1. Introduction

Fluid catalytic cracking (FCC) continues to be the dominant conversion process for the production of gasoline and light olefins from heavy oils. The FCC product slate is increasingly shifting towards light olefins production (mainly propylene), and refiners are under pressure to process heavier crude. Therefore, increasing the yield of the valuable light olefins, especially that of propylene produced by FCC, remains a major challenge for many refiners worldwide.

Average annual demand growth for propylene is expected to be around 5% during 2009-2013. Currently, 30% of the world’s propylene is supplied by refinery FCC operations, 64% is co-produced from thermal steam cracking of naphtha or other feedstock, and the remainder is produced on-purpose using metathesis or propane dehydrogenation processes.

Naphtha cracking is a thermal cracking process used to produce the major part of the propylene supply. However, the yield ratio of propylene/ethylene is only 0.50-0.65 mass/mass with naphtha cracking. Ethane cracking is very competitive for the production of ethylene in some oil production countries. However, ethane cracking does not produce propylene. Therefore, increased FCC propylene production is needed to meet the high growth demand for propylene.

Conventional FCC units typically produce about 3.6 wt% propylene depending on feed type, operating conditions, and type of catalyst. ZSM-5 containing additives were originally used to boost gasoline octanes, but are now frequently used to increase the yield of light olefins, specifically propylene. Propylene yield can be increased up to 10 mass% using ZSM-5 additive, in commercial applications. Minor changes in catalyst and FCC reaction conditions have been investigated in many studies to increase propylene production. Changes in equipment design, such as riser termination devices, were also studied. However, higher propylene yield is difficult to achieve with minor changes in the FCC process. Introduction of a new catalyst requires new reaction conditions, which in turn require a new reactor. Recent research of catalysts, reaction conditions and reactors has developed a new process called High Severity FCC (HS-FCC), and achieved more than...
20 mass% propylene yield. This paper discusses the initial phase of HS-FCC development, which includes catalyst development and optimization of reaction conditions.

2. Experimental

2.1. Fixed-bed MAT

Catalyst performance was measured by a micro activity test (MAT) according to ASTM D 3907. Figure 1 shows the typical schematics of a MAT system. The catalyst was kept in a fixed-bed reactor and feed oil is injected from the top of the reactor. Gas and liquid product were collected separately for further analysis. Reaction conditions were selected within the following range. The feed injection period is called "Time-on-stream."

- Temperature: 500-700°C
- Pressure: atmospheric
- Catalyst/Oil ratio (C/O): 3-6 mass/mass
- Time-on-stream (TOS): 10-60 s

Table 1 shows the typical properties of the vacuum gas oil (VGO) used as feed in MAT tests. The evaluation of catalysts containing ultrastable Y (USY) zeolite is discussed in Section 3.2. The catalysts were pretreated with 100% steam at 750°C to obtain pseudo-equilibrium catalysts. The steam condition was selected empirically to form steam-treated catalyst with the same activity as actual equilibrium catalyst in commercial FCC units.

Equilibrium catalyst withdrawn from a commercial FCC unit was used to study the effect of reaction conditions on product yields. The catalyst was convenient in providing the same catalyst activity for every experiment, especially in pilot plant testing which needs large amounts of catalyst.

2.2. 0.1 BPD Pilot Plant

Experiments were also conducted in a 0.1 BPD (barrel/day) pilot plant. Figure 2 shows a schematic flow diagram of the pilot plant which consisted of a riser reactor, stripper and regenerator. Feed oil is charged into the bottom part of the riser reactor together with dispersion steam. Regenerated catalyst is also charged at the bottom of the reactor from the regenerator. At the outlet of the riser reactor, product hydrocarbons are cooled and separated immediately from the catalyst in a stripper, where heavy oil adsorbed on the spent catalyst is stripped by steam, and spent catalyst is sent to the regenerator. The height of the riser reactor was around 2 m and the inner diameter was about 15 mm.

Reaction conditions were selected from the following range. Contact time was calculated by dividing the reactor volume by reactor outlet gas volume flow rate.

- Temperature: 470-700°C
- Pressure: 100-200 kPaG
- Catalyst/Oil ratio (C/O): 7-70 mass/mass
- Contact time: 0.2-2.0 s

The heat needed for the cracking reaction in an adiabatic commercial FCC unit is usually supplied by coke burning in a regenerator. However, the pilot plant was too small to be an adiabatic plant. Therefore, the vessels and piping of the plant were heated by electric heaters. As a result, the reaction temperature and C/O ratio could be adjusted independently in the pilot plant. However, the reactor outlet temperature is actually lower than the inlet temperature in the pilot plant because cracking is a highly endothermic reaction.
3. Results and Discussion

3.1. Optimization of Reaction Conditions

In order to optimize the reaction conditions to maximize propylene yield in a FCC unit, the effects of reaction temperature, contact time and catalyst/oil ratio on the reaction were investigated using commercial equilibrium FCC catalyst.

3.1.1. Reaction Temperature

The effect of reaction temperature was evaluated by the MAT using a commercial equilibrium FCC catalyst. Figure 3 shows the effect of reaction temperature on the yield of light olefins at similar C/O ratios and Time-on-stream. Ethylene yield increased significantly with increasing temperature, presumably due to the contribution of the thermal cracking reaction. Propylene yield also increased with temperature. Butenes yield also increased with temperature, but decreased at 700°C, presumably due to the thermal cracking of butenes, because butene is difficult to crack by β-scission.

Figure 4 shows the relationship between the isobutene/isobutane ratio and reaction temperature. Conversion was higher at high reaction temperature. The isobutene/isobutane ratio increased almost linearly with temperature. High olefin ratio reflects relatively low hydrogen transfer activity, although high temperature accelerates both cracking and hydrogen transfer reactions. This finding indicates that the activation energy of hydrogen transfer was lower than that of catalytic cracking.

According to these results, the temperature range of 550 to 650°C was selected as the reaction temperature for the HS-FCC process to maximize propylene yield. This range is considerably higher than the temperature range used in conventional FCC units.

3.1.2. Contact Time

The effect of contact time on yield profile was investigated using the 0.1 BPD pilot plant. To obtain short contact time, both feed rate and catalyst circulation rate were increased to maintain constant C/O ratio in the series of experiments. Reaction temperature was maintained at 600°C.

Figure 5 shows the results of the series of experiments. The olefin ratio became higher with shorter contact time showing that short contact time (less than 0.5 s) of the feed with catalysts in the reactor is favorable to minimize undesirable secondary reactions such as hydrogen-transfer reactions, which consume olefins.

3.1.3. Catalyst/Oil Ratio

Two competing cracking reactions, thermal cracking and catalytic cracking, occur at high reaction temperature. The thermal cracking reaction contributes to the formation of undesirable products such as dry gas and coke. A series of experiments was conducted with varied C/O ratios at a constant reaction temperature, 600°C, maintained using the heaters in the pilot plant, to eliminate the effect of temperature on the reaction.

Figure 6 shows that dry gas formation was decreased at high C/O ratio, indicating that high C/O ratio accelerated only catalytic cracking over thermal cracking. When the C/O ratio was increased to 40.7 from 17.5, coke deposition on spent catalyst decreased to 0.089 mass% from 0.107 mass%. Therefore coke yield increased with high conversion accompanying high C/O ratio, but coke amount on unit weight of catalyst became smaller with high C/O ratio. The lower rate of coke deposition on catalyst at high C/O ratio presumably enhanced catalytic cracking, so that ther-
mal cracking was relatively suppressed. In order to compensate for the inevitable decrease in conversion caused by use of low activity catalyst, as discussed in the next section, and short contact time, the HS-FCC process should be operated at high C/O ratio, in the range of 15 to 25. Another advantage of operating at high C/O ratio is the enhancement of catalytic cracking over thermal cracking as mentioned above. By increasing the C/O ratio, the effect of thermal cracking at high reaction temperature can be suppressed.

High C/O ratio has further importance in a commercial FCC unit as the heat transfer from the regenerator to the reactor is increased, thus achieving the high reaction temperature required for HS-FCC.

3.2. Catalyst Evaluation

The main objective of the HS-FCC process is to produce significantly more propylene and high-octane gasoline. Therefore, suitable catalysts to maximize propylene yield at high temperatures were identified.

Catalytic cracking, which is the main reaction of FCC, occurs on the acid sites of zeolites. Hydrogen transfer also occurs on the same acid sites. Olefins, such as propylene, are converted to paraffins by the hydrogen transfer reaction. Therefore, hydrogen transfer should be suppressed to maximize olefins production. Hydrogen transfer is a bimolecular reaction and catalytic cracking is a monomolecular reaction. Consequently, the hydrogen transfer reaction could be suppressed by using zeolite with low acid density, because the bimolecular reaction needs adjacent acid sites.

Six USY zeolites with small Unit Cell Size (UCS), including lower acid densities compared with the normal USY used for conventional FCC processes, were prepared. FCC catalysts were prepared from these USY zeolites. All catalysts were pretreated with 100% steam in MAT experiments to obtain pseudo-equilibrium catalysts. A series of MAT experiments was conducted on the catalysts using similar C/O ratio and Time-on-stream. Reaction temperature was fixed at 600°C according to the results of reaction conditions optimization, although conventional FCC is operated around 500°C.

Figure 7 shows the relationship between UCS of USY zeolite and isobutene/isobutane ratio. Conventional FCC catalysts have UCS in the range corresponding to the value shown as “Base” or higher in Fig. 7. Figure 7 shows that the isobutene/isobutane ratio increased with lower UCS, indicating that hydrogen transfer was reduced with the lower acid density of zeolites with low UCS. However, the cracking activity of the catalysts also decreased with lower UCS as shown in Fig. 8. The cracking activity, is shown with kinetic conversion $X/(1 - X)$, where $X$ is conversion, assuming the cracking reaction as a second order reaction.

These results agree well with previous conclusions. Since hydrogen transfer is a bimolecular reaction, the reduction of hydrogen transfer activity can be attributed to the lower density of acid sites. At the same time, cracking activity decreased because of the lower quantity of acid sites.

Use of the low UCS zeolite was expected to produce olefin-rich products, but the combination of the low UCS zeolite and the reaction conditions for enhancing cracking activity was thought necessary to compensate for the reduction in conversion to maximize propylene
production. Therefore, the HS-FCC proprietary catalyst with low UCS was compared with a conventional FCC catalyst in the 0.1 BPD pilot plant. Reaction temperature was fixed at 600°C, and conversion was varied by changing the C/O ratio. Figure 9 shows that the HS-FCC catalyst maintained higher isobutene/isobutane ratio throughout the conversion range in comparison with the conventional FCC catalyst. Therefore, the low UCS type zeolite was optimum for maximizing olefin yield even at a high conversion level in combination with the optimal reaction conditions and was chosen as the HS-FCC proprietary catalyst.

4. Conclusions

Optimization of reaction conditions and catalyst development were conducted to maximize FCC propylene yield through the development of a process called HS-FCC.

High reaction temperature accelerated catalytic cracking rather than thermal cracking. Short contact time suppressed undesirable reactions such as hydrogen transfer and thermal cracking. High C/O ratio accelerated catalytic cracking rather than thermal cracking, which is accelerated at high reaction temperatures. Operating at high C/O ratio is also necessary to maintain high reaction temperature in a commercial FCC unit.

A proprietary catalyst which contains low-acid density zeolite was developed. The catalyst could suppress hydrogen transfer reaction and has the potential to maximize propylene yield. However, the low-acid density zeolite has low cracking activity and requires a severe reaction conditions.

High temperature and high C/O ratio allow high conversion even using a low-acid density catalyst. Therefore, the HS-FCC process can maximize propylene yield with the optimum combination of catalyst and reaction conditions.

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References

要 旨

プロピレン生産のための高過酷度 FCC プロセスの開発
—触媒開発と反応条件の最適化—

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製油所でのプロピレン収率の増大を目指し, 高過酷度流動接
触分解（HS-FCC）と名づけたプロセスを開発した。本プロセ
スにおいては特殊な開発触媒、プロピレン生産のために最適化
した反応条件、ダウンフローリアクターの組合せによってプロ
ピレン収率を最大化する。本論文においては反応条件の最適化
および触媒開発について報告した。反応条件の検討について
は、反応温度を高くすることにより水素移行に比べ分解反応を
優勢にすことができる、生成物のオレフィン／パラフィン比を
高くできることを見出した。同時に短接触時間とすることで水
素移行や熱分解などの二次的に発生する応応を抑制した。さら
に、触媒／油比を高くすることで高温で加速される熱分解反応
の寄与を抑制することができた。商業装置では高触媒／油比は
熱バランス上、反応器を高温に保つために必要である。高温
で用いる場合に高いオレフィン収率をもたらそうる触媒の開発
を行った。酸密度の低いロジオライトを採用することでオレフィ
ン収率を低下させる原因となる水素移行反応を抑制でき、高い
オレフィン収率を達成しうる触媒組成を見出した。