Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 50 (1), 39-43, 2008

EVALUATION OF FCC UNIT PROCESS VARIABLES IMPACT ON YIELD DISTRIBUTION AND PRODUCT QUALITY

Part II. Evaluation of the impact of FCC Unit operating conditions on gasoline hydrocarbon composition and octane number

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Received October 12 19, 2007, accepted March 15, 2008

Abstract

This work evaluates the influence of the Lukoil Neftochim Bulgaria FCC unit variables on FCC gasoline quality while employing an octane-barrel catalyst. It was found that research octane number of the FCC gasoline directly correlated with the riser outlet temperature (ROT). FCC gasoline was found to consist of higher octane low boiling (that boil in the range 40-60^oC) and high boiling components (that boil in the range 160-200^oC). The high octane low boiling components are mainly olefins, whereas the high octane high boiling components are mainly aromatics. The raise of ROT leads to increase of ratio of β-cracking relative to hydrogen transfer which results in enhancement of the lower molecular hydrocarbon content in the FCC gasoline.

Key words: FCC gasoline, octane number, olefins, aromatics

1. Introduction

Reduction of high octane aromatics from gasoline, as well as continuous pressure for reduction of olefins content is very heavy burden on refiners, who must produce high-octane gasolines, required for modern automobile motors [1,2]. Catalytic cracking gasoline is 30 – 40 % of produced gasoline components and also has highest contribution of olefins content in gasoline pool [3].

For that reason, the issue for octane number and composition of cracking gasoline is of significant importance for satisfying the stringent gasoline quality specifications.

In another article has been discussed how process variables in FCC Unit impact the conversion and cracking products yields [4]. The article describes that during the period of investigation of FCC unit operation was used octane-barrel type of catalyst and that the quality of used feed stock is practically constant. Recycle quantity should not have any impact on gasoline octane number in spite of the fact that reduces gasoline precursor's content in combined feed, since it contains poly-aromatic structures, which can not be cracked to gasoline range products.

The objective of present investigation is to discuss impact of process variable parameters in FCC unit on the composition and octane number of cracking gasoline.

2. Experimental

We made our investigations on cracking gasoline samples, taken at different conditions in FCC Unit. Table 1 gives description of these conditions. The octane number of samples was determined in accordance with ASTM D 2699-97 on WIT – 65 motor. Hydrocarbon content in the samples 1, 2, and 5, expressed as normal paraffins, iso-paraffins, aromatics, naphthenes and olefins (PIANO analysis) is analyzed by means of Gas Chromatograph HP5880A, equipped with flame-ionization detector (FID).

In addition to that, on the basis of Gas Chromatograph data were calculated octane numbers of narrow fractions by means of octane model, which takes into account non-linear blending characteristics of hydrocarbons [5].
Distillation according to ASTM D- 2887 and group composition (PIANO analysis) of samples 1, 2 and 5 are shown in Table 2.

Table 1 Conditions at which FCC gasoline has been sampled

Sample	Riser outlet temperature, ^oC	Catalyst-to-Oil ratio t/t	Combined feed ratio, t/t	Conversion of fresh feed
1	511	6.2	1.29	74
2	518	7.0	1.08	81
3	521			
4	528			
5	534	7.2	1.08	82

Table 2 Boiling range and group hydrocarbon composition of cracking gasoline samples, taken at different operating conditions of FCC Unit.

	Sample 1	Sample 2	Sample 5
Distillation (ASTM D-2887)			
IBP	16	17	15
5	23	24	24
10	28	30	29
20	41	48	38
30	63	65	59
40	84	83	81
50	104	104	101
60	122	120	118
70	141	139	140
80	163	162	162
90	187	186	183
95	202	202	199
FBP	230	236	225
Content of fraction (IBP-215 ^oC), %	98.4	98.1	99,0
Content of fraction, boiling at >215 ^oC, %	1.6	1.9	1.0
PIANO analysis			
Paraffin	4.89	5.43	4,76
Iso-paraffins	31.62	33.24	31.95
Aromatics	25.04	28.42	29.07
Naphthenes	11.27	9.56	8.51
Olefins	27.18	23.35	25.70

3. Results and discussions

Catalytic cracking is complicated process with many variable parameters, that impact composition and octane number of gasoline [6]. For this set of data it was found out, that octane number (RON) correlates only with reactor temperature. This is shown on Figure 1.
As it can be seen, at every 10^oC temperature rise, octane number is increase by 1 point. The data, given in Table 2 also show that hydrocarbon content in gasoline depends not only on the reactor temperature, but also on remaining process variables in the unit.
Each change that takes place in the unit, which leads to reduction of reactions of hydrogen transfer against cracking reaction by the rule of β-breakage increases olefins content [7]. For example these can be reduction of catalyst-feed ratio, increase of reactor temperature. The tabulated data show that sample 1 is with highest olefins content. In spite of the fact, that reactor temperature, at which sample 1 was taken is the lowest (this actually helps reactions of hydrogen transfer), low catalyst-feed ratio and high content of recycle in combined feed lead to reduction of catalyst active centers and finally to reduction of hydrogen transfer reactions against cracking reaction by the rule of Beta-breakage. Increase in reactor temperature at constant conditions leads to increase of olefins content in the cracking gasoline [8].This is further confirmed by comparison of olefins content in sample 2 and 5. Higher temperature of taking sample 5 (534^oC) at identical content of recycle in combined feed and

close catalyst – feed ratio as sample 2 (518^{o}C) leads to increase of olefins content with 2.3 %. Therefore, it is possible to make the conclusion that olefins content in gasoline depends on the catalyst-feed ratio, on recycle quantity and on reactor temperature.

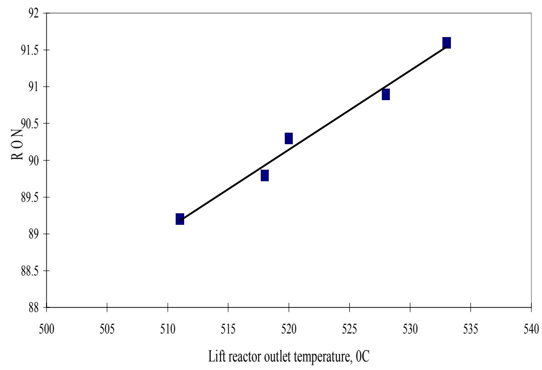

Figure 1 Dependence of FCC gasoline's RON from reactor temperature

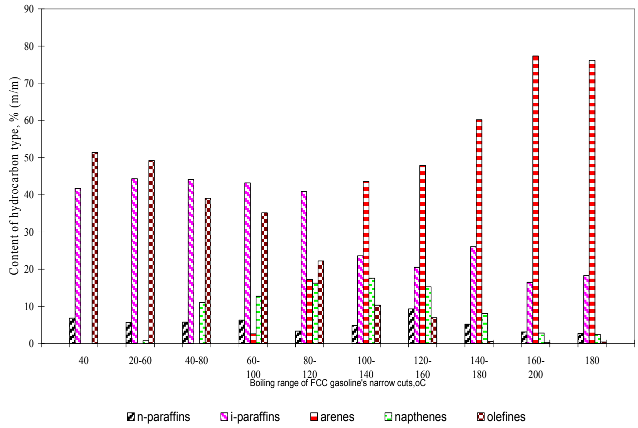

Figure 2 Hydrocarbon composition of FCC gasoline narrow fractions (sample 2)

Paraffins content is increased with rise of reactions of hydrogen transfer relation against cracking reactions by the rule of beta-breakage. For this set of data this is changed as follows: sample 2 > sample 5 > sample 1.The naphthenes are unstable products and this is the reason for reduction of naphthenes content when conversion is going up [9]. The highest naphthenes content is in sample 1, where the conversion is lowest. The lowest naphthenes content is in sample 5, where conversion is highest. Aromatic hydrocarbon content in the gasoline is increased by increase of conversion.
Distribution of hydrocarbons group in narrow 40^{o}C fractions of cracking gasoline (sample 2) are shown in Figure 2. From this data it can be seen that low-boiling fractions to 60^{o}C are with highest olefins content. The increase of boiling temperature leads to reduction of olefins content. The fractions, boiling in the range of 60-120◦C are rich in iso-paraffins. The fraction with higher boiling range, iso-paraffins content is lower, and local maximum content is observed in fraction 140-180^{o}C. Naphthenes can be seen first in fraction 20-60^{o}C and their content in fraction with higher boiling range increases gradually by reaching maximum content on fraction 100-140^{o}C. In the fractions with boiling range over 140^{o}C naphthenes content is going down. Aromatics content can be seen first in fraction 60-100^{o}C and they increases gradually and reaches maximum point in fraction 160-200 ◦C. Normal paraffins content in different fractions varies in more narrow range (2.7 -9.4 %), compared with the one of remaining hydrocarbons group. Their highest content is observed in fraction 120-160^{o}C and the lowest one in fraction, boiling at temperature over 180^{o}C.

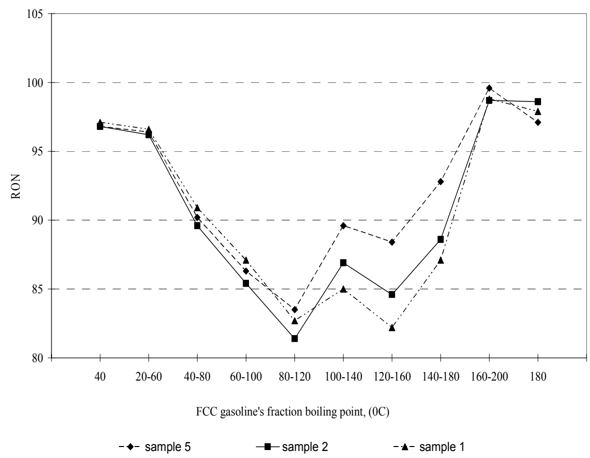

Figure 3 RON of FCC gasoline's narrow fractions, sampled at different operating conditions

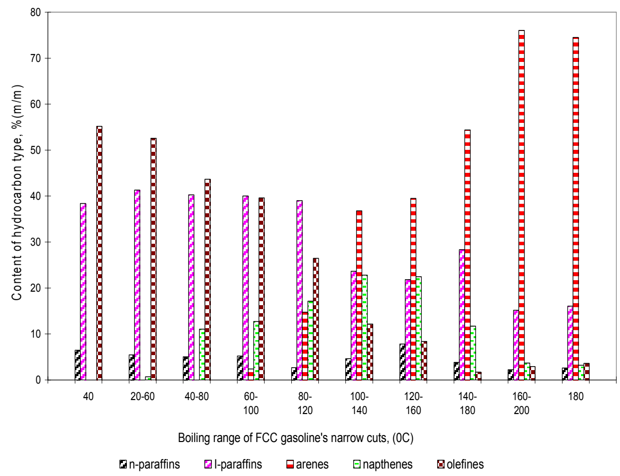

Figure 4 Hydrocarbon composition of FCC gasoline's narrow fractions (sample1)

Figure 3 shows variation of octane number of narrow fractions in samples 1, 2 and 5. From these figures become clear that cracking gasoline consists of low-boiling fractions (up to 60°C) and high boiling fractions and high octane fractions (temperature over 140°C).
High octane number of fractions with low boiling range is due to high olefins content and the one of high boiling fractions is due to high aromatic content. For all three analyzed samples the typical minimum octane number is observed in the temperature range of 80-120°C. This minimum value is due to high content of iso-paraffins and naphthenes (typically having low octane numbers), average olefins level and low content of aromatics (with high octane rating).
Sample 1 shows additional minimum in the range of 120-160°C. This minimum value is due to relatively high content of normal paraffins and naphthenes, average level of iso-paraffins and aromatics and low olefins content (Figure 4).

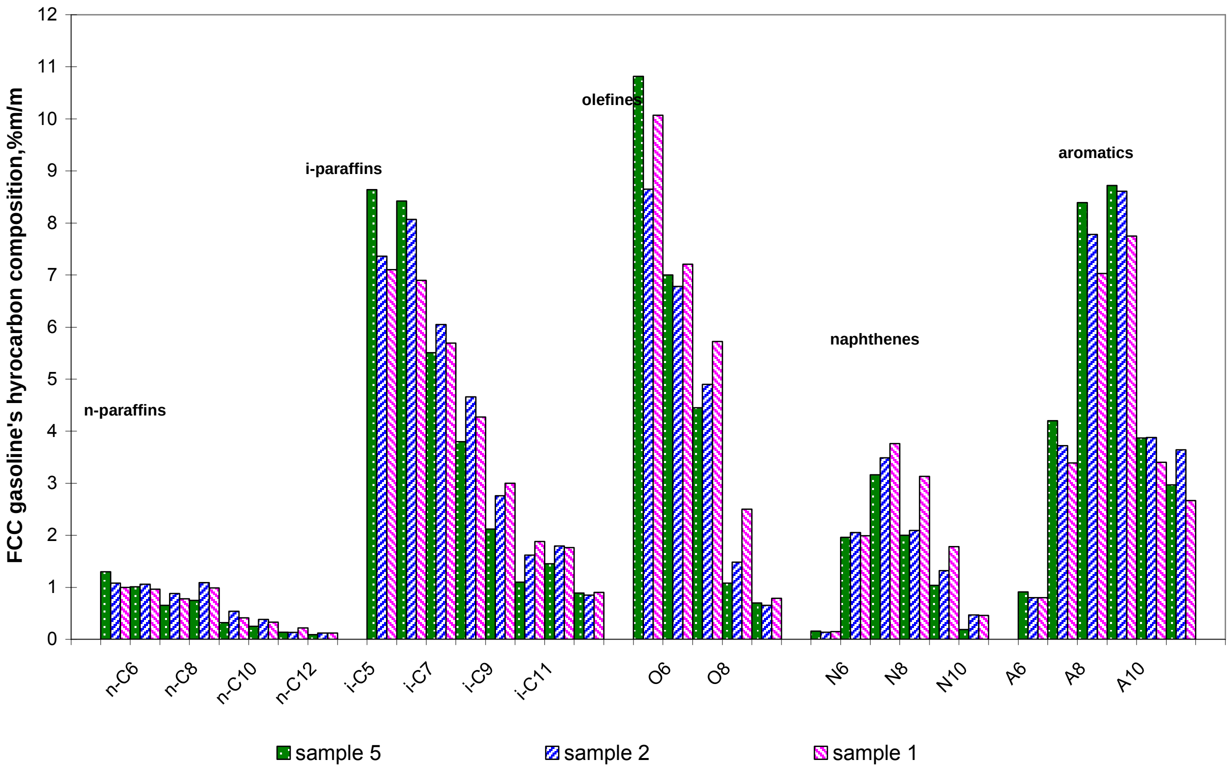

Figure 5 Distribution of hydrocarbon types and carbon number in FCC gasoline's samples at different operating conditions.

The highest content of olefins in sample 1 explains why the light part of this sample is with highest octane number, against the light parts of remaining samples. The highest content or aromatics ($A_7 – A_9$ – Figure 5) provides explanations of highest octane number of fractions 100-180°C of sample 5 compared to the same fractions of remaining samples.
Aromatic hydrocarbon distribution in groups and number of carbon atoms in all three samples, as given in Figure 5 shows that increase of reactor temperature leads to increase of relative hydrocarbon share with lower number of carbon atoms. This has favorable influence on octane number.

4. Conclusions

For some feed stocks and catalyst the octane number (by Research Method RON) of cracking gasoline from FCC unit is in direct correlation with reactor temperature. Each 10 % increase in reactor temperature leads to increase of octane number by 1 point. This is due to the increase of non-saturation degree of gasoline and increase of relative share of hydrocarbons with lower carbon number atoms, which are with higher octane numbers. Olefins content in cracking gasoline depends on reactor temperature, catalyst-feed ratio and recycle quantity. The increase of reactor temperature, reduction of catalyst-feed ratio and increase of recycle quantity lead to increase of non-saturation of cracking gasoline. Naphtenes and aromatic content depends on the conversion of fresh feed. With conversion increase the naphtenes content is reduced, but arenes content is going up.

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