Applications of zeolites in petroleum refining

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Zeolites, or more broadly molecular sieves, can be found in a majority of the major catalytic processes in today's petroleum refinery. This paper provides an overview of the use of zeolite catalysts in today's petroleum refineries, and emphasizes some of the newer refining applications including gasoline sulfur removal and dewaxing via isomerization. Zeolite catalysts are also finding new applications at the refinery–petrochemical complex interface. These applications will also be highlighted.

Keywords: petroleum refining, zeolites, catalysts

1. Introduction

Technology development is driven as much by economics and government regulation as it is by innovation. There is no better example of this than in the area of petroleum refining catalyst and process development. Over the past decade, the principal technology drivers have been: (1) increased process efficiency, (2) improved product selectivity, (3) product segmentation through quality enhancement, (4) more stringent sulfur specifications for fuel products, (5) increased aromatics and olefins to support a growing but cyclical petrochemical business, and (6) increased production of oxygenates to meet clean fuel mandates. The last of these is currently being revisited in light of growing concern from the environmental community of the environmental benefits vs. the liabilities incurred by mandatory incorporation of oxygenates in gasoline. The refining research and development community has responded to these challenges by introducing a number of new catalytic processes and finding ways to tailor many of the major refinery processes to produce the fuels, lubricants, petrochemicals, and special products required by a more value conscious and environmentally aware society. Many of these process innovations have come as a result of new applications of zeolite catalysis.

In the 40 years since their introduction into the refinery, zeolite catalysts have been the source of major improvements in gasoline yield and octane as well as in the production of cleaner fuels and lubricants with enhanced performance properties. Credible reviews zeolite catalysts in petroleum refining processes are already available in a text by Chen et al. [1] and in articles by Chen and Degnan [2], Maxwell [3,4] and Sie [5]. This review will cover the major areas highlighted by these earlier references, but it will focus primarily on recent catalytic improvements. It will also highlight several new areas where zeolites are providing improved petroleum products or where they are helping to reduce cost and production of wasteful by-products.

Figure 1 shows the major refining processes where zeolite catalysts find application. Current refinery processes that depend on zeolite catalysts are listed in table 1. In addition, there are several smaller, commercial zeolite-catalyzed process applications that have been the focus of significant technology development, and where, to date, there has been limited commercial implementation. These are listed in table 2.

2. Zeolite catalyzed refining processes

2.1. Fluid catalytic cracking (FCC)

Fluid catalytic cracking is by far the largest user of zeolite catalysts. Industrial estimates suggest that worldwide sales of zeolitic FCC catalysts are approximately $1 billion per year [6] and constitute a major portion of the $2.16 billion worldwide refinery catalyst market. Current worldwide capacity is approximately 585 000 mt and annual consumption is approximately 500 000 mt. North America alone consumes nearly half (204 000 mt/yr) followed by Asia-Pacific (110 000 mt/yr), and Western Europe (70 000 mt/yr). Zeolite Y continues to be the primary zeolitic component in FCC catalysts nearly 40 years after its first commercial introduction. While many research programs have attempted to identify alternative materials [7,8], zeolite Y continues to provide the greatest gasoline yield at the highest octane with the greatest degree of catalytic stability. Other zeolites and molecular sieves have failed principally because they have been deficient in stability or they have had poorer product selectivity.

Recent advances in FCC catalysts have concentrated on modifying zeolite Y for improved coke selectivity, higher cracking activity, and greater stability through manipulation of extraframework aluminum or through the generation of mesoporosity of the zeolite crystals. Extraframework aluminum is introduced either by steaming or via ion exchange. The development of improved FCC catalysts constitutes an interesting case study of the merits of selectively modifying a single crystal structure to achieve multiple catalytic objectives [9]. Figure 2 shows that the modifications in zeolite Y have continued to improve gasoline selectivity and octane [10].
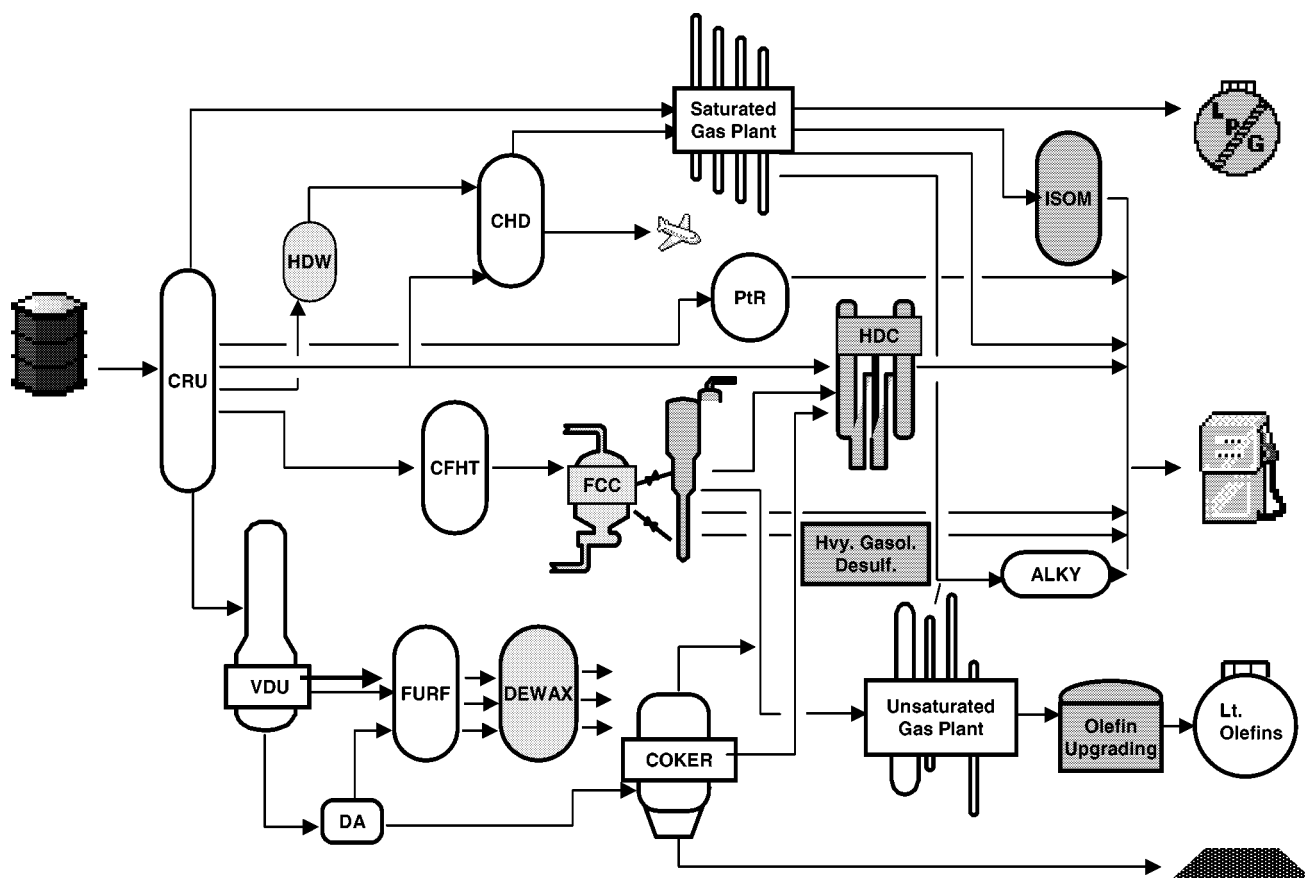
Figure 1. Zeolite-catalyzed processes in the refinery are shaded. CRU – crude distillation unit, HDW – hydrodewaxing, CHD – catalytic hydrodesulfurization, PtR – reforming, ISOM – isomerization, CFHT – catalytic feed hydrotreating, FCC – fluid catalytic cracking, HDC – hydrocracking, ALKY – alkylation, VDU – vacuum distillation unit, FURF – furfural extraction, DEWAX – lube hydrodewaxing, DA – deasphalting.

Table 1
Major zeolite-catalyzed processes found in today's refinery.

Fluid catalytic cracking	Distillate dewaxing by cracking
Hydrocracking	Lube dewaxing by cracking
Gasoline desulfurizaton	Distillate dewaxing by isomerization
Light paraffin isomerization	Lube dewaxing by isomerization
Reformate upgrading	Diesel aromatics saturation

Table 2
Zeolite processes that have found more limited commercial application.

Olefin (C_4/C_5) skeletal isomerization
Benzene reduction
Light olefin interconversion
Olefin oligomerization to fuels and lubes

Figure 2. Advances in zeolite Y design have led to improvements in octane and gasoline selectivity from [10].

2.2. FCC additives

The ability of small amounts of ZSM-5 added to the FCC unit to improve gasoline octane while producing more light olefins has prompted a substantial amount of process and catalyst research into zeolite-based FCC additives [11,12]. Significant advances have been made in stabilizing ZSM-5 to harsh FCC regenerator conditions which, in turn, have led to reductions in the level of ZSM-5 needed to achieve desired uplifts and wider use of the less expensive additives.
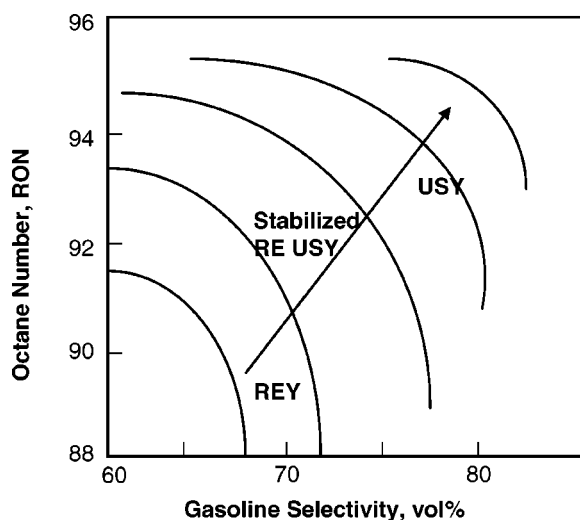
While the demand for incremental gasoline octane has diminished with increased oxygenate addition, the need for propylene has increased due to rapid growth in the market for polypropylene. As a result, FCC catalyst manufacturers and FCC process licensors have recently focused on catalyst – process systems that maximize C_3 and C_4 olefin
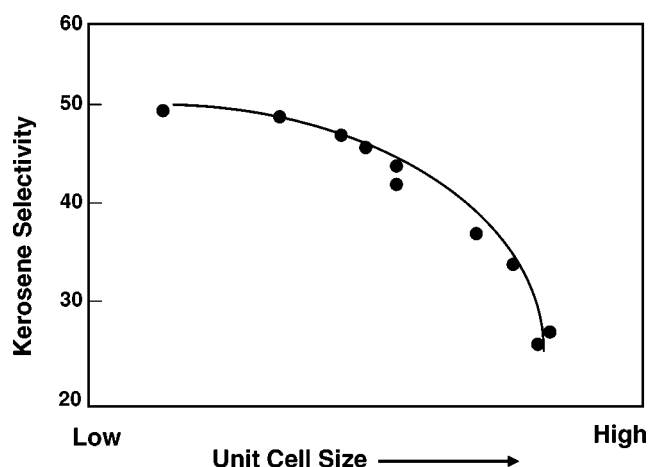
Figure 3. Selectivity to kerosene (distillate) improves with decreasing USY unit cell size (from [15]).

make [13]. The interest in C_4 olefins stems from the interchangeability of butene for propylene in light paraffin–olefin alkylation. Additional butene allows refiners to back out petrochemical propylene. Butenes are also needed for MTBE, although this is decreasing, as well as for polyisobutylene. This has led to the development of several butylene selective FCC additives by firms such as W.R. Grace.

2.3. Hydrocracking and hydrofinishing

Advances in zeolite-catalyzed hydrocracking processes have mainly been in the area of clean fuel production, i.e., lower aromatics and lower sulfur in gasoline and diesel. By using more highly dealuminated USY zeolites, catalyst manufacturers have been able to produce distillate selective hydrocracking catalysts that approach the desired selectivity of amorphous catalysts while enjoying substantially lengthened cycles and milder operating conditions (pressure and temperature) [14]. Figure 3 shows how distillate selectivity improves with decreasing framework aluminum (= decreasing USY unit cell size) [15]. This has led to the development of several moderate pressure hydrocracking (MPHC) processes.

These MPHC processes operate at temperatures in the 360–435 °C range and pressures as low as 5.5 MPa (55 bar). MPHC processes take advantage of the inherent coke re-

sistance of large pore, highly dealuminated Y-zeolites as well as improved base metal combinations that have been tailored to operate well at low hydrogen partial pressures. Processes have been developed around USY-based catalysts for partial conversion of vacuum gas oils, cracked gas oils, deasphalted oil, and FCC light cycle oil. The processes comprise a dual catalyst system consisting of an amorphous hydrotreating catalyst (normally NiMo/Al$_2$O$_3$) and a metal-containing USY-based hydrocracking catalyst. Single-stage, single pass conversions are typically in the range of 30–60 wt%. The process requirements are similar to those used in vacuum gas oil hydrodesulfurization (table 3), which has led to several catalytic hydrodesulfurization (CHD) revamps [16].

Strides have also been made in gasoline hydrotreating/mild hydrocracking mainly for the purposes of sulfur removal. Mobil's Octgain process reduces the sulfur and olefins in FCC gasoline without affecting octane. Commercialized in 1991 at ExxonMobil's Joliet, IL refinery, the Octgain process uses a shape-selective zeolite to convert the lower octane normal or near-normal paraffins and olefins to lighter products and a metal function to desulfurize the feed and keep the catalyst clean. The metal function also saturates some of the olefins generated during cracking. The process works best on heavier gasoline fractions, but also can be tailored to operate on full range FCC gasoline. Typical process conditions are LHSV = 1–4 h^{-1}, 290–425 °C and H$_2$ pressures greater than 2.1 MPa (20 bar). Table 4 shows some typical gasoline feed and hydrofinished gasoline and Octgain product properties.

2.4. Light olefins to gasoline

The search for a zeolite-catalyzed light paraffin–olefin process to replace current HF- and H$_2$SO$_4$-catalyzed processes continues. To date only supported liquid acid processes such Haldor Topsoe's alkylation process appear to be nearing commercialization [17]. Light olefins contained in lower value refinery streams can be oligomerized over a modified ZSM-5 catalyst in a dense fluid-bed reactor to produce high-octane gasoline in ExxonMobil's olefins to gasoline (MOG) process. The process is integrated into existing FCC gas plants. ZSM-5 converts the oligomers into C_5^+ components by acid-catalyzed oligomerization, hy-

Table 3
Typical conditions: desulfurization vs. hydrocracking.

	Desulfurization		Hydrocracking pressure	
	Middle distillate	Vacuum gas oil	Moderate (MPHC)	High
Pressure (kPa)	2750–5500	3450–10350	<10350	10350+
Liquid hourly space velocity (h^{-1})	2–4	1–2	0.4–1.0	0.4–1.0
Avg. rxr. temp. (°C)	315–370	360–415	360–425	315–400
Hydrogen rate (m^3/m^3)	85–200	170–340	500–850	675–1350
Hydrogen consumption (m^3/m^3)	15–50	50–85	62–170	250–600
Conversion (%)				
to naphtha	<1	1–5	5–25	100
to distillate		10–20	20–50	

Table 4
Typical feed and hydrofinished and octgain gasoline product properties.

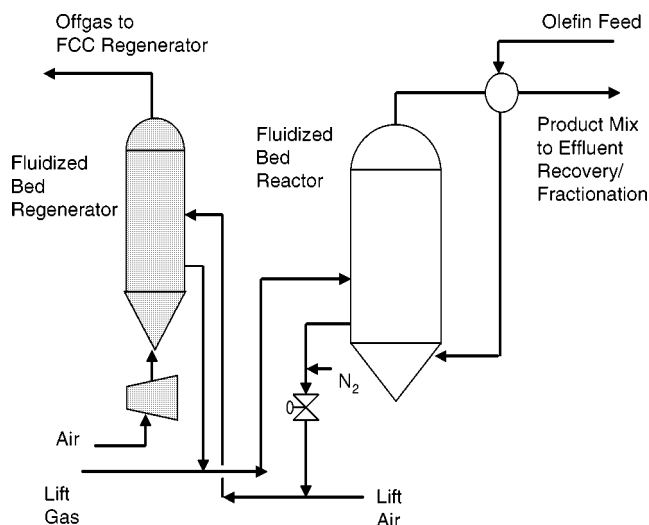| Feed properties | CARB FCC gasoline | | | | Heavy FCC | |
	Case A		Case B		gasoline (case C)	
Sulfur (ppm)	200		5 000		2 000	
RON	92		89		93	
MON	80		78		82	
Bromine No.	60		37		37	
Boiling range (°C)	C_5 −171°F		171–204		121–200	
Product yield	HDF	Octgain	HDF	Octgain	HDF	Octgain
C_{5+} vol% of feed	100	89	101	95	101	92
Sulfur (ppm)	<40	<40	<100	<100	<100	<100
RON	78	91	78	89	81	93
MON	72	81	68	79	73	82
Bromine No.	<1	<2	<1	<2	<1	<2

Figure 4. Olefins to gasoline (MOG) and olefin interconversion (MOI) processes incorporate recirculating dense fluid-bed reactor and regenerator process design.

drogen transfer, aromatization, and isomerization reactions. High-octane gasoline yields as high as 75% have been reported. The gasoline quality depends both on the process conditions and the distribution of the feed olefins. Typical gasoline properties are reported to be: RON = 94–98, MON = 81–85, API density = 62–57 and RVP = 0.72 psi/0.5 bar. A schematic of the process is shown in figure 4.

Shell has introduced a similar process which it calls its Polygasoline and Kero (SPGK) process [3,18]. Using a Ni/mordenite catalyst, the process converts C_2–C_5 olefins to gasoline, kerosene, and distillate at high pressures 1–5 MPa (10–50 bar) and low temperatures (200–280 °C). As in the MOG process, the product is primarily isoolefins and is very low in aromatics. The gasoline has a high octane (RON = 93) and is low in C_5–C_7 olefins. Distillate and gasoline selectivity can be varied by changing recycle composition. Consistent with their highly isomerized nature, the distillate products have very low pour points (<−50 °C) and very good cetane (cetane number >50).

2.5. Light olefin isomerizaton

The need for isobutene for methyl *tert*-butyl ether (MTBE) has diminished substantially as the environmental implications of MTBE contaminated groundwater are being debated. Nevertheless, there is a continuing need for isobutene for alklyate as well as for petrochemical applications including polyisobutylene. A similar need exists for isoamylene, a precursor for tertiary amyl methyl ether (TAME). Several zeolite catalyzed C_4 and C_5 olefin skeletal isomerization processes have been introduced in the past decade. These include: Mobil/BP/Kellogg's Isofin, Texaco's Isotex, Shell's butene isomerization, and UOPs Pentesom and Butesom processes. Mobil/BP/Kellogg's Isofin process operates in the vapor phase and uses a specially modified medium pore zeolite. The feed is typically a raffinate from an MTBE or TAME unit; the product is sent directly to an MTBE or a TAME unit for further ether production. The Isofin catalyst is reportedly highly selective to C_4 and C_5 olefins and requires no steam or halogen cofeeds. Texaco's Isotex process uses ferrierite as the active component for butene isomerization [19]. The catalyst is reportedly steam pretreated and bound in an alumina matrix. The Shell *n*-butene isomerization process also uses ferrierite as the active catalytic component [20].

Several mechanisms have been proposed to explain the unique selectivity that ferrierite exhibits for *n*-butene skeletal isomerization [21,22]. One mechanism involves the bimolecular reaction of two *n*-butene molecules to form a C_8 dimer which then undergoes isomerization and subsequent cracking to form the isobutene. The second mechanism involves the monomolecular rearrangement through a highly energetically unfavorable primary carbenium ion intermediate. The latter mechanism has recently gained increasing support [23]. Irrespective of the mechanism, one of the main requirements is that the zeolite acid site concentration be low or the that the acid sites themselves be fairly weak. Strong acid sites lead to oligomerization and catalyst fouling.

2.6. Paraffin isomerization

UOPs once through isomerization process for producing $C_4/C_5/C_6$ isoparaffins is an adaptation of the Pt/mordenite-based Hysomer process that Shell developed in the 1960s. Cepsa has recently introduced its own version of a mordenite-based light paraffin isomerization process. Both UOP and Cepsa have continuosusly improved upon the conventional mordenite catalysts once used by Shell. Much of the recent attention in this process has been focused on using Pt/sulfated zirconia or similar solid super acids as a means to achieve activity nearly commensurate with Pt/chlorided alumina catalysts, but without the need for continuous chloride injection that is required by these catalysts. If successful, these new super-acid catalysts may ultimately displace the need to use zeolite catalysts for light paraffin hydroisomerization.

2.7. Distillate dewaxing by cracking

ZSM-5-catalyzed distillate dewaxing was first introduced in 1978 and has been continuously improved upon. Today, the process is used worldwide by 27 licensees who have a combined dewaxing capacity in excess of 160 000 BPD. In the late 1980s Akzo-Fina improved upon this process by adding a desulfurization function to the ZSM-5 catalyst and placing a hydrotreating catalyst upstream of the ZSM-5 catalyst to reduce heteroatoms and saturate olefins and aromatics. The Akzo-Fina cold flow improvement (CFI) process was brought together with Mobil's MDDW process in 1992 under the Mobil Akzo Kellogg (MAK) hydroprocessing alliance. Recent improvements in the combined MDDW-CFI process have included optimized reactor design and incorporation of enhanced desulfurization technology. The process is used to upgrade waxy feedstocks, squeeze more gasoline and distillate from topping and reforming refineries, and produce high-value jet fuel from heavy gasoline. Table 5 provides a summary of typical feed and product properties for this process.

2.8. Lube dewaxing by cracking

As a means to reduce product pour point and improve flow properties, paraffin cracking is slowly being replaced by paraffin isomerization for both fuels and lubricants. Isomerzation improves product yield and product quality especially for lubricants where the isoparaffins are critical for achieving high-viscosity indices. However, the cracking and isomerization processes are not directly interchangeable. For example, the cracking processes tend to operate at higher temperatures. Isomerization catalysts rely on a strong metal function, most often a noble metal, for dehydrogenating and hydrogenating the olefinic intermediates. This noble metal function is more sensitive to poisons than the NiMo or CoMo catalysts frequently used for hydrotreating. Therefore, virtually all isomerization processes require a hydrogenation or a hydrocracking stage in front of the hydrodewaxing stage. The areas of fuel and lube hydroisomerization process development have been among the most active areas in refining technology within the past decade.

2.9. Distillate dewaxing by isomerization

Distillate dewaxing via bifunctional molecular sieve – metal-catalyzed isomerization was first introduced in ExxonMobil's Jurong refinery in 1990. The process produces low pour point, very low sulfur diesel at high yields by isomerizing hydrocrackate from a moderate pressure hydrocracker. Process conditions are fairly mild (2.4–4.0 MPa, LHSV = 0.5–1.0 h^{-1}). Details of the ExxonMobil Isomerization Dewaxing (MIDW) process are proprietary.

2.10. Lube dewaxing by isomerization

The need for higher quality lubricating oils has prompted many lubricant producers to look to hydroprocessing as a means to upgrade marginal feeds to quality lube stocks and to further upgrade stocks to near-synthetic quality. Within this area, there is a desire to obtain product yield and quality that exceeds those obtained via solvent dewaxing. This has been the principal motivation for the development of several bifunctional metal – molecular-sieve-based lube dewaxing technologies including Chevron's Isodewaxing and ExxonMobil's Selective Dewaxing (MSDW) and Wax Isomerization (MWI) processes [24]. The Isodewaxing and MSDW processes use hydroprocessed feedstocks and provide substantial increases to the base oil viscosity index (VI). The MSDW process uses a two-stage cascade reactor arrangement with a shape selective dewaxing catalyst in the first stage and a hydrofinishing catalyst in the second stage. It operates with hydrogen pressures ranging from 2.7 to 20 MPa (27–200 bar). At least two versions of MSDW

Table 5
Zeolite-catalyzed distillate dewaxing process conditions and performance.

Operating conditions		
Temperature (°C)	260–425	
Pressure (MPa)	2.75–5.5	
LHSV (h^{-1})	1–2	
H$_2$ circulation, scf/BBL	2000 (typ.)	
	Performance comparison	
	Arabian Gulf crude	North Sea crude
Feedstock		
Specific gravity	0.89	0.88
Pour point/cloud point (°C)	19/21	24/27
Sulfur (wt%)	1.85	0.33
Boiling range (°C)	310–445	
Product yields		
Distillate (165 °C+) (wt%)	81.8	81.9
Gasoline (C$_5$ to 165 °C)	11.2	11.3
Pour point/cloud point (°C)	−18/−15	−18/−15
Sulfur (wt%)	0.05	0.05

Table 6
Comparison of product distributions produced by lube dewaxing via cracking (MLDW) and isomerization (MSDW).

	MSDW-1	MLDW-3
Pour point (°C)	−12	−12
Yield (wt%)	90.5	82.9
Viscosity index	105	92
Kinematic viscosity, @ 100 °C, cSt	10.2	10.7
By-product selectivity (wt%)		
166–343 °C, distillate	17.5	9.9
52–165 °C, naphtha	37.9	28.2
C_4–C_5	33.0	43.1
C_3	10.7	17.7
C_1–C_2	0.9	1.1

catalysts have been developed, MSDW-1 and MSDW-2. Both are based on a constrained medium-pore zeolite with a strong metal function that balances the cracking activity of the zeolite [25]. Table 6 compares pilot plant yields of the same feedstock processed by ZSM-5-catalyzed dewaxing (MLDW) and bifunctional metal-zeolite-catalyzed dewaxing (MSDW-1). The advanges of isomerization over cracking as a means to achieve lower pour point are obvious.

Chevron's isodewaxing process reportedly uses SAPO-11 as the active component in its dewaxing catalyst [26,27]. The unidimensional SAPO-11 is very selective in producing highly branched products. This results in a low pour point and a correspondingly high viscosity index at high product yield. Its cracking activity is much lower than conventional zeolites such as ZSM-5.

The ExxonMobil wax isomerization (MWI) catalyst and accompanying process were developed to convert high-wax-content streams, such as slack wax, into very high-viscosity-index lubes. The original MWI process is configured to run at partial wax conversion. A bifunctional metal–zeolite catalyst is used to saturate residual aromatics, isomerize paraffins, and open some naphthene rings. A solvent dewaxing step is used downstream of the MWI unit to remove any remaining normal paraffins and reduce pour point to specifications. Recently, the MWI process has been refined so that a very selective catalytic-isomerization dewaxing step can be used in place of the solvent dewaxing step. This catalytic-isomerization dewaxing step is at least equivalent in its ability to produce very low pour points and very high viscosity indices. The high-quality lubes produced by the MWI catalyst system bridge the gap between conventional mineral-based lubes and synthetic lubes. The MWI catalyst system can process a wide range of feedstocks from light neutral stocks to bright stocks.

2.11. Reformate upgrading aromatics conversion and removal

The concept of alkylating benzene to increase gasoline yield and reduce benzene content is the basis for a ZSM-5-based process known as ExxonMobil benzene reduction (MBR). The fluid-bed process reduces refinery gasoline pool benzene below 1.0 vol% while increasing the pool octane by up to 1.0 number. Benzene conversion is carried out in a dense fluid-bed reactor with an adjoining fluid-bed continuous regenerator. The ZSM-5 catalyst alkylates benzene with light olefins such as ethylene and propylene in FCC off gas or coker fuel gas to produce a higher octane mixture of C_8–C_{10} alkylaromatics. The catalyst also cracks some low-octane paraffins further enhancing gasoline octane. Approximately 60–70% benzene reduction can be achieved with moderate recycle.

ExxonMobil's BTXtra^{SM} process is a variation of the well documented Selectoforming process wherein a zeolite catalyst is placed near in the last bed of a semi-regenerative reformer to improve product quality. Whereas erionite was used in the Selectoforming process to crack out normal paraffins to increase octane, in the BTXtra^{SM} process a shape selective zeolite increases the concentration primarily of toluene, and xylenes by transalkylation of the methyl groups from C_9 aromatics with benzene. Some additional benzene, toluene, and xylenes are produced as a result of dealkylation. The process was commercialized at ExxonMobil's Chalmette, LA refinery in 1996.

While not operating directly on benzene, Shell's middle distillate hydrogenation process uses cation-exchanged Y-zeolite as a support for noble metal to saturate heavier aromatics. The process was developed in response to tighter restrictions on aromatics in diesel, particularly in Europe. The process takes advantage of the reduced sensitivity of ion exchanged Pt and Pd to poisoning by sulfur and nitrogen compounds. The Shell catalyst can tolerate feed sulfur levels of at least 500 ppm with little impact on hydrogenation activity. The zeolitic function reportedly has very little cracking activity, commensurate with its goal of maximizing yield through aromatic saturation.

3. Processes at the refining–petrochemicals interface

Today, both semi-regenerative and continuous catalytic regeneration (CCR) reformers are the major source of aromatics for petrochemical complexes. As such, the reformer is considered as much a key petrochemical asset as it is a refinery asset. Processes such as the previously referenced BTXtra^{SM} fall into the ever growing classification of refinery/petrochemical interface processes. The same could be said of FCC units which supply a major portion of the C_3 and C_4 olefins to adjoining petrochemical complexes. The opportunity to tailor light olefin product composition has motivated companies, such as Phillips, to develop processes such as metathesis for $C_2/C_3/C_4$ olefin interconversion. Several companies are pursuing zeolite-catalyzed processes as alternatives.

Light olefin interconversion

Zeolite-catalyzed light olefin interconversion processes fit well into refineries that have accompanying petrochemical legs. The basis for these processes is the production

Table 7
Olefin interconversion (MOI) process performance comparison for steam cracker butenes and FCC light naphtha as feedstocks.

	Steam cracker C$_4$'s[a]		FCC light naphtha	
	Feed	Product	Feed	Product
Ethylene (wt%)		13.6		9.7
Propylene (wt%)		40.9		26.3
Butenes (wt%)	94.5	0.4		1.1
Pentenes (wt%)		27.0	98.0	46.0
Benzenes, toluenes, and xylenes in C$_{5+}$		12.9	6.1	13.7
Product quality		C$_{5+}$ MO gasoline		Delta
Ethylene purity	>75%	RON 92		+2
Propylene purity	>80%	MON 80		+2
		RvP 11.2 psi		−2

[a] After selective HDT.

of ethylene and propylene from lower value streams. Thermal and catalytic cracking processes produce a wide range of olefins and lighter streams whose value is lower than ethylene or propylene. Examples include steam cracker by-product streams and light cracked naphtha. ZSM-5-catalyzed processes have been developed to selectively convert these streams via olefin oligmerzation, cracking, and disproportionation into ethylene and propylene. The use of ZSM-5 limits the level of multi-ring aromatics in the product. Table 7 compares the product slates of the MOI process when C$_4$'s from a steam cracker or FCC light naphtha are used as feedstocks. The MOI process uses the same cyclic dense fluid-bed reactor–regenerator configuration as the ExxonMobil olefins to gasoline process shown in figure 4.

4. Future developments in zeolite-catalyzed refining processes

Advances in zeolite catalysis for refining applications will continue to be driven by the availability of new materials (i.e., leads) and the demands for improved fuels and lubricants (i.e., needs). In the leads area, zeolite catalysts for light paraffin–olefin alkylation continue to be a prime focus of many research groups. Most efforts center on the prolonging the longevity of the catalyst at conditions where attractive yields and selectivities have been observed with zeolites such as rare earth exchanged zeolite Y. Breakthroughs in this area will require the introduction of new materials which operate in a regime where oligomers are inhibited.

In fluid catalytic cracking, it is unlikely that zeolite Y and its variants USY and REY will be displaced in the near term because of their relatively low cost and versatility. Structures discovered in the last 5–10 years have been synthesized with complex and expensive structure directing agents at conditions requiring a pressure autoclave and are generally being evaluated initially in applications requiring less catalyst. Rather, it is more likely that developments will occur in FCC additive technology where there is an ability to tolerate expensive materials in exchange for attractive yield and product property shifts.

Hydrocracking is an area that has been ripe for the introduction of new, more selective zeolite catalysts. Like FCC, most of the commercial developments have focused on modifications of zeolite Y to produce either more gasoline or distillate selective catalysts. Catalyst aging is no longer a major concern, since most zeolite-Y-based hydrocracking catalysts have been refined to the degree that projected cycle lengths exceed the turnaround frequency of most hydrocracking units. Zeolite catalysts that operate under conditions where high levels of basic nitrogen or high levels of sulfur poison current bi-functional hydrocracking catalysts would be extremely valuable, allowing more streamlined and less capital intensive hydroprocessing schemes.

In lubricant hydroprocessing, the emphasis will be on the development of improved lube hydrocracking catalysts that are more effective in upgrading poorer quality, higher aromatic streams while maintaining product yield. Many
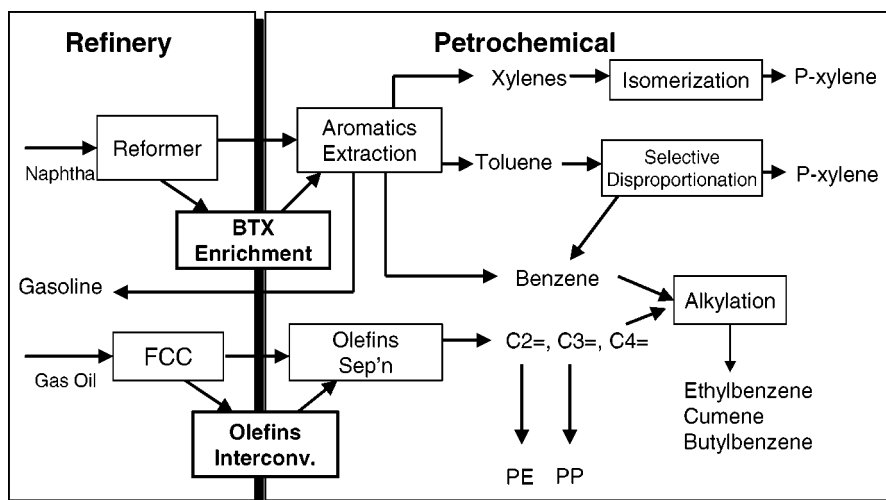

Figure 5. Modern refinery–petrochemical complex interface provides several process opportunities for aromatics and olefins upgrading.

of the current catalysts in this area are amorphous rather than zeolitic. In the hydrodewaxing area, the search continues for catalysts that produce even higher viscosity index lubricants and greater lubricant yields.

The major developmental opportunity area in the next decade may well be at the refinery–petrochemical interface. Processes which maximize olefins and aromatics while integrating clean fuels production will continue to look attractive to refiners who are seeing their fuels product margins come under increasing competitive pressure. Examples of processes that build upon FCC and reformer integration with the petrochemical complex are shown in figure 5.

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References

[1] N.Y. Chen, W.E. Garwood and F.G. Dwyer, *Shape Selective Catalysis in Industrial Applications* (Dekker, New York, 1996).

[2] N.Y. Chen and T.F. Degnan, Chem. Eng. Prog. 84 (1988) 32.

[3] I.E. Maxwell, in: *Stud. Surf. Sci. Catal.*, Vol. 58, eds. H. van Bekkum, E.M. Flanigen and J.C. Jansen (Elsevier, Amsterdam, 1991) ch. 12.

[4] I.E. Maxwell, CATTECH 1 (1997) 5.

[5] S.T. Sie, in: *Stud. Surf. Sci. Catal.*, Vol. 85, eds. J.C. Jansen, M. Stocker, H.G. Karge and J. Weitkamp (Elsevier, Amsterdam, 1994), ch. 17.

[6] Chemical Week 10 (17 March 1999) 32, 34–35.

[7] J. Scherzer, *Octane Enhancing, Zeolitic FCC Catalysts* (Dekker, New York, 1990) pp. 41–109.

[8] W.-C. Cheng, G. Kim, A.W. Peters, X. Zhao and K. Rajagopalan, Catal. Rev. Sci. Eng. 40 (1998) 39.

[9] A. Avidan, in: *Stud. Surf. Sci. Catal.*, Vol. 76, eds. J.S. Magee and M.M. Mitchell, Jr. (Elsevier, New York, 1993) ch. 1.

[10] B. deKroes, C.J. Groenenboom and P. O'Connor, in: *New Zeolites in FCC*, Ketjen Catalyst Symposium, Scheveningen, Netherlands (1986).

[11] F.G. Dwyer and T.F. Degnan, in: *Stud. Surf. Sci. Catal.*, Vol. 76, eds. J.S. Magee and M.M. Mitchell, Jr. (Elsevier, New York, 1993) ch. 13.

[12] R.J. Madon, J. Catal. 129 (1991) 273.

[13] P.K. Niccum, R.B. Miller, A.M. Claude, M.A. Silverman, N.A. Bhore, K. Liu, G.K. Chitnis and S.J. McCarthy, NPRA Annual Meeting, San Francisco (1998), paper AM-98-13.

[14] J. Ward, Fuel Process Technol. 35 (1993) 55.

[15] A. Hock, T. Huizinga, A.A. Esener, I.E. Maxwell and W. Stork, Oil Gas J. 89 (1991) 77.

[16] W.J. Tracy and W.R. Derr, Energy Progress 6 (1986) 15.

[17] P. Sogaard-Andersen, P.M. Geren and W.J. Hillier, NPRA Annual Meeting, San Antonio, TX (1996), paper AM-96-53.

[18] J.P. van den Berg, K.H.W. Roebschlaeger and I.M. Maxwell, 11th North Am. Meeting Catal. Soc., Dearborn, MI, 7–11 May 1989.

[19] E.J. Kuhlman, J.R. Pascoe and C.J. Thom, US Pat. 5 463 160.

[20] H.H. Mooiweer, K.P. de Jong, B. Kraushaar-Czarnetzki, W.H.J. Stork and B.C.H. Krutzen, in: *Stud. Surf. Sci. Catal.*, Vol. 84, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) p. 2327.

[21] J. Houzvicka and V. Ponec, Appl. Catal. A 145 (1996) 95.

[22] J. Houzvicka and V. Ponec, Catal. Rev. Sci. Eng. 39 (1997) 319.

[23] R. Byggningsbacka, N. Kumar and L.-E. Lindfors, J. Catal. 178 (1998) 611.

[24] C.L. Baker and M.P. McGuiness, NPRA Annual Meeting, San Francisco (1995), paper AM-95-56.

[25] T.E. Helton, T.F. Degnan, D.N. Mazzone, M.P. McGuiness, T.L. Hilbert and R.C. Dougherty, Oil Gas J. 96 (1998) 58.

[26] N.Y. Chen, in: *Shape Selective Catalysis*, ACS Symp. Ser. No. 738, eds. C. Song, J.M. Garces and Y. Sugi (Am. Chem. Soc., Washington, DC, 2000) ch. 3.

[27] S.J. Miller, in: *Stud. Surf. Sci. Catal.*, Vol. 84, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) p. 2319.

[28] C. Song, in: *Shape Selective Catalysis*, ACS Symp. Ser. No. 738, eds. C. Song, J.M. Garces and Y. Sugi (Am. Chem. Soc., Washington, DC, 2000) ch. 27.