting yields is given in Table 27-A. The treated VGOs have a content of hydrogen of 12.8 wt%, which corresponds to an H/C ratio of approximately 1.76, close to that of paraffins.

Increasing temperature from 580 to 640°C, the propylene to ethylene ratio could be shifted from 2.25 to 0.9. In this example, and probably due to larger residence time, maximum propylene production was observed at 580°C, while ethylene yield increased continuously with temperature. Residence time was not reported but the space velocities mentioned are in the range of 60-90 seconds, and seems that a fluidized bed, not riser cracking, is used for this operation. Gas residence time is not reported.

Laboratory results conducted on a fixed fluidized bed and rather short gas residence time (1-4 seconds) showed that propylene yield pass through a maximum in the range of 630-660°C, independently of the feed used, while ethylene yield increased continuously with temperature.[164-166] Residence time, catalyst to oil ratio and temperature were varied to shift product yield, although temperature changes had the largest effects (Table 28).

Table 27. Yields for different CPP operating conditions (A) and feedstocks (B).[23]

(A)	**Operating mode**			
	1	2	3	
Riser Outlet, °C	576	610	640	X
Regenerator, °C	720	725	760	X
Catalyst to oil ratio	14.5	16.9	21.1	X
Steam to oil ratio	0.30	0.37	0.51	X
Yields, wt%*				
Dry gas	17.6	26.3	37.1	X
LPG	43.7	36.6	28.5	X
Gasoline	17.8	17.6	14.8	X
LCO+HCO	11.8	9.0	7.9	X
Coke	8.4	9.7	10.7	X
Olefins yield, wt%				
Ethylene	9.8	13.7	20.4	X
Propylene	24.6	21.5	18.2	X
Butenes	13.2	11.3	7.5	X
(B)	**Feed**			
	VGO	AR	AR	VR
H/C mol ratio	1.89	1.82	1.79	1.76
Aromatic Carbon, wt%	6.8	10.9	13.0	13.8
Yields, wt%*				
Dry gas	26.3	24.1	28.2	27.4
LPG	41.7	42.2	37.1	35.2
Gasoline	16.3	16.9	14.9	16.5
LCO+HCO	4.5	5.1	5.4	6.2
Coke	11.2	11.18	14.3	14.8
Olefins yield, wt%				
Ethylene	13.5	13.8	12.2	12.1
Propylene	22.6	22.6	19.3	19.9
Butenes	11.9	10.7	10.4	8.4

Table 28. Yield pattern depending on process temperature, laboratory fixed bed.[164]

Reaction temperature (ºC) Yields, wt%*	600	620	640	660	680	700	716
Dry gas	12.8	16.1	19.6	23.1	27.7	32.4	35.6
LPG	45.7	46.6	45.8	43.2	39.3	33.9	30.1
Gasoline	24.2	20.0	18.3	16.9	15.1	15.5	14.1
LCO+HCO	8.3	7.9	6.7	6.1	6.3	6.2	5.7
Coke	9.0	9.5	9.6	10.8	11.6	12.0	14.4
Olefins yield, wt%							
Ethylene	8.7	10.8	12.4	13.8	15.6	17.3	18.3
Propylene	18.2	21.3	22.5	22.6	22.1	19.9	18.0
Butenes	10.8	11.2	11.2	10.7	9.7	8.2	6.8

The feedstock is the second largest influence on yields. Increasing aromatics content of the feed, measured by the weight percentage of hydrogen in fed or KUOP factor, will decrease small olefins yields. The feed tested had an H/C molar ratio between 1.76 and 1.89, which corresponds to hydrogen content in the feed between 12.8 and 13.6 wt%. Increasing steam to oil ratio from 0.3 to 1.6 was also reported as very beneficial, increasing small olefins yield (Table 27-B).

Also, the increase of conversion with increased steam to oil ratio (i.e. decreasing oil partial pressure) was explained by lower catalyst deactivation, although coke yield barely changed with steam to oil ratio (decreasing only 10 wt% at higher steam to oil ratio). The presence of a significant amount of aromatic rings, and especially dealkylated aromatic rings, may be the source of a significant deactivation that get lowered (diluted) with increasing steam.

While thermal cracking contribution is often obviated in fluid catalytic cracking (but for dry gas yield), its contribution may become significant in light olefins production owing the much higher processing temperatures. It was shown that thermal pyrolysis could reach yields of light olefins close to those of catalytic cracking when temperature reached 700^{o}C (Figure 12). Nevertheless, olefins distribution is much displaced toward ethylene, in thermal cracking, yielding lower P/E ratio, generally below 1.

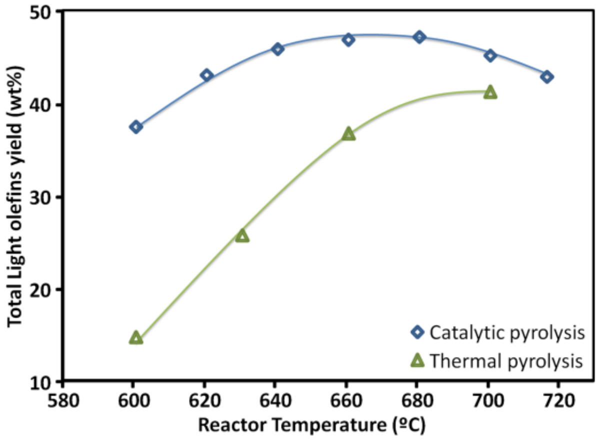

Figure 12. Light olefin yield with or without catalyst, against process temperature.[167]

Recycling of distillate streams such as naphtha and diesel is a common technique to increase light olefins yields. Nevertheless, in the case of Catalytic Pyrolysis, it showed little effects.[167,168] These streams are already largely aromatics, with little paraffin remaining. The source for small olefins is then mostly alkyl groups on aromatics, yielding around 10 wt% light olefins and increasing selectivity towards rings or ring systems with little alkyl groups (BTX, naphthalenes, phenanthrenes, etc…).

A large number of catalyst acronyms have been used by RIPP/Sinopec, yet formulation is rarely disclosed. As for any catalyst system aimed at maximizing light olefins, the matrix and first cracking component (for example Y zeolite) will be tailored with easily accessible pore system to enhance the conversion of large molecules with rapid diffusion of intermediate products, that are further cracked into small olefins on the second cracking component. Desirable properties of the second cracking component, based on ZSM-5 type structure, are enhanced hydrothermal stability, and high acidity and/or some dehydrogenation ability to promote small paraffin cracking into olefins.

Hydrothermal resistance of the zeolitic components may be stabilized by phosphorus (MFI) and La (FAU) as detailed in section 4.3.

A preparation of ZSM-5 structure incorporating rare earth ions, based on 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 a MFI type zeolite, was also claimed to give enhanced hydrothermal stability.[160] Resulting material, further modified under hydrothermal conditions, was denoted as ZRP. Phosphorus incorporation during synthesis resulted in the development of CEP-1 catalyst.[23]

Treatment with alkaline ions was found to enhance further the selectivity to ethylene by modifying acid site distribution and strength (PMZ materials).

Metals were also added to increase even further selectivity to small olefins. Phosphorus exchanged ZSM-5 was further impregnated with Mg and Ni, Zn or Cu and yielded more propylene and ethylene (and slightly more coke) at the expense of other components. Total C_2-C_4 olefins increased from 48 to 53 wt%.[169] Claimed compositions for the modified ZSM-5 were SiO_2/Al_2O_3 ratio between 15 and 60, 2-8 wt% P, 0.5-3 wt% alkaline earth (Mg or Ca), 0.5 to 3 wt% metal (Cr, Fe, Co, Ni, Cu, Zn), all based on corresponding oxide weight. Zn-bearing ZSM-5 was found most active, followed by Ni. Coke production was slightly higher with Ni. Silver-promoted ZSM-5 was also said to promote ethylene and propylene yields in thermal cracking of Gasoil at 650ºC.[23] An early patent from Pop et Al also reported enhanced activity and selectivity for Cu, Ag, Co-exchanged mordenite.[170] Cracking of a C_9-C_{14} paraffin cut was performed with high steam to hydrocarbon ratio (2 to 3), yielding 67 wt% C_2-C_4 olefins at 725ºC.

CEP catalyst is often compared with LCM materials, which are claimed as oxide based material designed for Heavy Oil cracking (HCC process). It is based on silica-alumina, which may be doped with alkaline or alkaline earth or transition metal oxides. It may also carry some molecular sieve catalyst.[171]

Several models of increasing complexity with detailed light olefins composition were developed for heavy oil cracking pyrolysis and fitted from laboratory results.[172-174] Deactivation was modelled by an exponential of time or coke on catalyst, with largely different values. Deactivation was found to be small by Liu et Al., but significant by Meng. Differences in catalyst type and process temperature may have explained the divergent findings. Thermal and catalytic contributions were not separated, so that intermediate activation energies were found, in the 100-200 kJ/mol range. Dry gas and ethylene formation presented higher activation energies probably because of a significant thermal contribution.

The CPP process may be used in combination with steam cracker (SC, on the lighter fraction of the feed) to yield maximum short olefins from full cut crude oil, as detailed in section 2. Paraffins yield much better results than naphthenes or aromatics (aromatics rings will hardly crack) so that paraffinic crudes are much preferred for increasing small olefins yields. Hydrotreatment of non-paraffinic crudes may be carried out, but this brings a number of problems related to metals and CCR in the crude oil. Naphthas from steam cracking or CPP are also very rich in BTX. Economic evaluation showed that CPP plants integrated with steam crackers will have a very fast payout.[23]

5.2.3. NEXCC process. The process concept was developed by Fortum Oil and Gas Oy (Neste Oy), and aimed primarily at producing light olefins.[175] It features both circulating bed for reactor and regenerator, allowing to reduce the catalyst inventory in the unit while maintaining the same throughput. It was designed to handle a large variety of feeds (LGO, HGO, VGO or Naphtha) to be cracked under relatively short residence time range (0.1 to 3 seconds). In order to take full advantage of short contact time, higher reaction temperature and catalyst to oil ratio are expected in this type of unit compared to traditional FCC process.

Spent catalyst can also be recycled to the reactor to increase the catalyst to oil ratio in the same way as PetroFCC design does. The use of baffled separation devices for both reactor and regenerator circulating beds allowed to design a very compact unit as shown in Figure 13, reducing catalyst inventory and improving heat transfer efficiency.[176,177]

Table 29. NExCC yield shifts compared to typical FCC, in wt%. Adapted from Ruottu et Al.[176]

	FCC	**NEXCC pilot plant**
Dry gases	Base	+1.6
Propylene	Base	+5.0
i-Butane	Base	-0.8
i-Butene	Base	+2.3
C_4 alkanes	Base	-1.3
C_4 olefins	Base	+4.9
total LPG	Base	+8.4
Gasoline	Base	-10.0
LCO + HCO	Base	0.0

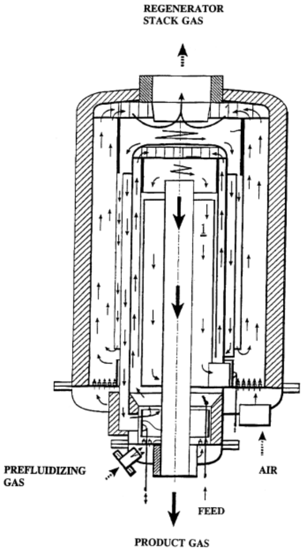

Figure 13. A simplified schema of the NEXCC process reaction system.[175]

It also permits maintaining a higher solid density in the circulating beds, allowing a higher conversion rate per volume. As solid catalyst, NEXCC process can use conventional cracking catalyst based on natural and synthetic aluminum silicates, zeolites, clays, Y and ZSM-5 zeolite, stabilized by Rare Earth and phosphorus. Short contact time and efficient separation and stripping enables the unit to use also improved cracking catalyst with higher loadings of zeolite. An increase of 10 points of propylene + butenes yields could be obtained while maintaining bottoms conversion (Table 29). It was also claimed that the flexibility of the design allowed extending operation to other reactions that may take advantage of short contact time, high temperature and efficient heat transfer between reactor and regenerator. For example, is was proposed to carry out thermal cracking of crude oil or heavy oil at short contact time of 0.2 to 0.5 s, high reactor temperature between 650 and 950ºC with an inner particulate heat carrier to yield light olefins and aromatics.

Dehydrogenation of small paraffins was also proposed as a process with high heat requirements. Ethane to butane feedstocks could be processed at temperature ranging from 650 to 750ºC, 0.5 to 4 seconds contact time, with typical Cr–alumina or Vanadium based dehydrogenation catalysts, yielding ethylene, propylene or butenes depending on the feed. Other reactions such as oxidative coupling of methane, or gasification of a variety of feedstock ranging from methane to biomass, coal or bottoms residues were also proposed.

5.2.4. High Severity FCC, HS-FCC. Developed by Nippon Oil Corporation, King Fahd University of Petroleum & Minerals and Saudi Aramco, the process was designed to maximize propylene by fluid catalytic cracking of crude oil fractions.[178-180] One of the prominent feature of the process is the proper control of dry gases generated by thermal cracking owing the very high reactor temperature involved.[34]

To accomplish this objective, HS-FCC process works at high reaction temperature (550-700ºC), short contact time (0.1-3 seconds) and high catalyst to oil ratio (15-50 wt/wt) in a downer type reactor. After reaction, the mixture of the products, unreacted materials and catalyst is forwarded into a separation zone (initially a box-type or a U-bent type), where at least 90 % of the catalyst is separated before the catalyst is precisely removed from the mixture in a cyclone separation zone. Separation system was later improved by the use of baffled separation system. After stripping, the catalyst is lifted by the circulating flow regenerator to a hopper from which it is fed back to the downer reactor. Feedstocks are the usually used in Fluid Catalytic Cracking.

A good management of temperature in the reactor and reactor inlet is more critical than in conventional FCC due to the higher mean temperature and shorter contact time involved.[181] Increasing reactor temperature for higher olefins yield and bottoms cracking implies raising sharply inlet temperature, leading to adverse effects such as increased thermal cracking, thus dry gas yield, and coke yield.

In order to mitigate this effect, it was proposed to have two or more catalyst inlets in the downer reactor. A first part of the regenerated catalyst, between 20 and 95 % of the total catalyst flow to reactor, is fed at the reaction zone inlet where it contacts with hydrocarbon, while the rest (5-80 wt-%) is fed downstream at one or several locations before separation device. A mixture of regenerated catalyst and incompletely regenerated catalyst can also be fed at the reaction zone inlet which allows decreasing catalyst inlet temperature. The raw oil is then cracked under mild conditions, restraining the generation of unsuitable by-products such as the dry gas and the coke. In another improvement, residual oil is recycled to the process and serves as quench oil at the inlet of the separation device.

While it is common to quench reaction mixture at reactor outlet, it becomes less effective at higher catalyst to oil ratio due to the larger thermal mass. Also, the higher reactor temperature would call for a higher temperature drop during the quench for being effective, increasing quench flow rate to unsustainable levels. It was found however that the use of residual oil, which is rich in heavy aromatics, was effective as quench media although temperature drop was minimal after quench.

Table 30. Comparison of ZSM-5 Addition in conventional FCC and HS-FCC.[24]

	FCC		**HS-FCC**	
	Base	+10wt%ZSM-5	Base	+10wt%ZSM-5
Dry gases	5.3	6.4	4.6	5.5
LPG	20.7	29.3	30.9	40.5
Propylene	***7.5***	***13.0***	***10.7***	***18.4***
Butenes	***8.8***	***13.6***	***16.1***	***17.8***
Gasoline	43.4	34.1	45.4	34.0
LCO	15.0	15.4	9.4	9.3
HCO	13.3	12.7	6.6	7.1
Coke	2.3	2.1	3.1	3.5

Catalyst used in these inventions contains the ultrastable Y-zeolite (2-60 wt-%), a matrix and a crystalline aluminosilicate zeolite or SAPO each having smaller pores than ultrastable Y-type zeolite. It may also be preferable to use a Y zeolite with a low Rare Earth content, for example lower than 0.5 wt%, in order to minimize hydrogen transfer reactions.[181] At the same time, larger amounts (5 to 40 wt-%) of shape selective zeolite, more preferably ZSM-5 zeolite, are recommended to take full advantage of the less saturated products yielded by low RE cracking catalysts, maximizing light olefins content.

Based on the intrinsic features of the HS-FCC, maximum light olefin yield can be obtained by the combination of optimized catalyst system and operation conditions. The yields of light olefins, LPG, gasoline, LCO, HCO and coke are presented in Table 30 for conventional FCC and HS-FCC.

In conventional FCC, the base catalyst yielded about 16 wt% light olefins and 43 wt% gasoline compared to 29 wt% light olefins and 45 wt% gasoline in HS-FCC. In the case of ZSM-5 addition, the yield of light olefins increased to more than 37 wt%, particularly propylene which showed an increase of 72 wt%. The results showed that, in both cases, the rise in light olefins was accompanied with a drop in gasoline yield since the addition of ZSM-5 accelerates the cracking of gasoline to lighter products.[182]

5.2.5. Other downer processes: Milli-Second Catalytic Cracking, MSCC and Quick Contact Process (Stone & Webster). Although not primarily designed for light olefins production, their downer configuration makes them interesting designs where to implement high severity cracking.

Milli-second catalytic cracking process was commercialized by UOP and CEPOC.[183] In this process a stream of hydrocarbons is sprayed perpendicularly into a downwards flow of catalyst (Figure 14). The mixture is then fed directly into a separation device located in front of the feed inlet, ensuring very low residence time of catalyst and feed in the reactor. In the MSCC process catalyst used is composed of at least 40 wt% of zeolitic component and contact times are less than 0.5 seconds. It was observed that the bottoms conversion was limited, hence the very high zeolite content in the catalyst formulation.

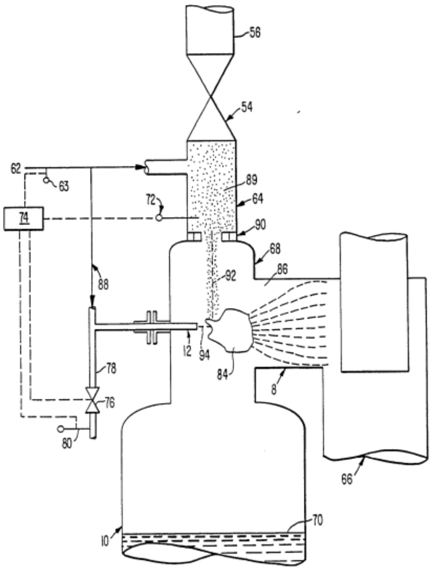

Figure 14. MSCC reactor - Enlarged view of the horizontal contactor.[183]

The solid down flow allows increasing significantly the catalyst to oil ratio as well as access to very short contact time, which allows in turn increasing the reactor temperature, while thermal cracking is maintained controlled. Although this is not its primary objective, this process arrangement is ideal to promote formation of light olefins when combined with the adequate catalyst.

In 1994, Cepoc revamped its conventional FCCU to a short-contact-time system known as the MSCC process and some of the benefits realized were:[184]

- Increased resid processing capability and improved yield structure through enhanced catalytic reactions.
- Increased overall liquid-volume yield and higher hydrogen content in the unconverted products.
- Higher LPG olefinicity, gasoline octane and Light-Cycle Oil (LCO) cetane. Reduced dry gas yield.
- Reduced dehydrogenation by contaminant metals even though metals levels increased.
- Reduced catalyst addition rate from 15 to 25 tons/day to 8-10 tons/day.

The TCR technology developed at the beginning of the 1980's by Stone & Webster was further extended, replacing the inert solid carrier by a catalyst.[185,186] While initially designed for olefins production, it was promoted later as a short contact time process with the advantages inherent to this call of process for the processing of VGO: reduced dry gas, higher gasoline yield, lower coke yield.[187]

The flow scheme is similar to the HS-FCC process. Its main feature is a downer reactor, with contact times claimed to be as short as 200 milliseconds.[188] The catalyst distributor, feed injection and downer outlet separator were carefully designed to ensure a good contact between hydrocarbons and catalyst as well as an efficient separation to take full advantage of short contact time. The solid is fed to the reactor from a hopper situated above the injection zone. Hydrocarbon is injected in the annular area surrounding the solid inlet, through angled openings to limit erosion of the wall.

A mixing plug creates several discrete mixing zones of reduced volume, ensuring more homogeneous distribution of solid and gas across the reactor section. If reaction time has to be kept minimal, solid separation must also be fast. Such a system is reported to separate more than 98 % of the solid within 30 milliseconds. The solid from the reactor impinges the lower wall of the separator, accumulating at the bottom and flowing by gravity to the stripping section. Gas is forced to turn upwards and enters a cyclone where the remains of solid are separated back to stripper.

The stripped catalyst is then contacted with air in an upwards transport bed, being regenerated and brought back to the catalyst hopper.[187] Operating parameters were claimed as 540-650°C reactor temperature, 5-15 catalyst to oil ratio, steam to hydrocarbon ratio 0.2 to 0.4, residence time in reactor from 0.02 to 5 seconds.

5.3. Dedicated catalytic cracking processes for light olefins: boosting small olefins yields through naphtha cracking

5.3.1. Standalone processes based on FCC technology for olefinic naphtha cracking. While reprocessing naphtha in a parallel riser minimizes costs, it has the disadvantage to use similar catalysts than VGO-based processes, and thus cannot take full advantage of a catalyst specially designed for naphtha cracking. Thus, several licensors also have proposed standalone units dedicated to crack naphtha. Olefinic streams such as light naphtha but also coker naphtha are cracked under optimized conditions and usually with a ZSM-5 based catalyst or similar shape selective catalyst. Processes based on an extension of FCC technology are:

- Superflex, as an extension of Maxofin process (KBR).
- Propylene Catalytic Cracker (ExxonMobil).

Superflex® is based on technology developed by ARCO Chemical Company (now LyondellBasell, patent owner) and is licensed by KBR with the same Orthoflow® reactor technology found for KBR FCC processes.[136] Its preferred feed is C_4-C_{10} streams with high content of olefins, and may be sourced from C_4-C_5 fractions from steam cracker, light cracked naphtha from FCC, coker naphtha or even olefinic stream from Fisher-Tropsch process. Non-aromatic, C_4 to C_6 fractions are recycled to extinction in the process to maximize small olefins and BTX output. Operating conditions may be in the range of 630-650°C reactor temperature, with typically 10 wt% steam added to the hydrocarbon. Depending on feedstock, propylene yield averages 40 wt% while total ethylene plus propylene yield averages 60 wt%. This process was proposed as a good synergy with a steam cracker based on naphtha or distillate, which generates a substantial amount of olefins in pyrolytic naphtha.[189] One unit is in operation in SASOL, running on an olefinic naphtha stream derived from FT operation. Yields of 10-15 wt% fuel gas, 15-20 wt% ethylene, 35-40 wt% propylene, 5-7 wt% propane and 20-25 wt% gasoline can be attained recycling C_4 to C_6 fractions to extinction. The naphtha stream produced from the process is highly aromatic, and thus may be used as a high octane, low olefin blend component for motor gasoline, or separated to valorise BTX.

Maintaining heat balance may be difficult with naphtha feed and low-coke making catalysts such as ZSM-5 or similar. Thus, additional heat has to be generated. This can be made directly by injecting a fuel, for example fuel oil recycled from the process, into the regenerator.[190]

Dual riser may also be used as in Maxofin™ process, in order to process paraffinic and olefinic stream under separate conditions, and where an amount of coke precursor, such as diolefins, is added to one of the feeds to provide enough coke for the process to be autothermal.[191] It has also been proposed to use the technology with a Ga-doped ZSM-5 catalyst to obtain BTX from small paraffins, for example propane.[192]

The Propylene Catalytic Cracker process from ExxonMobil is also based on a reactor regenerator system derived from Exxon FCC technology, and using ZSM-5 as main catalyst. Butylenes, C5 and/or Light Cracked Naphtha are fed to the reactor. Temperature is in a range that allows high conversion of olefins but that is not high enough to obtain high conversion of small paraffins, so that a fraction of naphtha is conserved.[193] Carefully designed riser reactor provides narrow residence time, that allow producing C_2 and C_3 streams with very high olefin content. Chemical grade (95 %) propylene stream may be produced directly from the unit, avoiding costly fractionation.

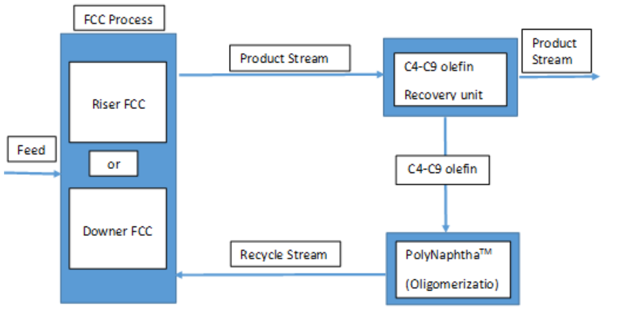

Figure 15. Integration of PolyNaphthaTM with FCC technology for propylene maximization. [196]

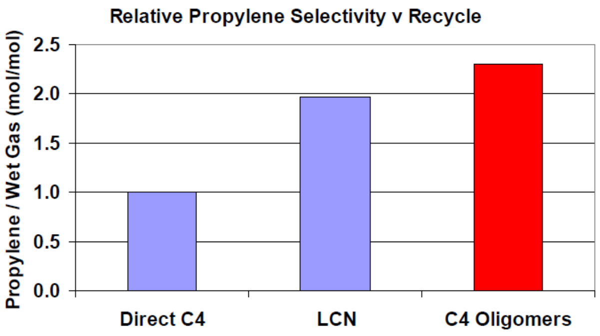

Figure 16. Enhancement of propylene selectivity with Flexene versus recycle.[194]

Other technologies may be used, for example fixed bed technology (Propylur process) or oligomerization/cracking technology (Flexene process).

The Flexene process licensed by AXENS is an integration between FCC and PolyNaphtha™ (Oligomerization process) unit to improve either propylene yield or middle distillate or gasoline (Figure 15). For maximum propylene mode, C_4 to C_9 olefins are recovered, oligomerized to higher C_8 and C_{12} olefins and recycled back to the FCC unit to be cracked to propylene. Based on the process condition, about 3-6 wt% of propylene can be added to the product stream.[180,194-196] Processing oligomerized olefins showed better selectivity for propylene production than recycling Light Cracked Naphtha (LCN) alone. The selectivity of the two options compared to the base case where direct C_4 is cracked is illustrated in Figure 16. The relative propylene selectivity when cracking oligomerized C_4 stream is about 2.3 compared to 1.9 for cracking LCN.

5.3.2. Standalone processes for small paraffins cracking: K-COT™ process. Small paraffins are found to be very refractory to cracking and require more severe conditions to be cracked than optimum conditions for olefin cracking. Higher severity, as well as improved catalysts, may be used in this kind of process. An example is the KBR's Catalytic Olefins Technology (K-COT™) process, based on the Orthoflow® design from KBR.[197,198]

This process was developed to produce short olefins from streams rich in small alkanes such as Light Straight Run Naphtha. It has the advantage over steam cracking to produce propylene and ethylene at a ratio of 1 to 1 or higher, whereas naphtha steam cracking is usually limited to 0.5 to 1.

Another advantage is a reduction in dienes, and particularly acetylene, which facilitates further purification of small olefins to polymer grade.[197]

K-COT™ process has similar or slightly lower ethylene yield than steam cracker (Figure 17) but with twice the yield of propylene. The total yield of ethylene and propylene can reach 60 to 65 wt%, similar or higher than a steam cracker.

It uses a robust, zeolite catalyst, most likely based on pentasil type, at a temperature between 600 and 700°C, with the injection of steam. The catalyst is specially formulated to show high performance with paraffinic feeds, and high hydrothermal resistance.

Compact Orthoflow® design is used in K-COT™ process. Typical features of high performance FCC, such as closed cyclones, are also used. As happens in cracking, the process is endothermic, yet the very low coke make from naphtha requires external heat to be supplied.

As Superflex process, the process may uses dual risers with the purpose of building coke and generating heat in the regenerator without the need of firing supplemental fuels. Propylene to Ethylene ratio decreases with temperature, from 1.1 to 0.7. Tail gas is lower than in thermal crackers.

Also, C_4-C_6 fraction can be recycled to the reactor without hydrogenation (but benzene). Gasoline is also richer in BTX than pyrolysis gasoline from steam cracker.

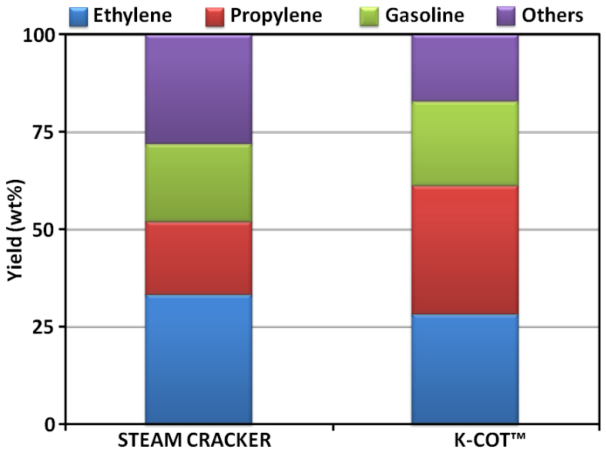

Figure 17. Yield pattern in ACO process compared with thermal cracking for LSR naphtha processing. [173]

A commercial trial was programmed for 2010 at Ulsan refinery in partnership with SK Energy. The operating conditions of this process are similar to that of Catalytic Pyrolysis Process described in an earlier section, but with the advantage of using a specialty catalyst designed for naphtha cracking.

As a kind of catalytically assisted steam cracking, it also has the advantage to run at substantially lower temperature, 650 to 750ºC compared with typically 850ºC for naphtha steam cracking.

As coke is formed on the catalyst, it is not affected by wall coking, as the catalyst is constantly regenerated. Also, the in-situ heat generation by coke combustion avoids the contact with extremely hot walls that accelerates the coke formation in steam crackers.

6. Summary and outlook

Today crude oil refining is centered on the production of fuel as main product, with collateral production of minor (but valuable) tonnage of sub-products such as petrochemicals. In certain areas, due to an increasing olefins market demand coupled with a limited supply from the refinery, new transformation complexes focalized on petrochemicals production directly from crude oil may appear, with fuels regarded as indirect secondary products. Central part of such complex could be a catalytic conversion unit such as an FCC like process optimized for light olefins.

The very limited flexibility of thermal processes, such as steam cracking, and in particular the low and relatively inflexible propylene to ethylene ratio, together with the difficulties to use low grade crude as feedstock due to excessive wall coking, indicates that future technologies based on catalytic cracking will be better positioned to fulfill impending market demand. The technology already existing in FCC field to boost light olefins production could be extended to process the whole crude oil fraction, propelling the direct petrochemicals production in the 30-50% yield range, which is far beyond the current levels in refinery. Process optimization for light olefins in FCC process were largely detailed in this review and, generally, features cracking temperature significantly above FCC range. As a consequence, short contact time and high catalyst-to-oil ratio will be used, making downer reactors ideal reactor configuration. The cracking component based on Y zeolite is tailored to have as low hydrogen transfer activity as possible. That means low Rare Earth, and high accessibility to favour bottoms conversion while limiting hydrogen transfer, yielding a maximum of material to be transformed further into light olefins by a shape selective catalyst. Active material content, including active matrix, in inventory may not require to be high since high CTO and temperature will bolster catalyst activity. This is even more true if one considers that coke make needs is reduced to minimum and, for instance, active ZSM-5 with optimized Si/Al ratio in the range of the hundreds and high accessibility may be used, to limit hydrogen transfer while keeping high activity.

The conversion of the lighter, naphtha range part of the crude oil, usually very paraffinic, may prove however more challenging using the same operating conditions and the same catalyst than for the heavier part of the crude oil. This stable light fraction may be cracked under conditions (higher temperature, very active catalysts), that would not be adequate with heavier feeds due to excessive coke and dry gas yields. It will remain challenging to find a catalyst formulation with an activity fully adapted to the whole range of the crude oil, from very stable, low molecular weight paraffins to high molecular weight, high coke make asphaltenes. Some may prefer to process the light fraction in a separate reactor. This is often carried out with the cracked naphtha, which is reprocessed in a reactor (riser or downer) in parallel to the main conversion reactor to crack the abundant stock of gasoline range olefins and increase further light olefins yields. Improving further the light olefins yield of this light fraction may be carried out in a separate process with a dedicated catalyst of high cracking activity, eventually improved with metals not allowed in traditional FCC for their coke make. Until a better catalyst is developed, multi-reactors units may remain an essential feature of such process.

As an alternative strategy, a number of units may come to support the catalytic cracking converter, with the objective of converting lighter fractions that may not crack efficiently towards olefins or aromatics in the catalytic cracker. Steam Cracker may be used in its traditional way, catalytic reformer may be used if more aromatics are sought. Methatesis units may be used to flexibilize further the ration between light olefins, transforming ethylene and butenes into more propylene. Finally, an important issue in the near future that may impact an olefins oriented catalytic cracker will be the incorporation of increasing amounts of unconventional feedstocks with diverse compositions such as extra heavy crude oils, light tight oils and/or biocrudes derived from biomass resources. The intrinsic properties of these feeds, will call for additional research to obtain optimized processes and catalytic systems adapted to each of these emerging feedstocks.[199] The high average molecular weight, low hydrogen to carbon ratio and high contaminants content for extra heavy crude oils will call for catalysts with better resistence to contaminants (metals) and ultra low coke make. Active cracking component amount may be reduced, and a significant part of the cracking performed thermally. By the contrary, low molecular, paraffinic tight oils may benefit from highly active materials, as small paraffins are difficult to crack. Also, increased resistance to Ca/Na/Fe was recommended. ZSM5 catalysts may be used for the direct conversion of acidic, high oxygen content and low thermal stability biocrudes to obtain preferentially aromatics or chemicals.[200,201] Meanwhile, hydrotreated, triglyceride-based oils yielding feedstocks similar to a paraffinic crude oil may be preferred to obtain light olefins.

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