Benzene Management in Refinery Gasoline Pool

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The paper present research that aims at reducing the benzene content from the catalytic reforming gasoline through a hydrofination process followed by a hydroisomerization. The feedstock obtained through fractionating of the catalytic reforming naphtha is a light gasoline with the final boiling point of 97°C, which is hydrofinated used Ni/Al_2O_3-SiO_2 as catalyst. After hydrofination there is a drop in octane number of the hydrofinated catalytic reforming (CR) light naphtha, phenomenon which is partially corrected by the hydroisomerization process in the presence of Pt /H-ZSM 5.

Keywords: light naphtha, hydrofination, benzene, hydroisomerization

Increasing the quality of fuels in order to protect the environment, shows a global concern at the level of research and technology but also at the decisional political level. For this purpose, reducing of the sulfur, benzene, aromatics and others are the most important measures to be taken in order to obtain a EURO type gasoline. The concept of Clean Fuel presume a quality increase of the fuels by modifying the chemical composition, reformulating of the recipes, adjustment of the physical characteristics and last but not the least the reduction of the benzene that is considered a carcinogen [1].

Currently the quality standard for gasoline EN 228, restricts the benzene content to 1% volume, but sure the EU would follow the new MSAT II regulations (Mobile Source Air Toxics) that US applies from 2011 and limit the benzene content from commercial gasoline to maximum of 0.62% volume.

In modern refineries the main source of benzene in the reformulation of the commercial gasoline, comes from the catalytic reforming and catalytic cracking processes (table 1). The catalytic reforming process is responsible for about 70 – 85% of the total benzene content from gasoline. This justifies the focus of finding new technologies regarding reduction of benzene resulting from catalytic reforming.

The options for benzene reducing include: fractioning of the feedstock for catalytic reforming or reformate, saturating the benzene fraction itself or combined with hydroisomerization and alkylation or the benzene extraction [2,3]. Also process severity reduction in the catalytic reforming associated with utilization of benzene low selectivity catalysts can be a cheap solution which allow diminish of benzene content.

In most of refineries, the C_6 fraction is eliminated from the gasoline which feed the catalytic reforming plant in order to avoid a partial transformation of it into benzene. During the reforming process from C_6 fraction the following are converted to benzene: the whole cyclohexane, close to 50% of the methylcyclopentane and 20% of the paraffin [4].

The refineries which are integrated with petrochemical plants are choosing for the separation through fractioning of a benzene fraction followed by benzene recovery through extraction and usage of it as a feedstock for the petrochemical industry [5]. In the absence of the petrochemical plants, this option can be associated with the export of the benzene on petrochemical plants feedstock market.

There are 2 extraction methods: Extractive Distillation (ED) and Liquid-Liquid Extraction (LLE). The main industrial methods for aromatic extraction out of gasoline uses as solvents superior glycols like tetraethylene glycol and polyglycols. For a better performance, it is used as a solvent a mixture of glycols. A procedure of this kind has been created by UOP called CAROM.

Many refineries have chosen to install facilities for benzene hydrogenation out of the benzene fraction from reformate [5]. Benzene removal out of the gasoline leads to a significant loss of octane number, which makes it necessary to reformulate the commercial gasoline, using oxygenated compounds or using octane compounds out of the isomerization and alkylation processes [6,7].

The UOP *BenSat* process is used for light fraction treatment out of reformate or a light fraction out of the straight run naphtha used as a feedstock for the catalytic reforming. The residual benzene from gasoline is less than 0.6%. Axens Group offers the benzene hydrogenation process *Benfree* on Ni catalysts.

In the CDTECH *CDHydro* process the hydrogenation take place in an extractive distillation system inside a *Benzene-Toluene split column* equipped with a layer of catalysts. Reformate and hydrogen feeding the same catalytic

Process stream	Range of benzene concentration, %vol.	Stream contribution in the pool, %vol.	Benzene contribution to the pool, %vol.
Reformate	0.2-8	40	70-85
FCC gasoline	0.5-1.3	40	10-15
Light straight run naphtha	0.8-8	2.5-6	2-5

Table 1
TYPICAL SOURCES OF BENZENE CONTRIBUTION IN GASOLINE POOL

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column. The conversion of benzene can reach up to 90% and is controlled with ease through the hydrogen flow controlling. The obtained reformate is formed from hydrogenated C_6, C_7+ and contain 0.78% benzene. Following the benzene saturation it is advantageously a isomerization reaction of cyclohexane (CH) to methylcyclopentane (MCP), which has the RON with 8 octanes more than the CH.

Other refineries have opted for benzene alkylation with olefins C_2-C_4 for producing alkylaromatics with a high octane number [8-10]. In this way, the BenzOUT process developed by ExxonMobil Research and Engineering Company, use the benzene fraction separated out of the reformate which is subject to a non-selective alkylation with alkenes C_2-C_4 contained into the catalytic cracking or thermal cracking gases [11,12]. This solution allows including of other fractions with a higher content of benzene in the alkylation feed. The non-selective alkylation is made in 2 ways: with a fixed bed catalyst or in a fluidized bed catalyst.

Fluidized bed catalyst process use a zeolitic catalyst ZSM-5 type, with a strong acidic character, at a pressure range 7-14 bar. The benzene conversion in this condition is 50-60%, COR raising from 80 to 90. This technology allows the transformation of the uneconomical C_2-C_5 fractions, in superoctane hydrocarbons, obtaining gasoline with a high octane number without using hydrogen and with a low benzene content (under 1% vol.).

The current paper aims increasing quality of the commercial gasoline in terms of reducing benzene content by hydrogenation of catalytic reforming light naphtha one of the main compounds used in formulating of fuel for spark ignition engines. Because benzene and partially alkylaromatics saturation is associated with octane number decrease, gasoline is subject to hydroisomerization in order to compensate the losses of octane. The influence of reaction conditions is analyzed for the two processes on the characteristics of hydrofinated and hydroisomerization gasoline with reference to benzene content and RON.

Experimental part

As a feedstock it was used, a light naphtha fraction, with the final boiling point 95°C, obtained by fractionating of CR naphtha which represent 15.6% wt. from total. feedstock's main characteristics is presented in table 2.

Table 2

CHARACTERISTICS OF CR LIGHT NAPHTHA

Characteristics	Value
Density, [g/cm³]	0.741
Octane number, [RON]	98.9
Final boiling point, [°C]	95
Vapor pressure, [kPa]	41.7
Composition, [% wt.]	
Benzene	9.2
Total aromatics compound	55.8
Saturated hydrocarbons	44.2

In the hydrogenated process was used a monometallic catalyst Ni/Al2O_3-SiO_2 whose main characteristics is presented in table 3.

The Ni/Al_2O_3-SiO_2 catalyst were prepared by multiple incipient wetness impregnation method, using nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%, Sigma-Aldrich). The support

Table 3

CHARACTERISTICS OF CATALYST TYPE Ni/AL_2O_3- SIO_2

Characteristics	Value
Density, [g/cm³]	1.1
Specific Surface [m²/g]	157.13
Total Pore Volume [cm³/g]	0.207
NiO, [%]	59.02
Al_2O_3, [%]	24.12
SiO_2, [%]	16.05
Na_2O, [%]	0.1
Fe_2O, [%]	0.9
Total acidity, [m echiv. NH_3/gcat].	0.2
Total acid sites number	1.2×10^{20}

was obtaining by mixing 1/1 Al_2O_3 with 100Å medium pore diameter, 100 m²/g Alfa Aesar and SiO_2 with 160Å medium pore diameter Alfa Aesar.

The dried support was impregnated with the corresponding aqueous metal nitrate precursors solution with concentration calculated according to the proposed metal content. After vacuum filtration, the catalysts were dried for 8 h at 150°C, calcined under air at 450°C for 6 hours and then kept in a desiccator under vacuum.

Chemical composition of catalyst was determined by atomic absorption using an atomic absorption spectrophotometer VARIAN AA 240 FS DUO and acid strength distribution of the catalyst which was determined by termodesorption of dimethylamine in the temperature range 20-700°C, performed on a *DuPont Instrument Thermal Analyst 2000/2100* coupled with a *module 951 Thermogravimetric Analyzer.* The specific surface areas of the samples were determined using the BET method.

Hydrogenation experiments were carried out into a micropilot plant (fig.1) with fixed bed catalytic reactor. The reactor's total volume is 80 cm³, from which 40 cm³ is volume filled by the catalyst distributed between two layers of an inert ceramic material.

The experiments have been carried out at 100, 150, 180°C, three LHSV 1.0 h^{-1}, 1.5 h^{-1}, 2.0 h^{-1} and 35 bar pressure.

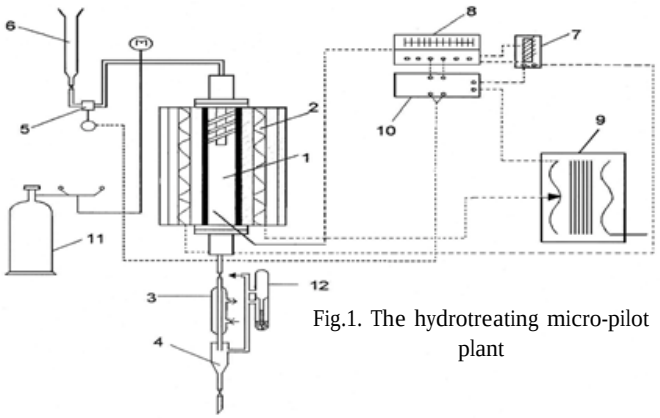

Fig.1. The hydrotreating micro-pilot plant

CR light naphtha fraction which was hydrogenated at 150°C and 1.5 h^{-1} LSHV subjected to a hydroisomerization process to convert cyclohexane (CH) to methylcyclopentane (MCP) in order to increase COR and to partially recover octane loss caused by saturation of aromatics. For isomerization a Pt (0.7%) / H-ZSM 5 (Si/Al = 150, from Union Carbide) was used. Platinum was incorporated into zeolite by impregnation method, using hexachloroplatinic acid (H_2PtCl_6 Merck) prepared at the

desirable equivalent Pt content by adding solution dropwise to the zeolite sample followed by the usual calcination and reduction treatments.

The hydroisomerization experiments have been carried out on the same micropilot plant (fig. 1) at 200, 250°C temperatures, 1.5h^{-1}, 2.5h^{-1} LHSV, 20 bar pressure and 500 cm^3/cm^3 H_2/feedstock ratio.

After each experiment, hydrogenated and hydroisomerization product were analyzed by IR spectrometry using a spectrometer type IROX 2000, in order to establish: the benzene content, total aromatics content and RON.

The measurement principle is based on measuring the infrared absorption (FTIR), by linking and comparing IR spectrogram of analyzed sample with IR matrix spectra, according to ASTM D 5845, in the 650 cm^{-1} la 3700cm^{-1} domain.

Results and discussions

The tests results obtained from light RC naphtha hydrogenation over Ni/Al_2O_3-SiO_2 catalyst and hydroisomerization of hydrogenated naphtha over Pt/ZSM-5 catalyst are depicted in tables 4 and 5.

Table 4 data shows a benzene content decrease in the hydrogenated CR light naphtha fraction at 0.9 %wt. for temperature 180°C and LHSV 1h^{-1} and 4.8 %wt. for temperature 100°C and LHSV 2h^{-1}. Considering that hydrogenated light naphtha is 15.6% wt. from catalytic reforming gasoline, the benzene content in whole reforming gasoline is about 0.14 to 0.74 % wt., facilitating formulation of a fuel which comply with the limit imposed by the EN 228 standard for commercial gasoline. The benzene and total aromatics hydrocarbons conversions in hydrogenation reactions is presented in table 6.

Benzene and total aromatics conversions after hydrogenation process due to reaction temperature over Ni/Al_2O_3-SiO_2 catalyst are presented in figures 2 and 3. At the investigated temperature, the catalyst prove excellent activity in benzene saturation. Temperature increasing determine increasing of benzene conversion.

Conversion increasing with temperature is kinetical justified by increasing the reaction rate. At a higher temperatures the conversion increase is lower because thermodynamic limitation occur due to exothermic character of the hydrogenation reactions. Benzene hydrogenation is achieved with greater conversion than hydrogenation of heavier aromatics like alkyl benzene type (table 6).

Hydrogenation of the benzene substituted with alkyl groups is more difficult than hydrogenation unsubstituted benzene because of steric hindrance effects induced by the alkyl groups. Also, increasing of substitution degree with alkyl groups lead to aromatic ring alkalinity increase by induction effect which produce a stronger adsorption of

Table 4
COMPOSITION AND CHARACTERISTICS OF HYDROGENATED CR LIGHT NAPHTHA

Temperature, [°C]	100			150			180		
LHSV, [h^{-1}]	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Characteristics									
Density, g/cm³	0.723	0.729	0.731	0.714	0.717	0.720	0.697	0.708	0.712
Research Octane Number (RON)	94.4	95.1	96.2	91.6	92.5	93.0	90.6	91.8	92.5
Composition, [%wt.]									
Benzene	3.6	4.3	4.8	1.8	2.2	2.7	0.9	1.3	1.9
Total aromatics	33.60	36.40	40.00	24.30	25.20	28.40	20.80	22.40	24.20
Total saturates	66.40	63.60	62.00	75.70	84.80	81.60	89.20	87.60	85.80

Table 5
COMPOSITION AND CHARACTERISTICS OF CR LIGHT NAPHTHA AFTER HYDROGENATION AND HYDROISOMERISATION

Temperature [°C]	200		250	
LHSV, [h^{-1}]	1.5	2.5	1.5	2.5
Characteristics				
Density [g/cm³]	0.710	0.7313	0.706	0.718
RON	96.5	98.2	97.6	98.8
Composition, [%wt.]				
Benzene	1.7	1.9	1.7	2.0
Total aromatics	24.40	25.00	23.60	24.50
Total saturates	75.6	75.00	76.40	75.50

Table 6
BENZENE AND TOTAL AROMATICS HYDROCARBONS CONVERSIONS IN HYDROGENATION REACTIONS

Temperature, [°C]	100			150			180		
LHSV, h^{-1}	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Conversie, [%wt.]									
Benzene	60.86	53.26	46.82	80.43	76.08	70.65	90.21	85.86	79.34
Total aromatics	39.47	34.76	28.31	56.45	54.83	49.10	62.72	59.85	56.63

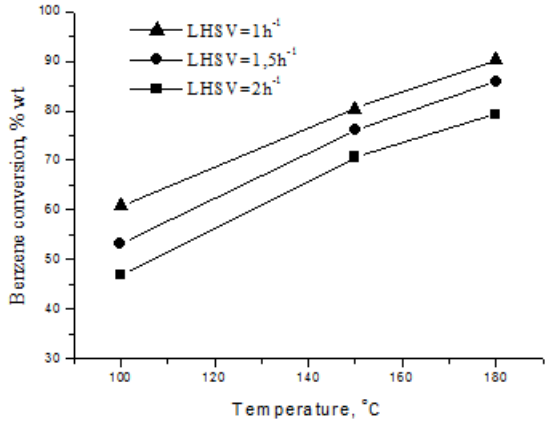

Fig. 2. Benzene conversion as function of temperature and LHSV

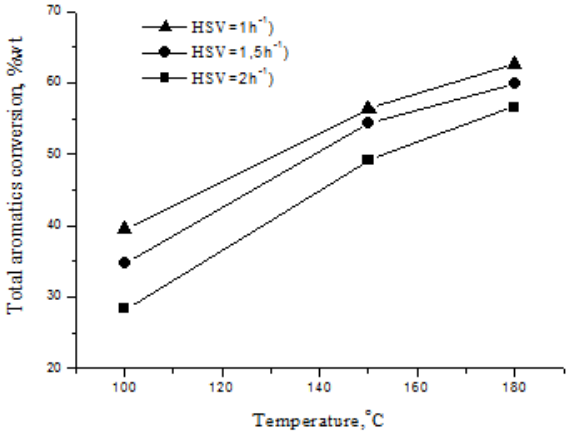

Fig. 3. Total aromatics conversion versus hydrogenation temperature and LHSV

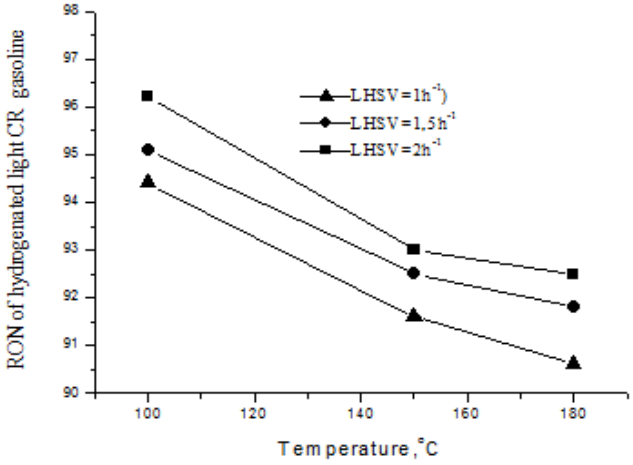

Fig. 4. Gasoline RON versus hydrogenation temperature and LHSW

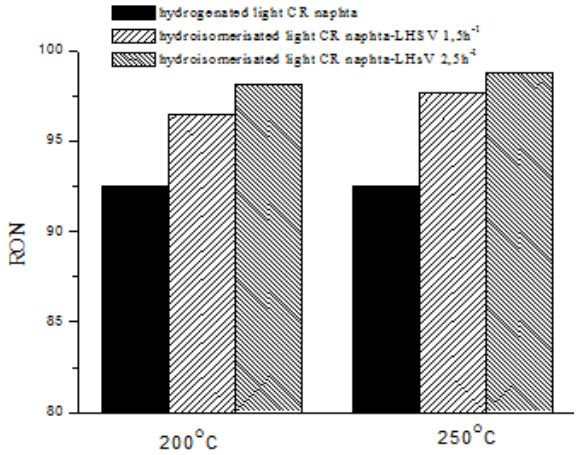

Fig. 5. Octane number of CR light naphtha before and after hydrogenation and hydroizomerization

the catalyst acid sites and higher energy consumption for desorption on metal sites [12,13]. Lower conversions for heavier aromatics than benzene are beneficial because their preservation provide a higher octane number for the hydrogenated CR naphtha.

At the same temperature, increasing the space velocity lead to conversions decreasing for benzene saturation reactions (fig.2.) and for total aromatics saturation reactions (fig. 3) as a result of lowering of the reaction time.

Analyzing the influence of the temperature and LHSV on the hydrogenation reaction conversion, highlight the need of the reaction to be performed at low temperatures and low LHSV. LHSV (1-1.5h^{-1}) provide a longer reaction time to substitute diminishing of reaction velocity due to low temperatures. The 150 °C temperature and 1.5 h^{-1} LHSV are the optimal reaction conditions which ensure a higher conversion for the benzene saturation, without excessive increase of heavier aromatic saturation conversion.

Removal of benzene by hydrogenation process is accompanied by octane number reduction of the hydrogenated CR light naphtha (fig.4). RON decreases by 2.7 to 8.3 octanes proportional with the saturation degree.

It is well known that the CH hydroisomerization over metal/acid bifunctional catalyst form MCP, these being a way to increase of the hydrogenated CR light naphtha RON.

After the CR light naphtha hydroisomerization, the octane number increase by 4.0 to 6.3 octane mainly due to conversion of the CH to MCP which has an octane number with 8 units higher than CH (table 5).

The temperature increase and LHSV decrease for the hydroisomerization reaction (fig.5) determine increasing of hydroisomerization naphtha RON as a results of the CH conversion to MCP.

The chemical composition of gasoline is slightly changed by hydroisomerization. As shown in table 5, after hydroisomerization, the total content of benzene and aromatics decrease from 2.2% to 1.7% wt. for benzene and 25.2% to 23.5% wt. for aromatics, as a result of aromatic hydrogenation side reactions. These reactions occur in the presence of catalyst with hydrogenated metallic function (Pt/HZSM-5) and hydrogen.

In another papers was studied the conversion of hydrocarbons over different HZSM-5 catalysts [15, 16].

Conclusions

Light naphtha from Catalytic Reforming hydrogenation over Ni/Al_2O_3-SiO_2 catalyst have been studied at different temperature and liquid hourly space velocity. The remarkable benzene saturation (less than 0.74 % wt. benzene in total CR naphtha were obtained at 150°C and 1.5 h^{-1} LSHV.

Benzene separation and saturation will result in an octane loss.

The decrease of CR light naphtha octane number can be recover by hydroisomerization over Pt/HZSM-5 catalyst.

The isomerization of cyclohexane to methylciclopentane increase the light naphtha RON with 4-6 octane.

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