

VARIOUS VARIANTS TO PROCESS THE GASOLINE FRACTION FROM THERMAL CRACKING

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ABSTRACT

The selection of the optimum technological scheme for processing gasoline from the thermal cracking depends on its content of alkenes and content of sulphur. Presently the best method for cleaning gasoline from nonsaturated hydrocarbons and sulphur compounds is the installation of hydrotreatment in the scheme of processing.

The hydrotreated fraction is a good raw material for the pyrolysis process. The hydrotreatment of a mixture of distillate naphtha and thermal cracking naphtha (25:75) at a volume rate of 2 h^{-1} gave a hydrogenate with a high degree of olefins saturation. This hydrogenate is suitable for feeding into the pyrolysis installation. Due to the low content of naphthenes, the hydrogenate is not recommended for use in reforming installations. The highest ΔT observed at the volume ratio used was about 40°C .

Keywords: selective absorption, thermal cracking, gasoline fraction, acid gas.

INTRODUCTION

Thermal cracking is carried out in the temperature interval from 470 to 540°C and pressure from 2 to 7 MPa . The main products are: hydrocarbon gas, cracking naphtha, kerosene-gasoil fraction and cracking residue. The gaseous products, as well as the naphtha obtained from thermal cracking contain significant amounts of unsaturated hydrocarbons, which could be used as raw materials for petrochemical synthesis [1]. The process of thermal cracking involves a complex of reactions between the various groups of the petroleum compounds [2, 3]. The effective energy of thermal decomposition of petroleum fractions is assumed to be $250 - 300 \text{ kJ/mol}$. It was found that, in many cases, the thermal decomposition of individual hydrocarbons in a mixture occurs at a higher rate than the decomposition rate of the pure compounds [4].

Under industrial conditions, petroleum fractions are subjected to pyrolysis rather than individual compounds. High yields of ethene, $\text{P}_3 - \text{P}_4$ alkenes and liquid product containing cycloalkenes, C_5 alkadienes and heavier $\text{P}_6 - \text{P}_8$ arenes, as well as polycyclic arenes can be obtained from petrol fractions with high content of n-alkanes [5-12].

EXPERIMENTAL AND DISCUSSION

Aiming to confirm the proper choice of the method of intermediate hydrogenation to process naphtha by pyrolysis process, experiments were carried out with naphthas from the installations for hydrotreatment, thermal cracking and for catalytic cracking (Table 1). Thus, the effects of the components in the raw materials for the ethene installation were determined.

It was observed that:

- the total amount of sulphur in the naphthas is determined mainly by the hydrogen sulphide contents in them (about 92 %);

- the naphtha obtained from thermal cracking contained 16 % N₂S vs the total amount of sulphur while the mercaptane sulphur was - 20 %;

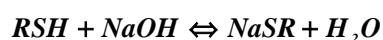
- the naphtha obtained from thermal cracking contained 43.83 %_{vol} alkenes, though they were not found in the petrol residue.

The total content of sulphur compounds in the mixtures of petroleum products is an additive value. Under alkali raffination with sodium hydroxide, mainly the hydrogen sulphide and low hydrocarbons (methyl, ethyl, propyl) are removed from the mixture.

The composite mixture (naphthas from the installations for hydrotreatment, thermal cracking and from catalytic cracking, presented in Table 1) subjected to sweetening with sodium hydroxide solution in this study contained the following sulphur compounds:

total sulphur	6016 ppm;
mercaptanic sulphur	1288 ppm;
hydrogen sulphide	754 ppm;
other	3977 ppm.

The stoichiometric amount of sodium hydroxide necessary for the reaction can be determined using the following reaction:



As can be seen, 1.6 g 100 % NaOH are necessary to remove 1.3 g mercaptanes. The suitable concentration of the NaOH aqueous solution was assumed to be 15 %, but the significance of the degree of base saturation should also not be neglected.

According to the requirements for the raw materials for the ethene installation, the alkenes content should not exceed 1 %. The addition of the mixture of petrol by-products and thermal cracking naphtha to the raw material for the pyrolysis should comply with the respective regulating documents.

The requirement for the sulphur content in the ethene raw material is 1000 ppm while in the composite mixture it was measured to be 7206 ppm. The other raw material components contained only 200 ppm sulphur. Therefore, to cover the standard requirements, the amount of the mixture of naphtha from hydrotreatment installation and thermal cracking naphtha in the raw

Table 1. Physical-chemical properties of different raw materials for catalytic hydrotreatment processes.

Properties	Low octane gasoline	Gasoline from the hydrotreatment installation	Gasoline from the thermal cracking process
Density at 20°C, g/cm ³	0.7510	0.7700	0.6865
Distillation characteristics, v/v:			
IBP, °C	105	49	35
5 %	112	99	52
10 %	116	118	56
15 %	117	128	59
20 %	119	133	61
25 %	120	138	64
30 %	121	141	66
35 %	123	144	68
40 %	124	147	70
45 %	126	150	71
50 %	128	153	73
55 %	130	156	75
60 %	132	159	77
65 %	134	162	79
70 %	136	166	81
75 %	138	170	83
80 %	142	174	85
85 %	146	181	88
90 %	150	190	91
95 %	158	207	96
FBP, °C	168	212	122
Yield, %	98	97	99
Bromine number, g Br ₂ /100 g	0.3	0.85	85.8
Total sulphur, ppm	540	64	3500
H ₂ S, ppm	< 1	< 1	< 1
Mercaptanes, ppm	140	2,3	812

material for the ethene production should not be more than 12 % of the total amount of raw material without preliminary treatment. Hydrogen sulphide and part of the mercaptanes could be removed by degassing and NaOH treatment but not the alkenes.

At present, the naphtha obtained from thermal cracking is not subjected to degassing and alkali purification, unlike the naphtha obtained from the hydrotreatment installations. Despite the degassing and alkali purification of all the components of the mixture, the performance of the ethene installation would not be easier.

Table 2. The composition of the fuel-gas.

Components	Molecular mass, kg/kmol	Composition, %	
		Volume %	Mass %
CH ₄	16	95.0	89.62
C ₂ H ₆	30	2.3	4.06
C ₃ H ₈	44	0.9	2.33
n-C ₄ H ₁₀	58	0.4	1.37
CO ₂	44	0.3	0.80
N ₂	28	1.1	1.82
		100.0	100.0

Table 3. Composition of the raw material and product from the pyrolysis process.

Components	Composition, % mole	
	Raw material	Gas
H ₂	1.0	18.3
CH ₄	6.8	28.7
C ₂ H ₂	-	0.4
C ₂ H ₄	3.3	28.5
C ₂ H ₆	14.8	7.6
C ₃ H ₆	10.3	7.3
C ₃ H ₈	56.6	5.2
C ₄	5.2	0.8
C ₅₊	2.0	3.2
	100.0	100.0

The general solution of the problem with the unsaturated hydrocarbons could be found only by hydrotreatment, which results in olefin saturation and removal of the sulphur present in various forms.

For the pyrolysis experiments in the present work, a pyrolysis tubular furnace of the gradient type equipped with a double serpentine with two-sided irradiation was used. An advantage of this kind of furnaces is the uniform heat transfer along the perimeter of the radiant tubes. As a fuel for the furnace for the pyrolysis process we use the composition, presented in Table 2.

The naphtha obtained from thermal cracking was 18.5 % of the initial material. The composition of the naphtha from thermal cracking process and products from pyrolysis process are presented in Table 3.

The hydrotreatment of a mixture of naphtha from hydrotreatment installation: thermal cracking naphtha = 25:75 at volume rate of 2 h⁻¹ gave hydrogenate (Table 4) with a high degree of olefins saturation. The hydrogenate is suitable for feeding into the pyrolysis installa-

Table 4. Physical-chemical properties of the gasoline mixture (gasoline fraction from hydrotreatment installation 25 % and gasoline fraction from thermal cracking process 75 %) and product from its hydrogenisation.

Properties	Gasoline mixture	Product – raw material for pyrolysis process
Density at 20°C, g/cm ³	0.7140	0.6980
Distillation characteristics, v/v:		
IBP, °C	38	36
5 %	56	54
10 %	60	60
15 %	64	64
20 %	68	68
25 %	70	70
30 %	72	72
35 %	76	76
40 %	80	80
45 %	82	82
50 %	85	86
55 %	89	90
60 %	94	94
65 %	98	98
70 %	104	106
75 %	114	116
80 %	122	136
85 %	148	155
90 %	162	171
95 %	188	195
FBP, °C	194	197
Yield, %	97.5	96.5
Bromine number, g Br ₂ /100 g	64.6	0.8
Total sulphur, ppm	150	18
Alkanes, %	25.1	36.9
Alkenes, %	27.7	0.7
Arenes, %	9.3	6.9
Iso-alkanes, %	19.3	31.9
Cycloalkanes, %	10.5	17.2
Other, %	8.1	6.4

tion. Due to the low content of naphthenes, the hydrogenate is not recommended for use in reforming installations. The highest ΔT observed at the volume ratio used was about 40°C.

The low content of arenes and naphthenes (2A+N=33.2) and the comparatively high content of sulphur in the hydrogenate (18 ppm) makes it unsuitable for reforming. The hydrotreatment of naphtha from thermal cracking with end boiling temperature 120°C gave a hydrogenate suitable for pyrolysis rather than reforming. Selecting heavier fraction with end boiling temperature 205°C from the thermal cracking, the characteristic index 2A+N would be equal to 57.6 provided the distribution of normal, iso- and cyclic structures was the same as in the light naphtha. Therefore, the heavy naphtha obtained from thermal cracking could be used in the reforming process after hydrotreatment.

The separation of the thermal cracking naphtha into light and heavy portions allows improving the potential of the high quality raw material for pyrolysis and reforming.

CONCLUSIONS

Aiming to confirm the proper choice of the method of intermediate hydrogenation to process naphtha by pyrolysis process experiments with naphthas from the installations for hydrotreatment, thermal cracking and for catalytic cracking have been made.

The hydrotreatment of a mixture of naphtha from hydrotreatment installation: thermal cracking naphtha = 25:75 at volume rate of 2 h⁻¹ gave a hydrogenate with a high degree of olefins saturation. The hydrogenate is suitable for feeding into the pyrolysis installation.

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REFERENCES

1. D.Minkov, P.Petkov, D.Valchev, Oil-compounds, properties and chemistry of the processes, Sofia, 2000, (in Bulgarian).
2. S. Nametkin, Chemistry of oil, Moscow, 1955, (in Russian).
3. E. Smidovitch, Technology of oil and gas, Technica, Sofia, 1972, (in Bulgarian).
4. M. Gerasimov, D. Valchev, D. Minkov, Chemistry and physics of oil and gas, Technica, Sofia, 1990, (in Bulgarian).
5. A. Amoreli, I. Amos, Oil, gas and petrochemistry, Moscow, 2001, (in Russian).
6. S. Gorislavec, D. Menov, Pyrolysis of hydrocarbons, Moscow, 1977, (in Russian).
7. N. Taylot, J. Hugill, Oil Auc Gaz Jurnal, 2001.
8. S. Sadrameli, A. Green, Journal of Analytical and Applied Pyrolysis, **73**, 2, 2005, 305-313.
9. E. Hájeková, B. Mlynková, M. Bajus, Journal of Analytical and Applied Pyrolysis, **79**, 1-2, 2007, 196-204.
10. X. Meng, Ch. Xu, J. Gao, Catalysis Communications, **8**, 8, 2007, 1197-1201.
11. T. Gauthier, P. Danial-Fortain, I. Merdrignac, I. Guibard, Catalysis Today, **130**, 2-4, 2008, 429-438.
12. X. Meng, C. Xu, J. Gao, Applied Catalysis A: General, **301**, 1, 2006, 32-38.