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Maximization of FCC light olefins by high severity operation and ZSM-5 addition

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Abstract

The effects of high severity operation and ZSM-5 addition on the FCC product yield structure have been studied in a MAT unit. VGO cracking at high reaction temperatures of 500–650°C increases the yield of light olefins (propylene and butenes) with a corresponding loss in gasoline yield and increase in dry gas formation. Similar behavior is observed with the addition of 0–20 wt.% ZSM-5 additive, however, with no increase in dry gas. The combination of the two effects (high severity and ZSM-5 addition) makes the FCC unit an excellent source of light olefins for downstream petrochemical and alkylation units. A novel downer reactor FCC configuration is proposed to suppress thermal cracking reactions and dry gas formation during high severity operation.

Keywords: FCC; Light olefins; ZSM-5 addition; High severity operation

1. Introduction

The FCC process continues to play an important role as gasoline producing unit in most oil refineries. Several FCC processes and catalysts are currently being developed to maximize the production of light olefins for petrochemical usage while maintaining high gasoline yield [1–4]. The increasing demand for light olefins is directing many FCC units towards maximizing their yields. Integrated petrochemical industry is continuously looking for processes with improved flexibility in producing various olefins (mainly propylene) from hydrocarbon feedstocks. Furthermore, the production of light olefins as petrochemical feedstocks is economically attractive for refineries integrated with petrochemical industries.

One of the FCC processes being developed is the high-severity FCC process (HS-FCC) that maximizes the selectivity to light olefins at high gasoline yield [5]. This process utilizes a down-flow reactor and operates above 550°C at short contact times and high catalyst/oil ratios. The process eliminates back-mixing in the downer reactor and obtains a narrower distribution of residence time. It is because of this optimum residence time that the yields of gasoline and light olefins can be maximized [6].

Light olefins are produced in the FCC unit mostly by beta-cracking of long chain paraffins, olefins, naphthenes and side chain of alkyl aromatics. Currently, the easiest FCC operation to maximize light olefins is to utilize a catalyst system that minimizes hydrogen transfer reaction in order to preserve olefins and maintain reasonable throughputs and good gasoline quality [7]. Usually, this is achieved by increasing the ratio of matrix cracking over zeolite cracking and by using

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dealuminated zeolites (low rare-earth content). The effectiveness of ZSM-5 is the highest with a catalyst having the lowest acid site density or lowest rare earth level on zeolite [8]. A reduction in hydrogen transfer is mostly effective for the production of *iso*-butene (at the expense of *iso*-butane). In case of propylene, thermal mechanisms also play a role [9].

One of the additives being used to maximize light olefins in conventional FCC units is ZSM-5. This zeolite was initially introduced into the FCC process as an additive for improving gasoline octane in the 1980s. ZSM-5 containing additives have been used in this combination in numerous commercial operations to date. As the current primary role of FCC as fuel producer is shifting towards a producer of light olefins and other petrochemical feedstocks, ZSM-5 is now used primarily to increase the yields of propylene and butenes. In commercial use, the additive is added in sufficient quantity to give 0.5–3.0 wt.% ZSM-5 (as crystal) in the circulating inventory with the primary Y-zeolite catalyst [10]. Typically, refiners have increased the reactor temperature and the ZSM-5 level to 1–3 wt.% and have increased propylene yields of 5–7 wt.% by 1–2 wt.% [3].

The present paper focuses on the effect of high severity FCC operation on product yield structure, mainly propylene and butenes. The paper also discusses the role of ZSM-5 additive in enhancing the production of light olefins as well as the associated loss in gasoline yield.

2. Experimental

2.1. Materials

A proprietary USY FCC catalyst specially designed for olefins maximization (supplied by CCIC) was used as a base catalyst in all microactivity tests (MATs). Grace Davison ZSM-5 additive was used in a diluted form that contained 25 wt.% ZSM-5 zeolite. The diluted form is preferable to using pure ZSM-5 in order to obtain a uniform dispersion of the small amount of ZSM-5 in the catalyst oil mixture [11]. The additive concentration in the base catalysts was varied from 0 to 20 wt.%. The ZSM-5 concentration used in this study is based on weight percent additive, not on crystal content.

Table 1
Chemical and physical properties of the FCC catalyst and ZSM-5 additive

Property	FCC catalyst	ZSM-5 additive
Chemical composition (wt.%)		
Al_2O_3	21.1	32.3
SiO_2	78.1	45.1
Re_2O_3	0.02	0.02
Fe	0.5	–
Loss on ignition (900°C, 3 h)	3.1	11.5
Physical properties (fresh catalyst)		
BET area (m^2/g)	237	33
Unit cell size (Å)	24.32	–
Physical properties (steamed at 810°C for 6 h)		
BET area (m^2/g)	184	–
Unit cell size (Å)	24.23	–

The chemical and physical properties of the catalyst and the additive are presented in Table 1. Alumina and sodium content of all the catalysts were determined by atomic absorption spectroscopy. The amount of rare earth oxide on catalyst (determined by spectrophotometric method) was about 0.02 wt.%. Loss of weight upon heating in air at 900°C for 3 h was 3.1 wt.% for the catalyst and 11.5 wt.% for the additive.

Surface area measurements were obtained on a Quantachrome Nova 1200 gas sorption apparatus following the BET procedure. The unit cell size (UCS) was determined using a Jeol X-ray diffraction system (JDX-3530) according to ASTM D-3942. The catalyst and the additive were steamed at 810°C for 6 h under 100% steam. This pretreatment is needed to equilibrate the activity of the catalyst to what is expected under industrial conditions.

A hydrotreated Arabian Light vacuum gas oil (VGO) was used in all MAT tests. The feed properties are presented in Table 2. Sulfur and nitrogen con-

Table 2
Properties of the hydrotreated vacuum gas oil feed

Density 15°C (g/cm^3)			0.896	
Sulfur (wt.%)			0.19	
Nitrogen (ppm)			440	
Conradson carbon (wt.%)			0.07	
Pour point (°C)			42.5	
Distillation curve (°C)				
IBP	10	50	90	FBP
321	378	447	537	620

tents in this paraffinic feed were about 0.19 wt.% and 440 ppm, respectively. The feed contains 0.07 wt.% of Conradson carbon and has a pour point of 42.5°C. The percentage of components boiling above 540°C was 7% compared to 10% for those boiling below 370°C.

2.2. Reaction procedure

VGO cracking was carried out in a fixed-bed MAT unit manufactured by Sakuragi Rikagaku, Japan, in accordance to ASTM D-3907. The operating conditions of the MAT unit are presented in Table 3. For each MAT test, a full mass balance was obtained. The cracking reaction was performed at three severities (500, 600 and 650°C), and the catalyst time on stream (TOS) in all experiments was 30 s. Conversion was varied by changing the catalyst to oil ratio (C/O) in the range 1.0–5.0 g/g. This variable was changed by keeping constant the amount of oil fed and changing the amount of catalyst between 1.0 and 5.0 g. Before each test, the system was purged for 30 min with a N_2 flow of 30 cm^3/min at the reaction temperature, and then about 1.0 g of VGO was fed. After this, stripping of the catalyst was carried out for 15 min using 30 cm^3/min of N_2. During the reaction and stripping, liquid products were collected in a glass receiver kept in ice-bath. Gaseous products were collected in a gas burette by water displacement.

A thorough gas chromatographic analysis of MAT products was conducted to provide detailed yield patterns and information on the selectivity of the catalyst being tested. The gaseous MAT product was analyzed using two Shimadzu GCs equipped with detectors (FID and TCD) for the quantitative determination of all light hydrocarbons up to C_4 and fixed gases. Three different liquid cuts were considered: gasoline (C_5, 221°C), LCO (light cycle oil, 221–343°C), and HCO (heavy cycle oil, +343°C). The weight percentage of these liquid products were determined by a simulated distillation GC according to ASTM D-2887 in order to calculate conversion and yield. The conversion was defined as 100% less the weight percent of LCO and HCO. Carbonaceous deposits on the catalyst were measured in a Strolein IR carbon analyzer.

Table 3
Operating conditions of the MAT test

Parameter	Value
Reactor temperature (°C)	500–650
VGO weight (g)	1.0
Catalyst/oil ratio (C/O) (g/g)	1.0–5.0
Contact time (s)	30
WHSV (h^{-1})	120/(C/O)

3. Results and discussion

3.1. Effect of reaction temperature

Conventional FCC units operate at around 500°C of the reactor outlet temperature. At this temperature, the simultaneous catalytic and thermal reactions have nearly equal contributions. In order to study the behavior at higher severity, the MAT reaction temperature was varied from 500 to 650°C. The results are presented in Table 4 and Fig. 1. In order to compare and interpret the results, the data are presented at constant conversion of 71 wt.%.

Although the yield of light olefins (propylene and butenes) increased significantly with increasing reaction temperature (10.8 wt.% at 500°C compared to 18.3 wt.% at 650°C), the corresponding gasoline yield decreased due to over-cracking (51.5–40.0 wt.%). Within this temperature range and at constant conversion, the increase in propylene and butene yields reached 93 and 52%, respectively. The increase in

Table 4
Effect of MAT temperature on product yields at 71 wt.% conversion and 0 wt.% additive

	Temperature (°C)		
	500	600	650
Catalyst/oil ratio (g/g)	4.5	2.7	2.0
Product yields (wt.%)			
Dry gas	1.1	5.3	9.1
Propylene	4.5	7.5	8.7
Total C_3's	5.1	8.5	9.7
Butenes	6.3	8.8	9.6
Total C_4's	11.6	12.2	11.0
Gasoline (C_5, 221°C)	51.5	43.4	40.0
LCO (221−343°C)	17.8	15.0	14.4
HCO (+343°C)	11.0	14.3	14.5
Coke	1.9	1.3	1.3

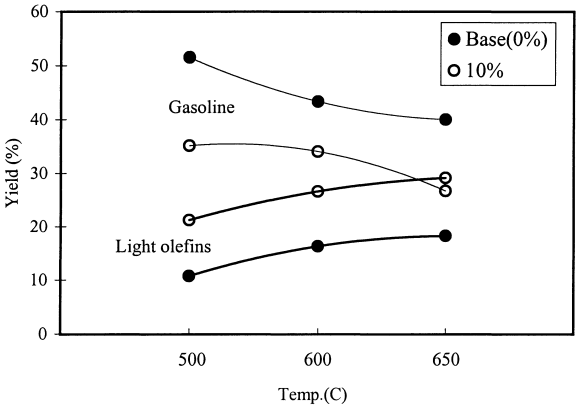

Fig. 1. Effect of reaction temperature on the yields of gasoline and light olefins at 71 wt.% conversion for base catalyst and 10 wt.% ZSM-5 additive.

total conversion is due to the significant increase in dry gas formation (thermal cracking effect). On the other hand, high severity operation had a much lower influence on HCO, LCO, and coke yields.

The increase in light olefins and dry gas coupled with the loss in gasoline yield is attributed to the paraffin dehydrogenation reaction which is more favorable at high temperature more than the hydrogenation of olefins to paraffins. The reaction rate of olefin production is faster at high severity than the rate of hydrogen migration on the catalyst surface from dehydrogenation sites to olefins hydrogenation sites. In commercial operation, the loss in gasoline yield at high reaction severity is partially compensated by a higher production rate of alkylate, if available. Furthermore, the loss in gasoline yield can be further compensated by adding a considerable amount of low-quality straight run naphtha to the gasoline pool. This is due to the fact that the research octane number (RON) of FCC gasoline obtained at high reaction temperature of 600–650°C is in the range 98–101 compared to 89–92 in a conventional FCC gasoline [6].

3.2. Effect of ZSM-5 addition

The effect of ZSM-5 addition on product yield structure at constant conversion and three reaction temperatures is presented in Tables 4–7. The effect of varying reaction temperature on the yields of gasoline and light olefins at 10 wt.% additive is shown in Fig. 1. Figs. 2–4 show the increase in the yields of C_2–C_4 light olefins as a function of ZSM-5 concentration and reaction temperature.

Table 5
Product yields at 500°C, 71 wt.% conversion and 0–20 wt.% additive

	Additive (wt.%)			
	Base 0	5.0	10.0	20.0
Catalyst/oil ratio (g/g)	4.5	4.5	4.3	4.0
Product yields (wt.%)				
Dry gas	1.1	+0.7	+1.3	+1.6
Propylene	4.5	+5.2	+6.4	+6.3
Total C_3's	5.1	+6.1	+7.7	+8.3
Butenes	6.3	+2.8	+4.0	+3.8
Total C_4's	11.6	+5.2	+7.2	+7.8
Gasoline (C_5, 221°C)	51.5	−12.3	−16.3	−17.6
LCO (221–343°C)	17.8	+0.3	−0.7	−0.9
HCO (+343°C)	11.0	0.0	+1.0	+1.2
Coke	1.9	+0.1	0.0	−0.3

The results show a significant increase in propylene and butenes associated with a decrease in gasoline yield. ZSM-5 addition increased propylene and butene yields by an amount approximately equivalent to gasoline yield loss. Such an effect of ZSM-5 is very well known and documented [12–14]. Of the four butenes, *iso*-butene showed the maximum yield. In general, ZSM-5 cracks the olefins before they undergo

Table 6
Product yields at 600°C, 71 wt.% conversion, and 0–20 wt.% additive

	Additive (wt.%)			
	Base 0	5.0	10.0	20.0
Catalyst/oil ratio (g/g)	2.7	2.4	2.0	4.0
Product yields (wt.%)				
Dry gas	5.3	+0.7	+1.1	+2.5
Propylene	7.5	+5.1	+5.5	+9.8
Total C_3's	8.5	+5.0	+5.8	+10.9
Butenes	8.8	+3.6	+4.8	+3.1
Total C_4's	12.2	+3.6	+3.6	+3.4
Gasoline (C_5, 221°C)	43.4	−8.9	−9.3	−16.6
LCO (221–343°C)	15.0	+0.3	+0.4	+2.0
HCO (+343°C)	14.3	−0.4	−0.9	−2.1
Coke	1.3	−0.3	−0.5	0.0

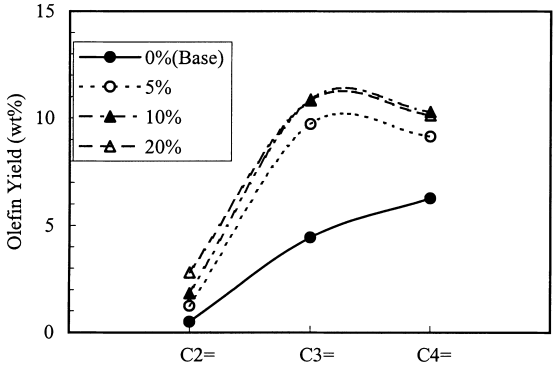

Fig. 2. Effect of ZSM-5 additive on the yields of C_2–C_4 light olefins at 500°C.

hydrogen transfer reactions as well as it enhances the isomerization of olefins as its activity drops. This explains why ZSM-5 loses its potential for the production of propylene while the gasoline octane is enhanced in many commercial FCC units [9]. ZSM-5 has a much lower potential to crack paraffins in the C_5–C_8 range and therefore unless reaction temperature is raised to 560–580°C, it will crack saturated gasoline only to a small extent.

Contrary to the effect of reaction temperature, ZSM-5 addition had lower influence on dry gas formation with a minor increase in ethylene yield at 650°C. However, at 500°C, ethylene yield increased with increase in the level of ZSM-5, indicating that Y-zeolite contributes little to the formation of ethylene [14]. There was also no major change in the yields of LCO, HCO, and coke yield within 5–20 wt.% additive. The propylene and butene yields showed a continuous increase with the increase in ZSM-5 concentration.

Table 7
Product yields at 650°C, 71 wt.% conversion, and 0–20 wt.% additive

	Additive (wt.%)			
	Base 0	5.0	10.0	20.0
Catalyst/oil ratio (g/g)	2.0	1.0	1.2	3.2
Product yields (wt.%)				
Dry gas	9.1	0.0	+0.5	+1.1
Propylene	8.7	+7.2	+7.8	+9.5
Total C_3's	9.7	+7.6	+8.5	+10.1
Butenes	9.6	+3.2	+3.0	+3.2
Total C_4's	11.0	+4.6	+4.0	+4.1
Gasoline (C_5, 221°C)	40.0	−12.3	−13.3	−15.6
LCO (221–343°C)	14.4	−0.6	+1.7	+0.7
HCO (+343°C)	14.5	+0.2	−1.7	−0.7
Coke	1.3	+0.6	+0.1	+0.3

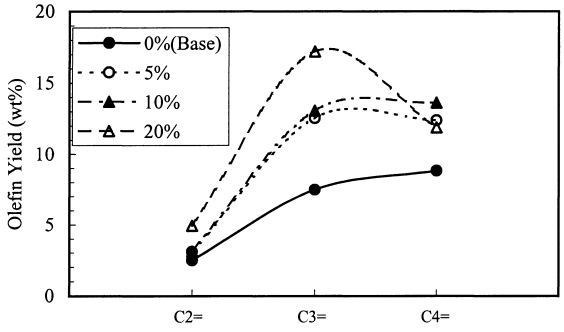

Fig. 3. Effect of ZSM-5 additive on the yields of C_2–C_4 light olefins at 600°C.

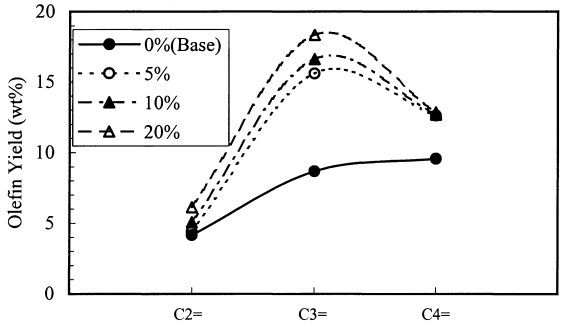

Fig. 4. Effect of ZSM-5 additive on the yields of C_2–C_4 light olefins at 650°C.

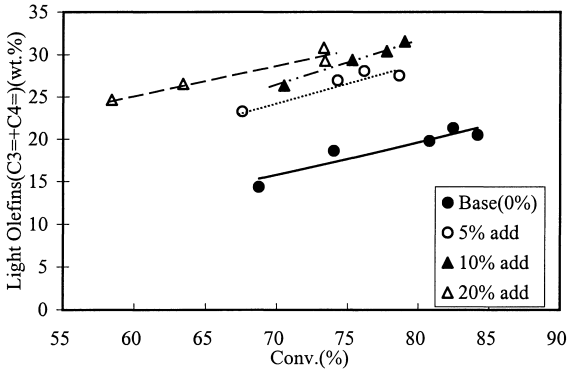

Fig. 5. Yields of light olefins versus conversion at 600°C.

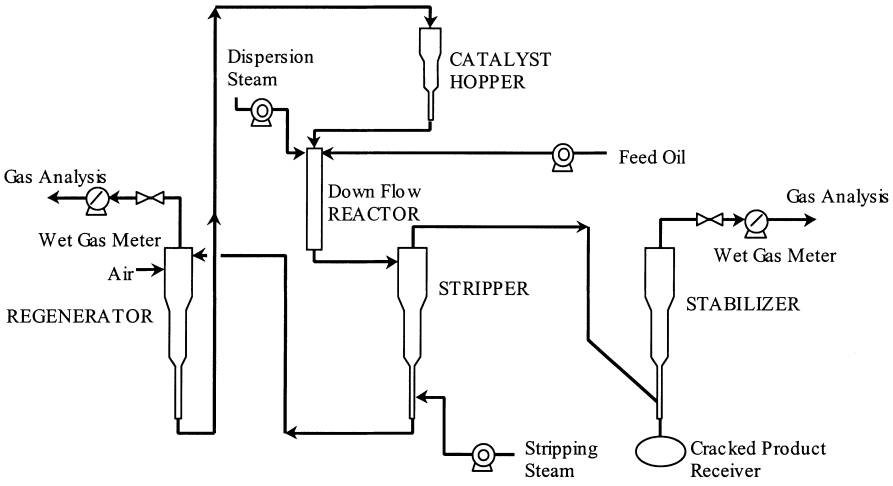

Fig. 6. Flow diagram of HS-FCC pilot plant.

Fig. 5 shows the increase in light olefin yields as a function of conversion level at 600°C. Minor drop in conversion level was observed within the range 0–20 wt.% ZSM-5 addition which is due to catalyst dilution.

At constant conversion of 71 wt.%, 500°C, and 10 wt.% additive (Table 5), the increase in propylene and butene yields reached 142 and 64%, respectively, compared with the base catalyst. However, at 650°C (Table 7), the increase was significant only for propylene at 90% compared to 3% for butenes. At 10 wt.% additive (Fig. 1), light olefins showed a continuous increase of about 10 wt.% between 500 and 650°C compared to an average loss of 13 wt.% in gasoline yield.

3.3. HS-FCC pilot plant

An HS-FCC process for maximizing light olefins is being developed by a joint research project between Petroleum Energy Center, Japan, and King Fahd University of Petroleum and Minerals, Saudi Arabia. A down-flow (downer) pilot plant was constructed by modifying the DCR (Davison circulating riser) unit to perform short contact time reactions. A schematic flow diagram of the pilot plant is shown in Fig. 6 [6]. The converter section consists of downer reactor, stripper, regenerator, and catalyst hopper. Catalyst circulation rates are controlled by three slide valves located below the stripper, regenerator, and catalyst hopper. The most important factors in this downer configuration are efficient catalyst-feed contacting, back-mixing, short contact time, and temperature. Preliminary testing results indicate that despite the fact that high reaction temperatures were used in the HS-FCC pilot plant, thermal cracking of hydrocarbons were suppressed because of negligible back-mixing in the downer reactor [6]. A 30 b/d HS-FCC demonstration plant is currently in the design stage. The unit will be constructed and operated near a Saudi refinery within the next 3 years.

4. Conclusion

Comparing the effects of high severity operation and ZSM-5 addition on FCC yield structure, it can be concluded that ZSM-5 addition is more efficient in increasing the yields of light olefins, mainly propylene. Increasing reaction temperature led to an increase in the yield of light olefins, however, it also produced unwanted dry gas coupled with high losses in gasoline yield. A temperature increase from 500 to 650°C only gave light olefins increase equivalent to about 5 wt.% ZSM-5 additive. On the other hand, combining the effects of high severity and ZSM-5 addition led to a significant increase in the yields of light olefins. Propylene and butene yields reached 17 and 13 wt.% at 650°C and 20 wt.% ZSM-5 additive, respectively.

With the increased demand for light olefins needed for petrochemicals, alkylate, and ether production, ZSM-5 usage is expected to increase in the coming years. However, in order to compensate for the inevitable loss in gasoline yield, a configuration with a downer reactor similar to the HS-FCC is needed in order to suppress thermal cracking and unwanted dry gas formation.

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