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SOLVING PROBLEMS IN REAL ZEOFORMING PLANT USING LABORATORY TESTS OF COMMERCIAL CATALYSTS

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Abstract

The zeoforming, a new process, is rarely used in petroleum industry. The zeoforming plant in ,,Glimar" S.A. refinery has been working during last few years. The differences of activity of two ZSM-5 catalysts (A and B) used in zeoforming process, have been found due to proposed laboratory tests carried out with use of industrial feed. Catalyst B appeared to be much more active than catalyst A. The conception of using catalyst B in one rector, in one line (A-B-A), and only one catalyst A in three reactors of second line (A-A-A) has been successfully applied in zeoforming plant in "Glimar" S.A. refinery.

Key words: *catalysts, zeolite, zeoforming*

Introduction

The zeoforming plant in „Glimar" S.A. refinery, located in the south of Poland, has been producing unleaded petrol component during the last few years.
The zeoforming process, is based on transformation of low octane feed to high octane product in the presence of the hydrogen form of ZSM-5 zeolite as catalyst, with the binder (γ-alumina)[1]. In this process mainly *n*-paraffin hydrocarbons are transformed to aromatic ones. Similar transformation of isoparaffines and naphthenic compounds is not so effective. The hydrogen practically is not produced in this process, but only light hydrocarbons can be found.
In the case of zeoforming plant in „Glimar" S.A. refinery two lines of reactors work alternatively. Both lines consist of three reactors. Each line of reactors works during 7-10 days and then the catalyst is regenerated. The total time of the catalyst work is about one and a half year.
There are not many test methods used for evaluating the catalysts in the refinery industry [2,3]. The methods used for evaluating catalysts activity usually are owned by companies producing these catalysts. Besides, zeoforming is a new process, rarely applied in the refinery industry. Our aim was to find a laboratory test selecting a proper catalyst for zeoforming plants.

Methods and results

Physicochemical investigation

Two catalysts (A and B) have been used in the investigation. The diffractometer PW 1060 with a copper lamp has been used for evaluating their crystal structure. The results are shown in Figure 1. Additionally the contents of aluminum and silicon have been investigated with the use of X-ray fluorescence method.

The activity test

The catalysts activity has been investigated in laboratory conditions in the set of only two reactors arranged in a line (instead of three reactors working in „Glimar" S.A. refinery in one line). There were two catalytic beds in the first reactor and one bed in the second one. The ratios of volumes of these beds were the same as in zeoforming plant in „Glimar" S.A. refinery, i.e. 1 : 1,5 : 2,3. The process was carried out at the pressure 1,6 MPa and LHSV = $1h^{-1}$. The SRG from „Glimar" S.A refinery was used as the feed for the activity test. Two kinds of test investigations have been performed:

- „short test"- some periods of ten degrees temperature increase with the rate 0,5°C/h; mean rate of temperature increase during the whole test was about 1°C/h,
- „long test" - some periods of ten degrees temperature increase with the rate 0,5°C/h; each of them followed the previous 24h period of constant temperature. The mean rate of temperature increase during the whole test was about 0,6°C/h.

The „short test" methods were used twice for A and B catalysts (Table 1). The „long test" method was applied to investigate the catalyst A as well as the mixed catalyst bed (A-B-A).

Table 1 The feed and stabilized petrol properties obtained in the case of A and B catalysts („short test").

	Feed	Temperature at the inlet to the first reactor							
		360 - 370 °C		400 - 410 °C		440 - 450 °C		450 - 460 °C	
Catalyst⇒		A	B	A	B	A	B	A	B
Research octane number, RON	61,0	90,2	-	93,5	>100	98,7	101,7	99,6	101,0
Motor octane number, MON	60,0	82,5	87,8	84,2	89,7	87,2	91,6	87,7	90,7
Vapour pressure, kPa	71,6	64,0	51,1	61,9	26,3	47,3	28,7	43,1	29,5
Density, 15°C, g/cm^3	0,7290	0,7640	-	0,7794	0,8300	0,8070	0,8404	0,8175	0,8380
Benzene, % (*m/m*)	0,70	1,01	2,56	1,77	3,94	3,64	5,95	4,62	6,09
Aromatics, % (m/m)	12,3	42,1	60,6	50,0	69,4	61,3	76,6	67,7	74,1
n-paraffins, C_3-C_{10} , % (*m/m*)	26,9	8,2	4,1	5,8	1,9	3,3	1,4	2,6	1,4

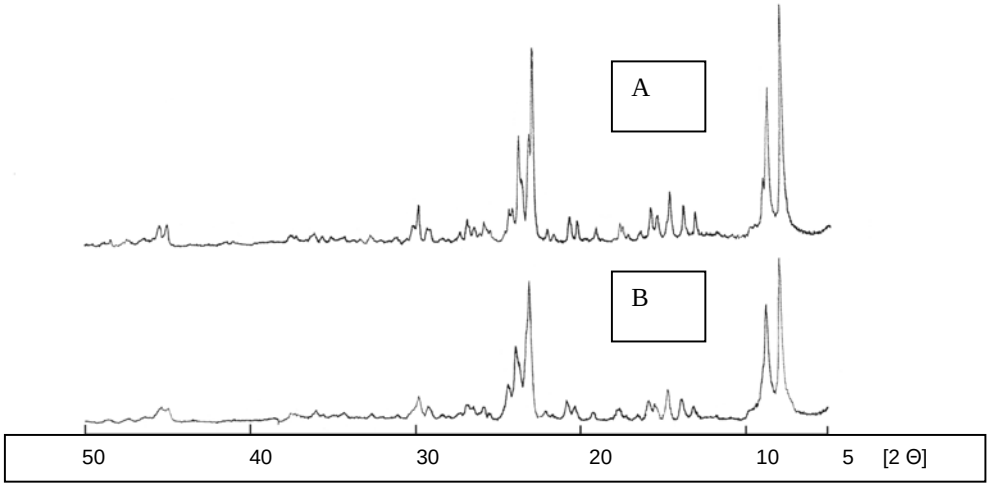

Figure 1. XRD graphs for two catalysts, ZSM – 5 type, used in zeoforming process.

Table 2 The comparison of activities in the case of A-A-A and A-B-A catalytic beds („long test").

Catalytic bed	A-A-A	A-B-A	A-A-A	A-B-A	A-A-A	A-B-A
Temperature, °C	405	390	417	405	422	415
Research octane number, RON	91,4	91,4	93,4	93,4	94,4	94,4
Motor octane number, MON	82,9	83,8	84,2	85,1	84,8	85,5
Benzene, % (*m/m*)	1,24	1,28	1,77	1,58	2,1	1,83
Aromatics, % (*m/m*)	44,6	43,8	49,8	48,0	52,4	49,8
n-paraffins, C_3-C_{10} , % (*m/m*)	7,6	7,9	6,3	6,7	5,7	5,9

Discussion

Discussion of experimental results

The X-ray diffraction results (Figure 1) for catalysts A and B show that ZSM-5 zeolites are the components of these two catalysts. Higher intensities of X-ray diffraction peaks (nearly 30 %) for A catalyst in comparison to peaks of B catalyst indicate the higher silicon module of ZSM-5 in the catalyst B [4]. The effective silicon module of catalyst B measured by X-ray fluorescence method is about 10% higher than in the case of catalyst A. The presence of γ-alumina binder in both catalysts have to be taken into consideration.

The „short" tests for both catalysts for the range of temperatures 360 - 460°C showed that catalyst B is much more active than catalyst A. It is expressed by the lower content of n-paraffins and the higher content of aromatics (in the same temperatures) in the case of catalyst B than in the case of catalyst A. In agreement with this fact are the observed values of octane numbers, vapour pressure, densities and benzene content. The analysis of the data in Table 1 shows that in the case of „short test" in the range of temperatures 360 - 460°C, the properties of petrol fractions obtained in the case of catalyst B are similar to those, obtained in the case of catalyst A, but the temperature should be up to 80°C higher.

The catalyst B is much more expensive than the catalyst A. This fact and the fact that there is no heater between the first and the second reactor (in zeoforming plant) suggested the usefulness of investigation of mixed catalyst bed during the „long test" (A and B catalyst in the first laboratory reactor and catalyst A in the second laboratory reactor, A-B-A). Besides that, the „long test" was applied to additional evaluation of A catalyst (A-A-A). Table 2 shows the comparison of selected results from both tests (the petrol fraction characterized the same RON values (91,4; 93,4; 94,4) obtained for mixed bed reactors and the reactor bed only with A catalyst). The obtained data show that the same values of RON were obtained for mixed bed in lower temperatures (7-15°C), at lower aromatic content and lower or the same benzene content.

The investigated conception of the catalyst arrangement has been proposed to be applied in industrial conditions in zeoforming plant in „Glimar" S.A.

Industrial application

The laboratory examined concept of mixed catalytic bed has been applied to Zeoforming plant in Glimar" SA. The aim of introducing catalyst B with high activity was to compensate lower work temperature of the second reactor in the line of reactors (L1) in this plant. On the other hand all reactors of line L2 were filled with catalyst A. In this way checking of the laboratory test results was possible. In the Table 3 the comparison of selected parameters for both lines and properties of the obtained products has been given. Due to the production requirements both lines did not work all the time at the same conditions. The periods at similar conditions were taken for the comparison.

During the beginning of the installation work (at similar mean temperatures for the two lines), the products obtained from line L1 had higher octane values than the ones from line L2. The octane index (arithmetic mean from RON and MON of petrol) for petrol products

obtained from line L1 are 1,3 to 2,4 units higher than those obtained from L2 line. In the late period of the cycle (for the time over 100 hours), the differences between both kinds of products are smaller. This can be the result of different values of the temperature increase. For line L1 the mean rate of temperature increase was 0,25 °C/h but for line L2 it was 0,44°C/h. At the end of the cycle for the same temperature of reaction in both lines the product properties were very similar (time of work of line L1 was 207 hours, the whole time of work of line L2 was 159 hours).

Table 3 The comparison of two catalytic lines performance in zeoforming plant.

Line	**L1**	**L2**	**L1**	**L2**	**L1**	**L2**	**L1**	**L2**	**L1**	**L1**	**L1**	**L2**
Time of work, h	39	39	47	47	71	71	103	103	159	199	207	159
Temp. of feed at the inlet, °C	412	408	414	415	425	425	439	437	450	453	452	456
Mean temp. of process, °C	390	389	394	393	404	403	413	413	424	427	430	430
LSHV, h^{-1}	0,94	0,94	0,97	0,93	0,94	0,97	0,91	0,90	0,68	0,85	0,85	0,82
Properties of products												
Research octane number, RON	95,5	91,6	94,2	94,0	94,0	93,0	94,4	93,8	96,0	94,3	93,6	94,5
Motor octane number, MON	86,3	85,1	87,0	85,6	86,5	84,8	86,7	84,0	86,6	85,8	85,4	83,5
Octane index	90,8	88,4	90,6	89,2	90,2	88,9	90,6	88,9	91,3	90,0	89,5	89,0
Density, 15°C, g/cm^3	0,784	0,775	0,770	0,774	0,771	0,782	0,774	0,790	0,790	0,785	0,784	0,779
Benzene, % (*V/V*)	2,4	1,8	2,0	2,3	2,2	2,4	2,4	2,4	3,2	2,7	2,7	2,4

Line L1 - catalytic bed A-B-A, Line L2 - catalytic bed A-A-A

The similar results of petrol octane numbers obtained in industrial conditions (Table 3) and in laboratory conditions (Table 2) were observed. In industrial conditions, however higher values of benzene content, particularly for catalyst bed A-B-A have been detected. Technical improvements made possible to maintain more stable operating conditions (stable LSHV and average reaction temperature increase) of two production lines of a commercial zeoforming plant. Though all operating cycles in the year 2002 every 24 hours two samples of the product (one sample from each line) were examined to assess the influence of these improvements on product quality. The properties of samples comes from one cycle are presented in table 4 and 5. From the analysis of the results presented in these tables it came out that the production line L2 was to be operated at higher reaction temperatures, as compared with line L1, to obtain products of analogous octane numbers (both RON and MON). At analogous octane numbers of products resulting from both production lines the content of benzene in products from line L2 was always higher as compared with line L1.

Table 4 Selected properties of samples of product produced in zeoforming plant in RN ,,Glimar" S.A.

	Line L1					
Date	6.09.02	7.09.02	8.09.02	9.09.02	10.09.02	11.09.02
RON	90,9	90,8	91,0	92,1	93,5	93,7
MON	83,9	83,9	83,8	84,4	84,9	84,6
Distillation:						
Initial point, ^{o}C	30,2	28,2	28,1	27,6	27,7	28,0
Up to:						
70 ^{o}C distilled, % (*V/V*)	22,8	24,7	23,5	24,7	25,9	24,9
100 ^{o}C, % (*V/V*)	36,5	37,5	36,7	39,5	37,8	35,7
150 ^{o}C, % (*V/V*)	76,6	78,0	77,3	78,6	79,0	76,3
180 ^{o}C, % (*V/V*)	94,7	95,0	95,0	95,0	95,0	94,7
End-point , ^{o}C	217	213	213	210	207	216
Residue, % (*V/V*)	1,0	1,1	1,1	0,9	0,9	0,9
Vapour pressure, kPa	82,4	85,5	82,9	93,5	93,5	93,0
Sulfur content, mg/kg	10	13	13	14	14	16
Density, 15^{o}C, kg/m^{3}	756	756	757	760	760	760
Benzene content, % (*V/V*)	1,4	1,5	1,6	2,0	2,0	1,9
HC content (FIA):, % (*V/V*)						
- aromatics	29,5	29,0		34,8	37,5	38,5
- olefins	-	-		-	-	-
- paraffin - naphthenes,	70,5	71		65,2	62,5	61,5
Temperature after furnace ^{o}C	404	412	421	429	437	443
Average temperature in reactor 1, ^{o}C	381,0	388,0	396,7	402,8	410,0	414,8
Average temperature in reactor 2, ^{o}C	368,2	376,9	385,0	390,3	396,5	401,8
Average temperature in reactor 3, ^{o}C	390,8	403,2	412,5	418,7	426,4	432,9
Average temperature of reaction, ^{o}C	381,8	392,0	400,5	406,7	413,8	419,6
Day of cycle	1	2	3	4	5	6
Feeding, m^{3}/h	10,0	10,0	9,8	9,6	9,3	9,3

Conclusions

The differences of activity of two ZSM-5 catalysts (A and B) used in zeoforming process, have been found due to proposed laboratory tests carried out with the use of industrial feed. Catalyst B appeared to be much more active than catalyst A. The conception of using catalyst B in one line and only in one reactor was performed in zeoforming plant in „Glimar" S.A. refinery.

The comparison of the two industrial lines showed the higher activity of catalyst line A-B-A than the line A-A-A. In comparable conditions the product obtained from A-B-A line has got octane index about 1,5 unit higher than from A-A-A line and the possibility of achieving longer time of work between the following catalyst regenerations increases.

As the activity of catalyst B was not known earlier, the laboratory investigations made it possible to compare the activities of both catalysts. Thanks to the results laboratory tests, the conception of using mixed catalyst bed (A-B-A) in the zeoforming plant has been proposed and successfully performed.

Table 5 Selected properties of samples of product produced in zeoforming plant in RN ,,Glimar" S.A.

	Line L2					
Date	11.09.02	13.09.02	15.09.02	16.09.02	17.09.02	18.09.02
RON	90,9	91,6	92,0	91,9	91,0	93,0
MON	82,7	-	83,6	-	83,9	84,5
Distillation:						
Initial point , ^{o}C	29,0	28,0	30,6	28,7	33,5	31,0
Up to:						
70 ^{o}C distilled, % (*V/V*)	27,0	26,7	23,4	24,4	16,3	20,6
100 ^{o}C, % (*V/V*)	40,3	39,0	35,9	36,1	29,6	32,6
150 ^{o}C, % (*V/V*)	79,7	79,4	77,1	77,3	76,0	76,3
180 ^{o}C, % (*V/V*)	95,9	95,4	94,7	94,6	94,7	93,6
End-point, ^{o}C	207	218	215	214	215,6	211
Residue, % (*V/V*)	0,8	0,8	1,1	1,1	1,0	1,2
Vapour pressure, kPa	97,1	96,5	89,1	90,9	96,9	76,4
Sulfur content, mg/kg	15	15	14	14	15	14
Density, 15^{o}C, kg/m^{3}	745	750	759	756	754	769
Benzene content, % (*V/V*)	1,5	1,8	2,0	2,0	2,2	2,8
HC content (FIA):, % (*V/V*)						
- aromatics	28,7	-	34,2	35,0	30,1	40,8
- olefins	-		-	-	-	-
- paraffin - naphthenes,	71,3		65,8	65,0	69,9	59,2
Temperature after furnace ^{o}C	407	423	435	438	445	452
Average temperature in reactor 1, ^{o}C	382,1	395,6	406,3	407,7	413,3	421,0
Average temperature in reactor 2, ^{o}C	372,0	384,2	393,2	396,0	401,1	407,0
Average temperature in reactor 3, ^{o}C	399,7	414,3	425,0	428,3	434,6	438,8
Average temperature of reaction, ^{o}C	387,5	401,2	411,4	414,1	419,9	425,3
Day of cycle	1	2	3	4	5	6
Feeding, m^{3}/h	9,6	9,4	9,4	9,2	9,1	9,1

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