Effect of feedstock properties on the performance of ZSM-5 additive in catalytic cracking reaction

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Abstract

In this study, we present our recent laboratory experimental results regarding the application of ZSM-5 additive in catalytic cracking reactions. Our results show that the nature of feedstock significantly influences the performance of ZSM-5. For paraffinic feedstock, ZSM-5 additive not only increases propylene yield and gasoline octane but also improves the bottom cracking ability of Fluid Catalytic Cracking (FCC) catalysts. The conversion of paraffinic feedstock could increase up to 10wt% while that of aromatic feedstock remains almost unchanged upon the addition of ZSM-5 additive to the FCC catalyst. Mixing 5wt% of ZSM-5 additive with the FCC catalyst also results in increased propylene yields of 13wt% and 8wt% for paraffinic and aromatic feedstock, respectively. Our results can serve as guidance for refineries to flexibly control product yields by adjusting the processed feedstock or the amount of ZSM-5 additive used in the FCC unit.

Introduction

Propylene is one of the key products of refineries, particularly for those which integrate petrochemical plants such as a polypropylene (PP) plant. Due to the decline of crude oil resources, refineries are now facing the challenge of adapting their operation to a variety of feedstocks in which assuring a stable supply for downstream petrochemical plants such as the PP plant is a key issue. On the other hand, the continuous change in market demand also requires refineries to have certain operating flexibilities in order to maximize their profit. For example, depending on the relative prices of their main products such as gasoline, diesel, and propylene in the market, refiners often have to adjust the product slate to maximize the margin. Therefore, a flexible solution to adjust those product yields is of vital importance for refineries nowadays. Fig.1 shows the changing relative prices of the main refining products in the period of 2008 - 2011.

In order to adjust the propylene yields, it is quite common that ZSM-5 additive for catalyst is applied in FCC units, from which most of propylene in the refinery is produced [1]. ZSM-5 is a small pore (5 - 6Å) and high Si/Al (30 - 200) zeolite compared to those of Y zeolite (7 - 8Å pore and Si/Al of 3 - 6). As a result, ZSM-5 selectively cracks the gasoline hydrocarbon (C5 - C12) to light olefins such as propylene and butene [2]. On the other hand, ZSM-5 also facilitates the isomerization of straight olefin to branched olefin in the gasoline fraction. The resulting effect is the improvement of light olefin yields and of gasoline octane at the expense of gasoline yield [3]. However, the effectiveness of ZSM-5 is largely dependent on the feedstock nature and the applied concentration. Therefore, in this study, we investigated the effect of feedstock properties and ZSM-5

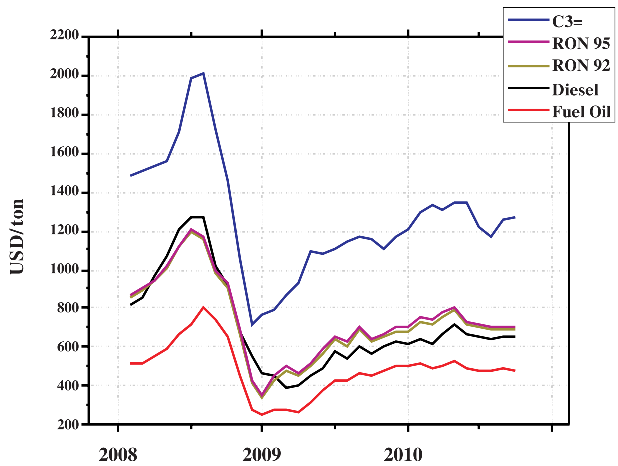

Fig.1. *Relative price of different refining products in the period of 2008 - 2011*

additive concentration on the product yields of catalytic cracking reactions. Our results can serve as guidance for refineries to flexibly control product yields by adjusting the processed feedstock or the amount of ZSM-5 additive used in FCC units.

Experiment

FCC catalyst and ZSM-5 additive samples are commercial products obtained from Grace Davison. The feedstocks were obtained by distillation of different commercial crude oils, from which the residue fraction (370°C+) was collected. The main properties of the FCC catalyst, ZSM-5 additive and feedstocks are shown in Table 1 and 2, respectively. Four feedstocks used in this study show different properties ranging from very paraffinic (AR1, AR2) to aromatic in nature (VGO2) as can be seen by some main properties such as aniline point and wax content.

The FCC catalyst and ZSM-5 additive were separately steam deactivated for 12 hours at 816°C prior to the cracking experiment. The properties of deactivated catalyst and ZSM-5 additive are shown in Table 3. For the cracking experiments, the FCC catalyst/ZSM-5 blends (~ 10g each) were prepared by mechanical mixing of deactivated FCC catalyst and ZSM-5 additive. The concentration of ZSM-5 in the blend was varied between 0 - 20wt% by changing the amount of ZSM-5 additive in the mixture.

Cracking experiments were performed by a fixed bed short contact time Micro Activity Test (SCT-MAT) designed and built by Grace Davison. All experiments were performed at the temperature of 560°C and the same catalyst/oil ratio with the amount of feed and time-on-stream were kept constant at 1.75g and 12s, respectively. Gaseous cracking products were analyzed by Refinery Gas Analysis Gas Chromatography (GC RGA) according to ASTM D-1945-3 standard, whereas Simulated Distillation Gas Chromatography (GC SIMDIS) and carbon analyzer were used for the liquid fraction and for coke analysis according to ASTM D-2887 and ASTM E-1915 standards, respectively. The gasoline octane was calculated from the detailed hydrocarbon analysis (DHA) performed by Gas Chromatography (GC DHA). The conversion is defined as:

Conversion = 100% - LCO (%) - HCO (%) where:

LCO is Light Cycle Oil, which is the liquid fraction with the boiling point in the range from 216 - 360°C;

HCO is Heavy Cycle Oil, which is the liquid fraction with the boiling point above 360°C.

Results and Discussion

The effects of ZSM-5 concentration on the propylene yield in cracking products and the conversion of 4 different FCC feedstocks are shown in Fig. 2 and 3, respectively. It is clear that upon the addition of ZSM-5 to the FCC catalyst, a large increase of propylene yield is observed for all feedstocks. The maximum increase is obtained at the ZSM-5 concentration of 5wt%, at which propylene yield increases by 13wt% for paraffinic feedstocks (AR1, AR2) and 8wt% for aromatic feedstock (VGO2). The higher increase of propylene yield for paraffinic feedstock is due to the fact that the gasoline fraction in the cracking products of paraffinic feedstock contains higher olefin content (42%) compared to that (23.6%) of aromatic feedstock as shown in Table 3. Since the cracking rate of olefin on ZSM-5

Table 1. *FCC catalyst and ZSM-5 additive propertie*

Catalyst	FCC catalyst	ZSM-5 additive
Zeolite surface area, m^2/g	131.22	136.59
Matrix surface area, m^2/g	116.06	22.97
P_2O_5, %wt	-	8.88
RE_2O_3, %wt	0.99	-
Al_2O_3, %wt	56.35	24.02
Unit cell size, Å	24.57	-
ZSM-5, wt%	-	50.00
Pore volume, cc/g	0.25	0.09
Average particle size, µm	62.80	77.90
Attrition Index	4.85	1.20

Table 2. *Feedstock properties*

Feedstock	VGO 1	VGO 2	AR 1	AR 2
Density at 15°C (g/ml)	0.8983	0.9104	0.9158	0.9176
API°	25.90	23.80	22.90	22.60
Conradson carbon, wt%	0.06	0.23	4.37	2.03
Wax, wt%	24.29	13.13	35.60	42.80
Aniline point, °C	97.00	86.00	121.40	118.60

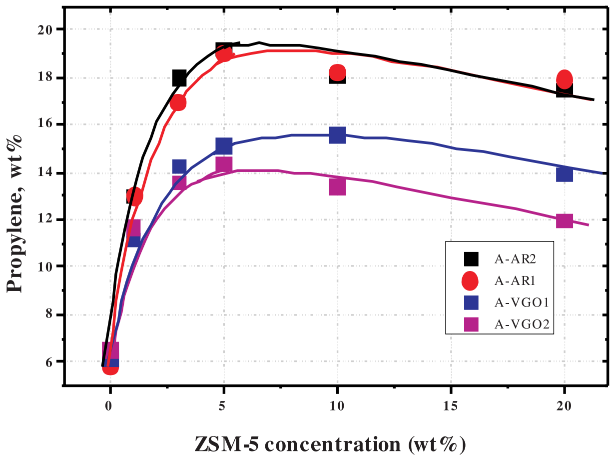

Fig.2. *Propylene yield in cracking products of different FCC feedstocks as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend*

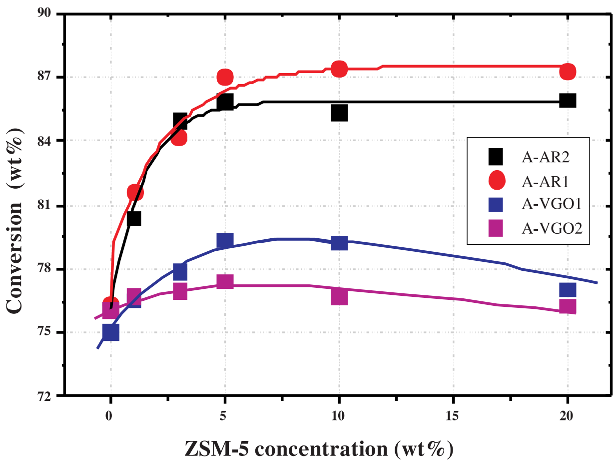

Fig.3. *Conversion of different FCC feedstocks as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend*

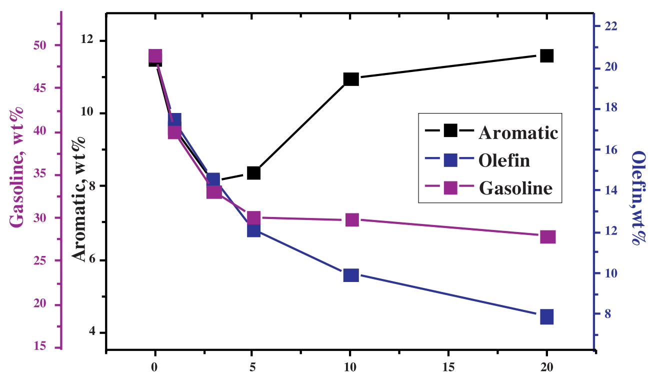

Fig.4. *Gasoline aromatic and olefin yields (AR2 feedstock) as a function of ZSM-5 additive concentration in FCC/ZSM-5 blend*

is faster than the other hydrocarbon types, this leads to a higher increase of propylene yield [4, 5]. At the ZSM-5 concentration higher than 5wt%, the propylene yields start decreasing due to other competing reactions on ZSM-5 such as oligomerization or aromatization of propylene. Both oligomerization and aromatization of light olefin on ZSM-5 catalyst have been observed, however, the oligomerization is facilitated at high pressure and low temperature while the latter is favored at low pressure and high temperature. At the reaction temperature of 560°C in this case, therefore, aromatization is much more favorable than oligomerization. This is supported by the fact that the aromatic content in the gasoline fraction increases quickly when the ZSM-5 concentration exceeds 5wt% as shown in Fig.4.

The effect of ZSM-5 on the conversion also depends on the nature of the feedstock. As shown in Fig.3, the conversion of paraffinic feedstock (AR2) could increase up to 10wt% at ZSM-5 concentration of 5wt%, while that of aromatic feedstock (VGO2) remains almost unchanged upon addition of ZSM-5 additive to the FCC catalyst. In the ZSM-5 concentration range between 5 - 20wt%, the conversion of paraffinic feedstock remains constant, whereas that of aromatic feedstock starts decreasing. The increase of conversion upon addition of ZSM-5 to FCC catalyst is a surprising result since it is usually believed that ZSM-5 does not affect the conversion in the cracking reaction due to its small pore structure which prevents the large hydrocarbon molecules in LCO, HCO fraction from diffusing into the pore and reaching the reactive sites. This can be seen in Fig. 6; as the ZSM-5 concentration increases, the gasoline yield decreases quickly while there is a slight decrease in LCO and HCO yields. The HCO yield starts increasing at the ZSM-5 concentration of 3wt% due to the diluted active matrix content in the catalyst mixture at increasing ZSM-5 concentration, which leads to a lower bottom cracking ability. In the other words, for aromatic feedstock, the reactivity on ZSM-5 is in the order: Gasoline > LCO > HCO. The LCO and HCO fraction of aromatic feedstock contains mainly the aromatic hydrocarbon, which is too large to get into the pore of ZSM-5.

On the other hand, the order of reactivity on ZSM-5 of paraffinic feedstock is quite different (HCO > LCO ≈ Gasoline) as shown in Fig. 5. Here the result indicates that the HCO fraction is consumed more rapidly than the Gasoline and LCO fractions as ZSM-5 concentration increases. As a result, a large increase of conversion is observed for paraffinic feedstock upon addition of ZSM-5 to FCC catalyst. This opposite effect observed on paraffinic feedstock is due to the fact that the HCO fraction of paraffinic feedstock contains a high amount of long, straight chain paraffins with small kinetic diameter, which can more easily penetrate into the small pore of ZSM-5 than their aromatic counterparts [5, 6]. The higher reactivity of HCO fraction, compared to that of LCO and Gasoline fractions, is reasonable since the longer the length of the hydrocarbon molecule, the faster it is cracked on zeolite [7]. The HCO yield starts increasing at ZSM-5 concentration of 5wt% which again is again due to the dilution effect mentioned above.

Our results are also in agreement with Dupain et al.'s study [6], in which cracking of highly paraffinic Fischer-Tropsch (FT) wax was investigated. They observed that the FCC catalyst/ZSM-5 blend displays higher reactivity than that of FCC catalyst for the cracking reaction of highly paraffinic FT wax [6]. This is due to the fact that HCO range olefins, which are produced by pre-cracking on the FCC catalyst, are crackable on ZSM-5 and there is a synergy effect between FCC catalyst and ZSM-5 additive.

Table 4 shows the effect of ZSM-5 additive on the gasoline octane in cracking product of 4 different feedstocks. Aromatic feedstock (VGO2) shows a larger improvement of gasoline octane (ΔRON = 3.4) compared to that (ΔRON = 1.37) of paraffinic feedstock (AR2) when ZSM-5 concentration increases from 0 to 5wt%. The rate of gasoline octane increase, however, is similar for all feedstocks in the ZSM-5 concentration region of 5 - 20wt%. The larger octane enhancement of aromatic feedstock compared to that of paraffinic feedstock can be explained from the difference in gasoline components. By adding ZSM-5 at 5wt%, the aromatic content of the gasoline fraction in cracking products of aromatic feedstock (VGO2) increases by a factor of 1.37 (from 38.79 - 53.04), while that of paraffinic feedstock (AR2) only increases by a factor of 1.19 (from 23.38 - 27.85%). As a result, the effect of ZSM-5 addition on the gasoline octane improvement for aromatic feedstocks is more profound than that for paraffinic feedstocks.

Conclusions

Our results have shown that using ZSM-5 additive for FCC catalyst could improve the propylene yield and gasoline octane for all feedstocks investigated. ZSM-5 additive was found to be the most effective on paraffinic feedstock as both propylene yield and conversion are significantly increased upon addition of ZSM-5 to the FCC catalyst. At ZSM-5 concentration of 5wt%, the propylene yield and conversion could increase by 13wt% and 10wt%, respectively. Particularly, the effect of ZSM-5 on bottom (HCO) cracking ability of FCC catalyst for paraffinic feedstock, observed in this study, is unprecedented. The fact that ZSM-5 could improves propylene yield and conversion of paraffinic feedstock at the same time is a very beneficial effect for refineries. In contrast, it was found that gasoline octane improvement by ZSM-5 is higher for aromatic feedstocks compared to that of paraffinic feedstocks. To further clarify the mechanism by which cracking of paraffinic feedstock is enhanced by addition of ZSM-5 to FCC catalyst, synthetic feedstocks with varied paraffinicity can be prepared by mixing

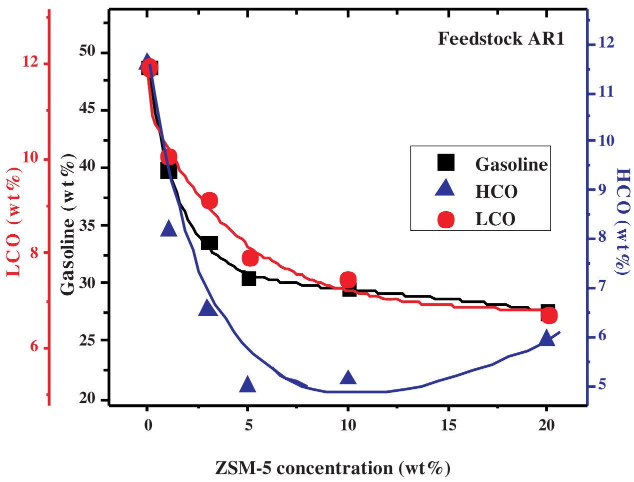

Fig.5. *Main cracking products of paraffinic feedstock (AR1) as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend*

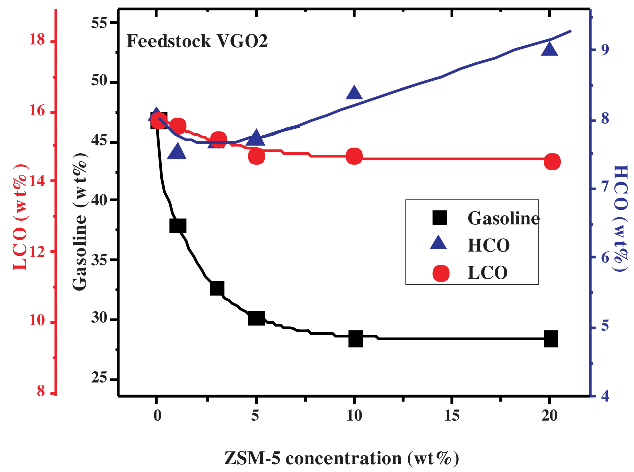

Fig.6. *Main cracking products of aromatic feedstock (VGO2) as a function of ZSM-5 additive concentration in FCC catalyst/ZSM-5 blend*

Table 4. *Gasoline octane and composition in cracking products of 4 feedstocks at different ZSM-5 additive concentration*

Additive, wt%	Conversion, wt%	Dry gas, wt%	Propylen, wt%	LPG, wt%	Gasoline, wt%	LCO, wt%	HCO, wt%	Coke, wt%
A-AR1								
0	76.42	2.65	5.88	19.96	48.79	11.95	11.58	4.87
1	81.67	3.15	13.02	33.24	39.94	10.08	8.18	5.04
3	84.24	4.11	17.02	40.70	33.61	9.15	6.54	5.51
5	87.06	5.30	19.11	45.40	30.47	7.92	4.97	5.56
10	87.39	6.70	18.30	44.75	29.56	7.45	5.11	6.05
20	87.31	7.96	17.97	45.82	27.62	6.71	5.93	5.58
A-AR2								
0	76.17	2.46	6.19	20.65	48.99	11.88	11.86	3.79
1	80.45	2.94	13.05	33.31	40.07	10.54	8.94	3.83
3	84.97	4.26	18.01	42.95	33.07	8.66	6.31	4.38
5	85.88	5.20	19.24	45.90	30.09	8.53	5.54	4.37
10	85.39	6.52	18.11	44.26	29.84	8.56	5.98	4.45
20	85.95	8.00	17.50	45.21	27.96	7.51	6.48	4.46
A-VGO1								
0	75.10	2.34	6.11	19.74	50.14	14.48	10.33	2.60
1	76.57	2.80	11.21	28.91	42.02	13.64	9.69	2.56
3	77.88	3.76	14.29	34.45	36.79	13.04	8.99	2.59
5	79.40	4.38	15.17	36.83	35.12	12.44	8.09	2.78
10	79.24	6.01	15.59	38.53	31.50	12.16	8.51	2.90
20	77.05	6.77	13.94	36.95	30.38	11.97	10.90	2.66
A-VGO2								
0	76.08	3.30	6.54	20.91	46.93	15.77	8.06	4.65
1	76.76	4.04	11.69	29.19	38.07	15.62	7.52	5.18
3	77.01	5.30	13.62	33.09	32.72	15.25	7.65	5.61
5	77.44	6.40	14.40	35.14	30.16	14.76	7.72	5.46
10	76.76	7.69	13.41	35.02	28.49	14.78	8.37	5.27
20	76.32	8.18	12.00	34.55	28.50	14.60	8.99	4.81

the above feedstocks with model compounds such as n-paraffin mixture (C32 - C40). The synthetic feedstocks cracking will be carried out using the ZSM-5 additive/FCC catalyst mixture, the results of which may reveal a greater insight into the role of ZSM-5 in paraffinic feedstock cracking mechanism.

The maximal ZSM-5 concentration which should be used for those four feedstocks with the selected FCC catalyst is about 5wt% because above this concentration, there is no further improvement in terms of propylene yield as well as conversion. Depending on the processed feedstock and refinery objectives, the refiner can flexibly control the product yields by changing the ZSM-5 additive concentration in the unit in the range between 0 and 5wt%. The exact ZSM-5 concentration, however, must be determined by detailed economic evaluation for the whole refinery.

Table 3. Conversion and products yields of 4 feedstocks at different ZSM-5 additive concentration

Additive, wt%	RON	Paraffin	Isoparaffin	Aromatic	Naphthene	Olefin
A-AR1						
0	89.52	7.73	24.80	21.96	4.73	40.78
1	90.81	8.43	20.58	23.16	3.35	44.48
3	91.50	9.73	19.00	26.68	2.64	41.94
5	91.74	10.29	19.56	26.91	2.37	40.88
10	92.67	10.96	18.59	33.17	2.78	34.50
20	95.00	10.00	16.75	39.54	2.26	31.45
A-AR2						
0	91.28	5.96	23.59	23.38	5.02	42.05
1	91.48	7.06	21.33	24.04	3.92	43.65
3	92.28	8.50	19.71	24.66	2.95	44.17
5	92.65	9.18	19.93	27.85	2.63	40.41
10	94.22	9.30	17.92	36.64	2.75	33.40
20	95.49	9.26	18.63	41.38	2.41	28.32
A- VGO1						
0	92.68	4.20	23.54	32.50	6.60	33.17
1	93.55	4.47	23.86	36.52	5.99	29.17
3	93.94	4.96	24.66	38.39	5.11	26.88
5	95.02	5.06	23.69	41.44	4.19	25.62
10	96.07	5.23	21.83	46.45	4.18	22.31
20	97.96	4.97	19.58	53.11	3.16	19.19
A-VGO2						
0	92.70	4.13	27.64	38.79	5.83	23.61
1	94.30	4.22	24.91	45.42	5.62	19.83
3	95.10	4.52	23.80	49.98	5.04	16.66
5	96.10	4.49	22.56	53.04	4.58	15.33
10	97.50	4.21	20.67	58.17	3.87	13.07
20	99.20	3.81	18.15	63.40	3.14	11.49

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