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PREFRACTIONATION OF HIGH BENZENE PRECURSORS' FEED FOR HYBRID REFORMER UNIT

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Abstract

Benzene is toxic air pollutant and that's why is set a constraint to 1% (v/v) in gasoline. Refiners have to lower benzene in its gasoline pool components. High benzene contributors are reformate and FCC gasoline. Worldwide practice is to optimize the reformate benzene content. Some light crude oils, like Samgori from Georgia contain more fraction with boiling temperature interval from 60 to 85°C. This fraction is an indicator for benzene precursors content in gasoline. There is a possibility in LNB of prefractionation the reformer feed in columns K 105 from ADU and K1 from hydrotreating of catalytic reforming.

A simulation was run with both aims: lowering benzene precursors and not to decrease reformer feed. The best solution is using K1 for its high potential reboiler's duty.

Key words: benzene precursors, reformate, simulation, light crude oil

1. Introduction

Benzene is one of the key aromatic hydrocarbons desirable in gasoline for its high octane (RON=113). It is present in automotive evaporation and refueling vapors as well as in their exhausts. The positive octane impact has been offset by its tendency to induce severe health hazards as it is a known carcinogenic. In fact benzene was identified as a potent carcinogen and toxic air pollutant (TAP) by the US Clean Air Act of 1990. The actual atmospheric benzene levels in the most highly polluted cities range between 50 and 150 ppm (parts per million). Such high amounts of benzene in the atmosphere are known to cause leukemia, lung, and skin cancer. Also, children and people in the age group of 50-70 are more prone to the risk of developing breathing problems due to idiopathic pulmonary fibrosis, which hardens the air sacs in the lungs causing thickening and scarring. In view of such severe health impact, the European Union has set the safe limit of benzene in air at 10 ppm. [1]. To attain such low benzene levels, directive 2003/17/EU of the European Parliament, concerning fuels quality and World Wide Fuel Charter (WWFC Jan 2000) set constraints in gasoline benzene content to 1% (v/v). New regulations proposed by the EPA under Mobile Sources Air Toxics (MSAT) Phase 2 are expected to reduce benzene in all US gasoline to 0.62 vol % starting Jan. 1,2011. This requirement applies to both US refiners and importers [2].

Lukoil Neftochim Bourgas (LNB) gasoline pool consists of 12 components, which physical and chemical properties are presented in table 1. Components' benzene contribution to gasoline pool is: reformate – 43,9 %; fluid catalytic cracking (FCC) gasoline – 54,6 %; fraction C5 and raffinate from aromatic extraction unit (AEU) respectively – 1,2 % and 0,2 %. Concerning the limit of 1 vol % in the gasoline pool, benzene reduction in the reformate has great effect in meeting the specifications nevertheless the contribution from FCC naphtha is the highest. Lowering the level in FCC naphtha require refiners to look at more expensive benzene- reduction solutions [2].

The two basic approaches to reduce benzene from the reforming unit and thereby reduce the benzene content of the gasoline pool are postfractionation and prefractionation.

Postfractionation offers the best control of gasoline benzene. In postfractionation, reformate is split into a light and heavy stream in a reformate splitter that typically has 40-50 trays.

Table 1 Physical and chemical properties of LNB gasoline components

Components	% in LNB gasoline pool	Density at 15°C, kg/m^3	Benzene content, % (v/v)	RON	MON	Distillation		
						Evaporate at 70°C, % (v/v)	Evaporate at 100°C, % (v/v)	Evaporate at 150°C, % (v/v)
FCC gasoline	52,83	742	0,9	92,7	81,2	31,0	54,6	82,0
Reformate	21,24	800	1,80	98,5	88,0	8,5	24,7	73,5
Alkylate	11,69	705	0,00	95,0	91,0	7,5	27,0	91,0
MTBE	3,76	738	0,00	120,0	111,0	100,0	100,0	100,0
C_5 from AEU	0,51	656	2,00	86,0	76,0	82,0	100,0	100,0
Fr. C_5-86°C	2,91	700	0,00	68,0	63,0	64,0	100,0	100,0
Highly aromatic stream from AEU	1,11	879	0,00	108,0	98,0	0,0	0,0	0,0
Reformate from AEU	2,03	879	0,00	105,0	95,0	0,0	0,0	1,0
Ethylbenzene	0,52	743	0,00	99,0	89,0	0,0	0,0	100,0
Raffinate from AEU	3,23	716	0,06	76,0	68,0	9,0	71,0	94,0
Stream from hydrocarbon resin unit	0,17	891	0,00	127,8	112,8	0,0	10,0	50,0

Benzene is concentrated into the light reformate, and the heavy reformate is blended directly into the gasoline pool. There isn't such a possibility in LNB and it will be a point of a large investment to design and built such a column.

Prefractionation is the only available option with which benzene precursors are removed from the reforming unit feed to prevent or reduce benzene formation. Benzene precursors are primarily C_6 and C_5 naphthenes like cyclohexane, methylcyclopentane and to a far lesser extent C_6 paraffins.

In LNB research laboratory was studied the possibilities to reduce benzene precursors content in catalytic reforming unit feed. Two situations were analyzed:

- Optimizing technological parameters of column K105 from Atmospheric distillation (AD) unit.
- Optimizing technological parameters of column K1 after hydrodesulphurization unit of Catalytic Reforming (CR) unit.

Table 2 Physical and chemical properties of feed and products from columns K105 (normal working conditions)

Property	Method	Feed	Top prod.	Boom prod.
Density at 15°C, kg/m^3	ASTM D 1298	728,0	676,0	751,0
Flow rate, kg/h		39 556	11 400	28 156
Distillation, °C	ASTM D 86	(v/v) evaporate at		
IBP		48	43	106
5%		57	52	112
10%		81	54	114
20%		87	56	118
30%		99	58	121
40%		106	60	125
50%		113	63	129
60%		122	66	134
70%		131	70	140
80%		139	74	146
90%		150	79	155
FBP		183	91.5	180
Hydrocarbon content, %	ASTM D 5134			
Methylcyclopentane		2,73	8,00	0,60
Benzene		0,50	1,56	0,08
Cyclohexane		2,07	5,08	0,86
Σ benzene precursors		5,30	14,64	1,54

2. Experimental

A commercially available software simulator was used in order to calculate benzene precursors' distribution and to describe the technological parameters of two columns K105 in AD and column K1 in CR.

Columns K105 splits fraction 35-180°C into top product –light naphtha (35-100°C) and bottom product –heavy naphtha (100-180°C). The bottom fraction is used as CR unit feed. Distillations of fractions is let according to ASTM D 86, density is analyzed according to ASTM D 1298. Physical and chemical characteristics and hydrocarbon type, analyzed according to ASTM D 5134 are reported in table 2. The normal working conditions of column K105 are presented in figure 1 and the reflux ratio is 1,3. The reboiler consists of two sections. The heat from heavy straight run gas oil (HSRGO) is utilized in the lower and the heat from middle straight run gas oil (MSRGO) - in the upper section.

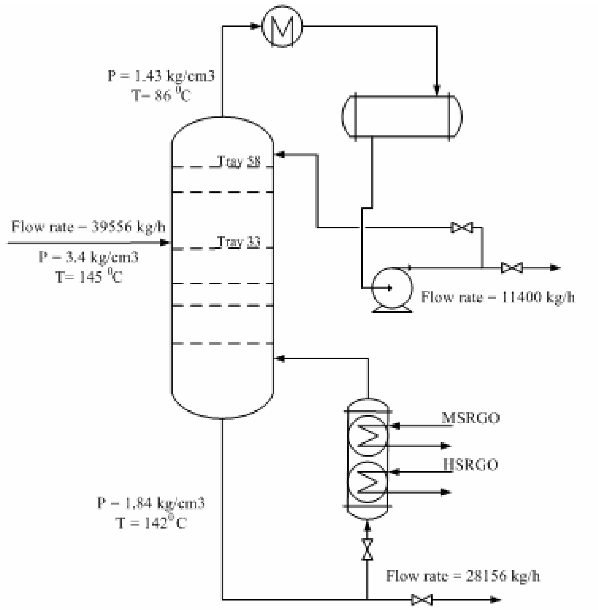

Figure 1 Normal technological parameters of columns K 105

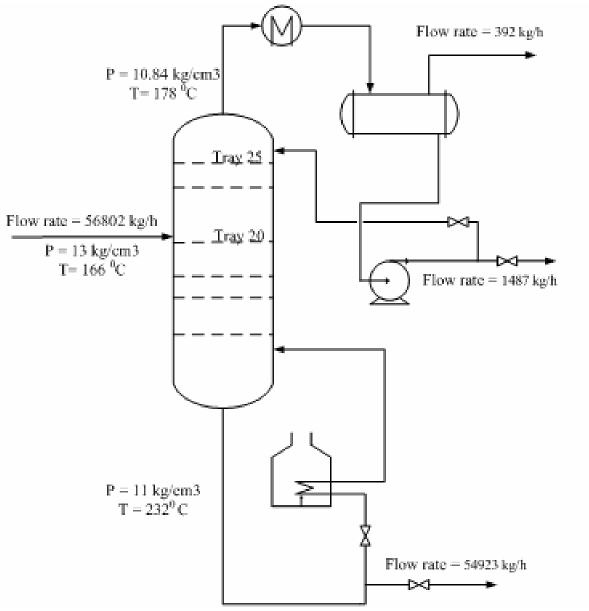

Figure 2 Normal technological parameters of columns K 1

Column K1 stabilizes heavy naphtha (fraction 100-180°C), feed for CR after it is hydrotreated. The normal working conditions of column K105 are presented in figure 2 and the reflux ratio is 10.3. Physical and chemical characteristics and hydrocarbon type of feed and products from column K1 are reported in table 3. A furnace is used for reboiler with normally used duty of 5,5 KW.

Bottom product from columns K105 after passing trough unit for hydrotreating fed column K1. The scheme is described in figure 3.

Table 3 Physical and chemical properties of feed and products from columns K1 (normal working conditions)

Property	Method	Feed	Gas	Top prod.	Bottom prod.
Density at 15°C, kg/m^3	ASTM D 1298	737,0	0,687	662,0	751,8
Flow rate, kg/h		56 802	392	1 487	54 923
Distillation, °C	ASTM D 86	(v/v) evaporate at			
IBP		-267		30	110
5%		109		59	116
10%		114		65	119
20%		121		70	123
30%		125		73	127
40%		127		74	130
50%		129		76	134
60%		138		77	139
70%		146		80	144
80%		155		83	150
90%		172		91	159
FBP		197		104	174
Hydrocarbon content, %	ASTM D 5134				
Methylcyclopentane		0,49		14,70	0,08
Benzene		0,07		2,85	0
Cyclohexane		0,72		8,10	0,52
Σ benzene precursors		1,28		25,65	0,60

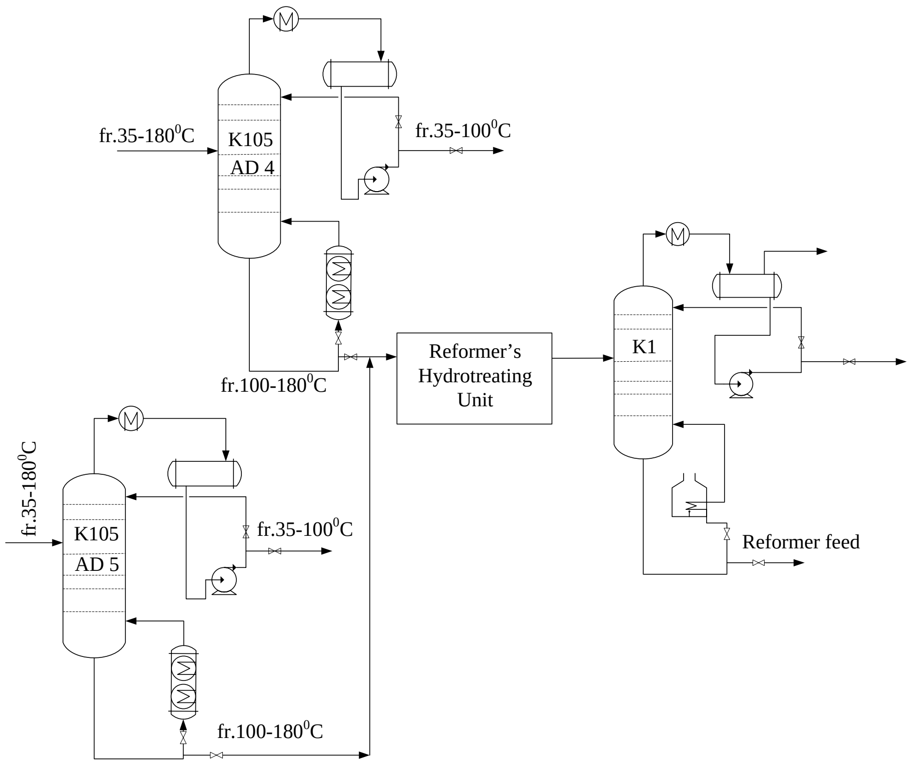

Figure 3 Pipe communications between ADU and CR

3. Results and discussion

In LNB were processed mainly Russian Export Blend Crude Oil (REBCO) and individual crude oils from Former Soviet Union countries (FSU). TBP analyses showed that fraction 60-85^{o}C was 9,5 % from fraction IBP-180^{o}C. According to data published in [3], benzene precursors' content for most crude oils from FSU in fraction 60-85^{0}C varies in the rage 40-53 %. This statement was confirmed by a hydrocarbon type analyses of REBCO's fraction IBP-180. The result was 5,05%. Benzene precursors' content in this fraction could be easily calculated as the quantity of fraction 60-85^{o}C in fraction IBP-180^{0}C was known:

$$BP = 0.53^{*}\ (FR60\text{-}85^{o}C) \qquad (1)$$

Where,

BP = benzene precursors, % (v/v)

FR60-85^{o}C = content of fraction 60-85^{o}C in fraction IBP-180 ^{0}C, % (m/m)

Removing benzene and its precursors from the reformer feedstock limits the benzene produced in reformer. Low pressure reformers (less than 100 psig) have a low level of dealkylation reactions, so the prefractionation strategy may produce an appropriate low benzene product. For higher pressure reforming unit a splitter is needed for postfractionation of reformate [4]. LNB hybrid reformer has four reactors working in series. Three of them are fixed bed with working pressure of 1,69MPa (230 psig) and the last one is with continuous catalytic regeneration -1,3 MPa (188,5 psig). Table 4 presents hydrocarbon content of both hydrotreated, stabilized feed and reformate from five LNB reformer's samples. A correlation is observed between the feed content of methyl cyclopentane (naphthene with five carbon atoms), cyclohexane (naphthene with six) and benzene (aromatic hydrocarbon with six carbon atoms) and benzene content in reformate:

$$Benzene_{ref.} = BP_{feed}/\ (RY/100) \qquad (2)$$

Where,

$Benzene_{ref.}$ = Benzene content in reformat, % (v/v)

BP_{feed} = benzene precursors (methyl cyclopentane, cyclohexane and benzene) content in feed, % (m/m)

RY = Reformate yield, %

This correlation revealed that all (almost 100%) of benzene precursors were transformed into benzene at the working conditions of LNB hybrid reformer. No reactions of high molecular weight arenes dealkylation were observed.

The benzene content in reformat reached values up to 1,80 % when processing REBCO. LNB philosophy was maximum utilization the heat of streams. MSRGO and heavy straight run gas oil HSRGO passed through column K105's reboiler in order to minimize energy expenses. The maximum flow rate of MSRGO was 16 933 kg/h, inlet temperature of 255°C and outlet temperatures of 178^{0}C at pressure 10 kg/cm^2. Exchanged heat was 3 534MJ/h. The maximum flow rate of HSRGO was 44 941 kg/h, inlet temperature of 206°C and outlet temperatures of 187°C at pressure 8,9 kg/cm^2. Total exchanged heat was 2 212 MJ/h. Total calculated duty of column K105's reboiler was 5 746 MJ/h. This maximum value was used in column simulation. Result is shown in table 2. The heat from two GO streams was enough to lower benzene precursors' content in K105's bottom product (1,54%). This low level allowed the K105's entire bottom product to be fed into reformer reactor after hydrotreating. That means that benzene in reformate would stay under 1,80%. Then the role of K1 was only to stabilize reformer feed and there would be no need to separate wild naphtha.

Table 4 Hydrocarbon type of reformate and reformer feed

	Feed	Reform.	Feed	Reform.	Feed	Reform.	Feed	Reform.
Composition, wt,%	Sample1		Sample2		Sample3		Sample4	
Total n-Paraffins	29,48	11,20	26,95	9,32	24,13	9,83	24,29	10,20
Total I-Paraffins	32,15	19,68	32,01	17,96	33,03	18,59	32,05	18,87
Naphthenes (Nf)								
C_5	0,01		0,01		0,00		0,01	
C_6	1,14		1,24		1,16		1,12	
C_7	7,85		8,24		10,46		8,36	
C_8	7,13		9,49		8,06		7,37	
C_9	8,17		7,46		8,41		8,88	
C_{10}	1,51		1,18		1,32		1,64	
C_{11}	0,06		0,43		0,27		0,09	
C_{12}	0,00		0,00		0,00		0,00	
Total naphthenes	25,88	1,25	28,04	0,82	29,69	1,06	27,48	1,91
Aromatics (Ar)								
C_6	0,09	1,50	0,09	1,60	0,07	1,49	0,10	1,50
C_7	1,74	15,32	1,46	14,30	1,91	16,70	1,86	15,42
C_8	4,63	23,73	4,20	24,44	4,43	24,19	5,27	23,50
C_9	3,88	10,92	4,80	19,28	4,08	17,03	3,46	10,52
C_{10}	1,97	14,60	2,16	9,77	1,49	7,95	1,94	15,02
C_{11}	0,11	1,50	0,20	2,15	0,07	1,50	0,10	0,69
C_{12}	0,07	0,29	0,08	0,38	0,02	0,37	0,05	0,50
Total aromatics	12,49	67,86	12,99	71,91	12,07	69,22	12,78	67,16
Total hydrocarbons	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00
Reformate yield (C5+), wt%		83,00		84,00		83,00		83,00
Nf (C_5+ C_6) +Ar(C_6) , wt%	1,24		1,34		1,24		1,24	
Ar(C_6) , wt%		1,50		1,60		1,49		1,50

A problem arises when lighter crude oils were processed (higher content of fraction 60-85°C in fraction IBP-180°C). Typical crude oil was Samgori from Georgia. According to TBP analyses the content of fraction 60-85°C in fraction IBP-180°C was 14.3%. Benzene precursors can be calculated by equation 1.

BP = 0.53*14.3 = 7,58 %

There were two possibilities when simulating column K105 with new feed (7,58 % benzene precursors) and maximum reboiler duty of 5 746 MJ/h : to increase quantity of top fraction (13 500 kg/h) aiming at 1,54% benzene precursors in bottom product; to distil the same quantity of top fraction (11 400 kg/h) but with higher content of benzene precursors. Normal conditions are processing REBCO with benzene precursors 5,05% in fraction IBP-180°C and products quality described in tables II and III.

The first solution was quite unacceptable and was presented in table 5. The level of benzene precursors in bottom product was maintained but it decreased in quantity.

Table 5 Physical and chemical properties of feed and products from columns K105 (maximum reboiler duty = 5 746 MJ/h, 1,54 % benzene precursors in bottom fraction)

Property	Method	Feed	Top prod.	Boom prod.
Density at 15°C, kg/m^3	ASTM D 1298	729,0	686,0	753,0
Flow rate, kg/h		39 556	13 500	26 056
Distillation, °C	ASTM D 86		(v/v) evaporate at	
IBP		48	48	104,5
5%		56	50	113
10%		80	51	118
20%		86	59	121
30%		98	69	124
40%		104	69,5	127
50%		110	70	131
60%		120	73	136
70%		129	83	141
80%		138	87	147
90%		149	93	158
FBP		183	100,5	183
Hydrocarbon content, %	ASTM D 5134			
Methylcyclopentane		3,87	10,39	0,48
Benzene		0,72	2,00	0,06
Cyclohexane		2,99	6,82	1,00
Σ benzene precursors		7,58	19,21	1,54

The RON of LNB gasoline pool was under 95. In order to meet the requirements in [5] it was very important to save and even increase quantity of components with high RON. That's why the decrease of feed for reformer would have a negative effect towards LNB gasoline pool.

Applying the second solution saved the quantity but increased benzene precursors in reformer feed (2,39%) – table 6.

Table 6 Physical and chemical properties of feed and products from columns K105 (maximum reboiler duty = 5 746 MJ/h , quantity of top prod = 11 400 kg/h)

Property	Method	Feed	Top prod.	Boom prod.
Density at 15°C, kg/m^3	ASTM D 1298	729,0	681,0	751,0
Flow rate, kg/h		39 556	11 400	28 157
Distillation, °C	ASTM D 86		(v/v) evaporate at	
IBP		48	48	79
5%		56	49	109,5
10%		80	50	114
20%		86	55	117
30%		98	64	120
40%		104	66	124
50%		110	68	128
60%		120	70	133
70%		129	73,5	139
80%		138	82	146
90%		149	85	156
FBP		183	97,5	184
Hydrocarbon content, %	ASTM D 5134			
Methylcyclopentane		3,87	11,06	0,95
Benzene		0,72	2,16	0,13
Cyclohexane		2,99	7,14	1,31
Σ benzene precursors		7,58	20,36	2,39

That means that feed for reformer should be fraction furthermore in K1 because technological target was under 1,50 % benzene precursors. K 1 reboiler was a furnace. Normally this furnace duty was 19 800 MJ/h (5,5 MW). It had extra heat capacity up to 21 132 MJ/h (5,87 MW) maximum. The excess of benzene precursors in bottom fraction (2,39-1,54 = 0,85 %) should be distill with wild naphtha picked out from the column K 1 reflux drum. Table 7 describes simulation results for column K 1 with maximum duty of its reboiler.

Table 7 Physical and chemical properties of feed and products from columns K1 (maximum reboiler duty = 21 132 MJ/h , 1,49% benzene precursors in bottom fraction)

Property	Method	Feed	Gas	Top prod.	Bottom prod.
Density at 15°C, kg/m^3	ASTM D 1298	737,0	341	710	744
Flow rate, kg/h		56 802	401	1 274	55 127
Distillation, °C	ASTM D 86		(v/v) evaporate at		
IBP		-267,1		-50	104
5%		107		9	113
10%		113		72	118
20%		120		76	122
30%		125		77	125
40%		127		77,5	128
50%		129		78	130
60%		137		78,5	139
70%		146		79	146
80%		154		85	156
90%		171		91	172
FBP		197		127	197
Hydrocarbon content, %	ASTM D 5134				
Methylcyclopentane		0,95		26,38	0,33
Benzene		0,13		4,44	0,02
Cyclohexane		1,31		8,72	1,14
Σ benzene precursors		2,39		39,54	1,49

Analyzing the opportunities of decreasing benzene precursors content with restriction to save the quantity of reformate a conclusion can be made. Distilling benzene precursors from lighter Samgori crude oil in K1 would not let reformer feed to decrease with 3 015 kg/h as it would happen when K105 was used to obtain benzene precursors' level of 1.50%.

$SRF = BP_{K1} - 2^* BP_{K105}$

SRF = 55 127-2*26 056 = 3 015 kg/h

Where,

SRF – saved reformer feed, kg/h

BP_{K1} – bottom product from column K1, kg/h

BP_{K105} – bottom product from column K105, kg/h

The multiplier 2 – means that there are two identical columns K 105

4. Conclusion

Almost 100% of benzene precursors were transformed into benzene at the working conditions of LNB hybrid catalytic reforming. No reactions of high molecular weight arenes dealkylation are observed.

Lighter crude oils are desired in refinery crude diet in terms of high yield of white fractions (ibp-360°C) but some of them posses higher content of fraction 60-85°C (benzene precursors) too. An optimization of column parameters for reformer feed preparation were required. The most effective way of decreasing benzene precursors in CR feed and saving its quantity is to increase reboiler's duty.

Target of 0,62 % benzene in gasoline pool (0,66 % in reformat) with prefractionation of reformer feed was not a possible solution for hybrid type LNB unit.

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