The characteristics and the effect of ZSM-5 additive to increase light olefin fraction in fluid catalytic cracking (FCC)

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Abstract:
ZSM-5 additive is usually used to increase light olefins yield in fluid catalytic cracking [1]. In this work, the performance of our commercial ZSM-5 additives are compared by using laboratory testing unit ACE-MAT. Our new ZSM-5 additives are able to improve the butene selectivity or the propylene yield under high contaminant metal (nickel and vanadium) condition such as RFCC reaction as compared with our conventional ZSM-5 additives.

Keywords: Light olefin, Fluid Catalytic Cracking (FCC), ZSM-5 additive

1. Introduction

Fluid Catalytic Cracking (FCC) is one of the most important conversion processes in the oil refinery. In FCC unit, heavy oil is cracked to valuable lighter fractions (e.g. middle distillate, gasoline, and LPG). Usually, the operation of a commercial FCC unit must be continuously adjusted to increase the margin for the change of feedstock and target yield. Recently, the demands of light olefins such as propylene and butene for petrochemicals have increased. Refineries usually use ZSM-5 additive to increase light olefins yield. We have developed various ZSM-5 additives to meet such refiner's needs to increase light olefins and commercialized them as "OCTUP" series[2]. In this work, the performance of our ZSM-5 additives (OCTUP-α, OCTUP-C4, and OCTUP-MT) are compared by using laboratory testing unit ACE-MAT.

2. Experimental

In this work, the latest three our commercial ZSM-5 additives (OCTUP-α, OCTUP-C4, OCTUP-MT) were evaluated as follows. Prior to the reaction test, each additive sample was deactivated at 750℃ for 13hr under 100% steam condition without metals (OCTUP-α and OCTUP-C4) or deactivated at 810℃ for 12hr under 100% steam after impregnated with nickel and vanadium (Ni ppm/V ppm=0/0, 1000/2000, 2000/4000) on additives (OCTUP-α, OCTUP-MT). Those deactivated samples were mixed with a FCC equilibrium catalyst at the rate of 2.4% and/or 5.0% in the total catalyst. FCC reaction test were carried out with a fixed-fluidized micro activity test unit (ACE- R+ MAT unit: purchased from Zytel corporation in the United States) using refinery's DSVGO(sulfur=0.2%, density=0.904g/ml@15℃) at 510℃ reactor temperature, and Cat/Oil =5.

3. Results and discussion

OCTUP-α is high activity type ZSM-5 additives and has widely used in the world. Table 1 shows the test results of three ZSM-5 additives, indicated as the delta of each yield and RON from those without the additives. OCTUP-C4 was designed to improve butene selectivity more than our conventional ZSM-5 additives by controlling the solid acidity of incorporated ZSM-5 crystal. OCTUP-C4 indicated the same propylene yield, higher butene/LPG ratio and RON compared to OCTUP-α at same LPG yield. Figure 1 shows the carbon number distribution of hydrocarbons in gasoline range measured by GC-FID-GPI system. With OCTUP-C4, cracked gasoline contains less C8-C9 but more C5-C7 than that compared with OCTUP-α. These results suggest that OCTUP-C4 cracked C8-C9 in gasoline selectively and on the other hand it suppresses the cracking of C5-C7, which leads to the observed higher RON gain of OCTUP-C4 over OCTUP-α

OCTUP-MT was designed to possess the higher metal tolerance by incorporation of metal-trap agents into ZSM-5 additive. Figure 2 shows the change of propylene yield versus increase of metal (nickel and vanadium) deposition level on ZSM-5 additives. OCTUP-MT was able to suppress the decrease of propylene yield as the metal content increased compared with OCTUP-α.

Table 1. Performance result of the ZSM-5 additives in JGC C&C

ZSM-5 Additive of JGC C&C	Additive Input (%)	Metal free, 750℃-13hr steaming					Ni/V=2000ppm/4000ppm 810℃-12hr steaming	
		ΔC3= (%)	ΔC4= (%)	ΔLPG (%)	ΔC4=/ΔLPG	ΔRON (%)	ΔC3= (%)	ΔLPG (%)
OCTUP-α	2.4	+3.7	+2.3	+7.7	0.30	+2.1	+1.7	+4.0
OCTUP-C4	5.0	+3.8	+2.6	+7.9	0.33	+3.1	–	–
OCTUP-MT	2.4			–			+2.4	+5.7

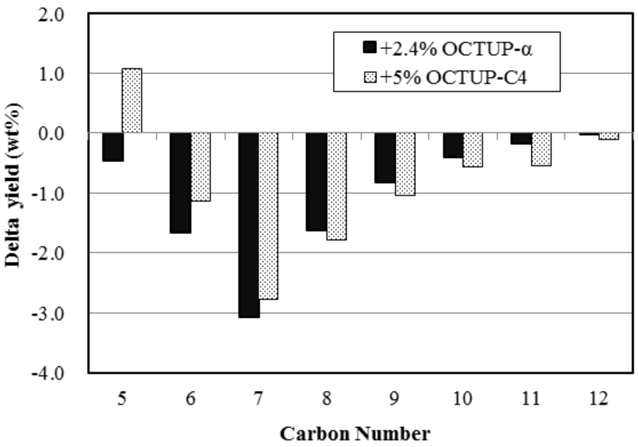

Figure 1. Carbon number distribution of chain hydrocarbons in produced gasoline fraction.
Delta yield (%)=[Yield with ZSM-5 additive]-[Yield without ZSM-5 additive]

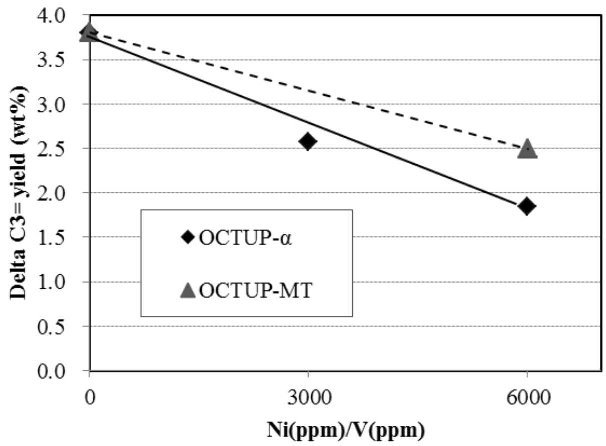

Figure 2. The change of delta propylene yield versus increase of metal (nickel and vanadium) contents of OCTUP-α and OCTUP-MT

4. Conclusions

We have developed various ZSM-5 additives to meet refiner's needs. In this work, our commercial ZSM-5 additives (OCTUP series) are evaluated by using laboratory testing unit ACE-MAT. OCTUP-α has higher activity to increase propylene yield with a little addition amount. On the other hand, OCTUP-C4 shows higher butene/LPG ratio and RON than OCTUP-α due to the modified acid property. OCTUP-MT has improved metal tolerance compared with OCTUP-α, and refineries can expect more light olefins yield under high contaminant metal (nickel and vanadium) condition such as RFCC reaction.

References

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