



The study of the effect of the concentration of propylene in the PPF to the liquid yield of the reaction

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ABSTRACT

The results of the study of the effect of the concentration of propylene to propane-propylene fraction to a liquid yield of the reaction depending on the feed space velocity are presented. The results in the presence of a chromia-alumina catalyst in oxides of Ni, Co, Cr are examined. The optimal reaction conditions ($T=280^{\circ}\text{C}$, $V_{\text{overall velocity}} 50\text{-}200 \text{ h}^{-1}$), in which the liquid yield of the reaction was determined depending on the concentration of C_3H_8 and C_3H_6 in the raw feedstock, were set.

Indexing terms/Keywords

Paraffin, olefins of alkylation, liquid yield of the reaction



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One of the most important tasks of oil refining from both the environmental as well as economic points of view is the effective use of hydrocarbon residue gas of refineries and the chemical industry for the production of light oil products and raw materials for the petrochemical industry. The problem of using gases of catalytic cracking can be solved to a great degree by the introduction of new processes of their alkylation over zeolite-containing catalysts in oil refining. In this regard, the problem of expansion of production of alkylation gasoline, which share now accounts for about one seventh of the total volume of the world's gasoline production, arises.

Most part of alkylation gasoline is produced by reacting isobutane with C_2 - C_5 olefins in the presence of a catalyst. A drawback of these productions is the formation of acid sludge as well as the use of solely isoparaffins as a raw material. In this regard, the importance of developing new processes using heterogeneous catalysts is increasing. Development and implementation of recycling process of gases of oil refineries would allow production of an additional amount of automobile gasoline and drastic reduction of the amount of harmful emissions into the atmosphere.

Modern automobile gasoline is prepared by mixing the components obtained by direct distillation, catalytic cracking and reforming, alkylation, isomerization, polymerization and other refining processes [1]. Alkylate, obtained by alkylating isobutane with C_3 - C_5 olefins, is one of the most promising components among them. Alkylate is a component satisfying the technical-operational and environmental requirements of modern European standards for fuel. This process significantly reduces manufacturing costs and provides high-quality gasoline [2].

Currently, one of the most important areas of modern petro chemistry is the development of new solid acid catalysts of alkylation over zeolites. Zeolites have sufficient activity, stability and the ability to regenerate, which is essential for the practical implementation of the process. It is commonly known, zeolites are multifunctional. They possess isomerizing, hydrogenating and dehydrogenating properties and can lead reaction to oligomerization of cracking, cyclization. Unlike mineral acids, zeolite catalysts may be modified and promoted. At that, there is no need to separate the catalyst from the reaction mixture, and it becomes possible to carry out the process in continuous conditions and the environmental conditions significantly improve [3,4,5].

Of all the existing methods for producing unsaturated hydrocarbons, the main share is accounted for the catalytic dehydrogenation of n-paraffins. This is due to the large number of studies conducted on the improvement and development of new catalysts [6,7].

EXPERIMENTAL PART

The purpose of this study is to investigate the activity of the chromia-alumina catalyst promoted with oxides of Ni, Co, Cr and study of the effect of the concentration of propylene to propane-propylene fraction to a liquid yield of the reaction depending on the feed space velocity.

One of the characteristics of the recommended process, developed in Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, is the involvement of paraffins contained in the gases of the catalytic cracking in the alkylation reaction via their dehydrogenation to the corresponding olefins. The resulting propylene C_3 - C_4 participates in the alkylation reaction of paraffins. With this purpose, modifiers Ni, Cu, Co in an amount of 10% are added into composition of the industrial zeolite catalyst OMNIKAT-210П by applying them to a base, γ - Al_2O_3 in an amount of 10% is taken as the binder. The reactor was charged with the catalyst in an amount of 30 cm^3 . We have found that in the catalyst subjected to calcination under vacuum at a temperature ~ 500 - 550°C , $NiAl_2O_4$ and $CoAl_2O_4$ are formed, presence of which leads to formation of olefins by dehydrogenation of the corresponding paraffins.

In order to study the effect of the concentration of C_3H_6 in the initial fraction to yield liquid reaction products, artificial mixture of from pure propane and propylene was prepared (95-96% purity). The concentration of propylene in the artificial mixture was varied from 40 to 60% at a constant feed space velocity of PPF ($50\div 200\text{ h}^{-1}$). The volume of the loaded zeolite catalyst - 30 cm^3 . Studies were carried out at a temperature of 280°C . The contact time at a feed space velocity of PPF 50 h^{-1} is 22.4 seconds (Table 1).

As shown in Table 2, when changing the concentration of C_3H_6 from 40 to 60% of volume concentration of C_3H_8 changes from 60 to 40%. At a feed space velocity of PPF 50 h^{-1} , 100% conversion of C_3H_6 is observed. Conversion of C_3H_8 thus increases from 9.8% at its content in the initial fraction of 60% to 28.7% at its content of 50%. Then conversion of C_3H_8 is somewhat reduced to 24.4% at 40 % concentration of C_3H_8 . With increasing concentrations of C_3H_6 in the mixture of 40 to 60%, yield of liquid product per unit weight of the catalyst increases from 0.068 g/hr to 0.1 g/hr. The yield of liquid to the original PPF increased from 42.4 to 69.8%. The yield of liquid on C_3H_6 increased from 117.3 wt% at a concentration of C_3H_6 in the initial mixture in 40 wt% to 124.37 wt% at 50% concentration of C_3H_6 , and then liquid propylene yield decreased to 116.3% (Table 3).



Table 1. Change of technological parameters of process of conversion of C₃H₆ and C₃H₈ into the liquid yield of reaction (t=280°C): (Cross-section of reactor-3.14 cm², catalyst weight -18.1 g, Catalyst volume -30 cm³, height of catalyst layer -6 cm)

Indicators	Composition of raw material, l/h			
	C ₃ H ₆	0.6	0.75	0.9
	C ₃ H ₈	0.9	0.75	0.6
V _{overall velocity} , h ⁻¹	50.0			
V _{steam volume} , l/h	1.5			
V _{steam volume (t)} , l/h	3.04			
V _{overall velocity (t)} , h ⁻¹	101.3			
V _{linear velocity} , cm/s	0.268			
τ _K , sec	22.4			

Table 2. Change of conversion of C₃H₈ and C₃H₆ depending on their concentration in raw material composition (t=280°C)

Indicators	Units of meas.	Concentration of components in raw material, wt%			
		C ₃ H ₆	40	50	60
		C ₃ H ₈	60	50	40
C ₃ H ₈ init.	g/h	1.885	1.178	1.125	
C ₃ H ₈ prom.	g/h	1.7	0.84	0.85	
C ₃ H ₆ init.	g/h	1.068	1.387	1.687	
C ₃ H ₆ from dehyd.C ₃ H ₈	g/h	0.176	0.32	0.262	
C ₃ H ₆ prom.	g/h	-	-	-	
Conversion of Σ C ₃ H ₆	g/h	1.244	1.707	1.95	
Conversion of C ₃ H ₈	g/h	0.185	0.338	0.275	
Conversion of C ₃ H ₈	wt%	9.8	28.7	24.4	
Conversion of C ₃ H ₆	wt%	100	100	100	

Table 3. Change of conversion rate of C₃H₈ и C₃H₆ and the liquid yield of reaction depending on concentration of C₃H₈ and C₃H₆ in raw material (t=280°C)

Indicators	Units of meas.	Composition of raw material, %			
		C ₃ H ₆	40	50	60
		C ₃ H ₈	60	50	40
Conversion of C ₃ H ₆	mole/h	0.03	0.04	0.046	
Conversion rate of Σ C ₃ H ₆ ·10 ⁻⁴	mole/l _K ·sec	2.74	3.76	4.26	
Conversion of C ₃ H ₈	mole/h	0.0042	0.0077	0.00625	
Conversion rate of Σ C ₃ H ₈ ·10 ⁻⁴	mole/l _K ·sec	0.39	0.71	0.58	
Quantity of liquid product	g/h	1.253	1.725	1.962	
Yield of liquid product per unit weight of the catalyst	g/h	0.068	0.094	0.1	
Yield of liquid raw product	wt%	42.43	67.25	69.77	
Yield of liquid original propylene	wt%	117.32	124.37	116.3	



From the above it follows that the C_3H_6 is fully involved in the reaction and C_3H_8 is alkylated, the maximum amount thereof that is involved in the reaction is achieved at 50% content in the original mixture. Further reduction of the concentration of C_3H_8 in the original mixture leads to a reduction of alkylation reaction of C_3H_8 by propylene and therefore the yield of liquid is reducing based on the initial C_3H_6 .

When the feed space velocity of 100 h^{-1} (process indicators are given in Table 4) yield of liquid per unit of weight of the catalyst increases from 0.105 to 0.257 g/h. at a 50% concentration of C_3H_6 , and then reduces to 0.1 g/h. The yield of liquid to original propylene is respectively changed from 84.8 to 152.46 wt% and then reduced to 58.5 wt%. The conversion of C_3H_6 (wt%) thus varies from 70.2 to 99.2% and then reduced to 39.6 wt%. Conversion C_3H_8 increases from 9.3 to 61.1% and then decreased to 27.3 wt% (Table 5). Consequently, in this case, there is a saturation of the catalyst with propylene and further increase of the concentration of C_3H_6 in the feedstock does not lead to increase of the yield of liquid products (see Table 6). The yield of liquid product on feedstock from increase the concentration of C_3H_6 in the feedstock increases from 33.02 to 80.9 wt% to 50% of C_3H_6 content in the feedstock then is reduced to 34.6 wt% at the content of C_3H_6 in 60% by volume.

By increasing the feed space velocity from 50 to 200 h^{-1} , conversion of C_3H_8 increases from ~9.5 to 10.5 wt%, while reducing the yield of liquid products both to C_3H_6 and all the feedstock, wherein the concentration of C_3H_6 accounts for 40%, the rest is C_3H_8 . Consequently, with increasing of partial pressure of C_3H_8 , alkylation reaction of C_3H_8 by propylene also increases.

With the content of C_3H_8 the feedstock in amount of 50%, the conversion of C_3H_8 increases to feed space velocity of 100 h^{-1} . Then C_3H_8 conversion decreases from 61 to ~8%. As a consequence, the yield of liquid raw material initially increases and after 100 h^{-1} decreases. Decrease the concentration of C_3H_8 in the feed to 40% leads to reduction the conversion of C_3H_8 , caused by the decrease of its partial pressure. This leads to a reduction of alkylation reaction of C_3H_8 by propylene. The yield of liquid to the source C_3H_8 decreases from ~120 to 15%. This decrease means a reduction of alkylation reaction of C_3H_6 by propylene.

The contact time of hydrocarbon vapors with the catalyst is 11.2 sec (Table 4). With increase of contact time (5.6-11.2-22.4 s) or decrease of feed space velocity (PPF) ($200-100-50\text{ h}^{-1}$) from 5.6 to 11.2, yield of liquid product per unit weight of the catalyst increases from 0.128 to 0.257 g/h but further increase of the contact time to 22.4 leads to decrease in the yield of liquid per unit weight of the catalyst.

Table 4. Change of technological parameters of process of conversion of C_3H_6 and C_3H_8 into the liquid yield of reaction ($t=280^\circ\text{C}$)

Indicators	Composition of raw material, l/h			
	C_3H_6	1.2	1.5	1.8
	C_3H_8	1.8	1.5	1.2
$V_{\text{overall velocity, h}^{-1}}$	100			
$V_{\text{steam volume, l/h}}$	3			
$V_{\text{steam volume(t), l/h}}$	6.07			
$V_{\text{overall velocity (t), h}^{-1}}$	202.56			
$V_{\text{linear velocity cm/sec}}$	0.537			
τ_k, sec	11.2			


Table 5. Change of conversion of C_3H_8 and C_3H_6 depending on their concentration in raw material composition ($t=280^\circ C$)

Indicators	Units of meas.	Concentration of components in raw material, wt%			
		C_3H_6	40	50	60
		C_3H_8	60	50	40
C_3H_8 init.	g/h		3.528	2.7	2.27
C_3H_8 prom.	g/h		3.2	1.05	1.65
C_3H_6 init.	g/h		2.25	3.05	3.287
C_3H_6 from dehyd. C_3H_8	g/h		0.313	1.575	0.592
C_3H_6 prom.	g/h		0.67	0.025	1.984
Conversion of ΣC_3H_6	g/h		1.893	4.6	1.895
Conversion of C_3H_8	g/h		0.328	1.65	0.62
Conversion of C_3H_8	wt%		9.3	61.1	27.3
Conversion of C_3H_6	wt%		70.2	99.2	39.6

This is explained by the fact that with increase of the contact time, emerging dimers were further converted with emergence of trimers, cyclic hydrocarbons, etc. These compounds are adsorbing on the catalyst surface at the reaction temperature ($280^\circ C$) and are not desorbing, thereby lowering the number of active centers and reducing the active surface, which leads to a decrease in the yield of liquid per unit weight of the catalyst. The yield of liquid to the source C_3H_6 with increase of a contact time from 11.2 seconds to 22.4 seconds, which corresponds to the feed space velocity from 100 to 50 h^{-1} (Table. 1, 4), is reduced from 152.5 to 124.4 %.

With feed space velocity of 200 h^{-1} (Table 7), which corresponds to a contact time of 5.58 s, yield of liquids to introduced C_3H_6 is also reduced from 152.5% at $\tau_k=11,2\text{ s}$. (Table 4) to 40% at 5.58 s. Essentially doubly reducing the contact time results in fact that the residence time of C_3H_6 on the surface is not enough for both dimerization like reaction and involving of C_3H_8 in alkylation reaction. And increasing the contact time from 5.6 to 22.4 leads to increased conversion of C_3H_8 from 6.8 to 61.1%. Thus, with 50% concentration of propane, increasing the contact time promotes the alkylation reaction of C_3H_8 by propylene. Table 8 presents the value of the conversion of propane and propylene, depending on their initial concentration in the feedstock. Table 9 presents the value of the transformation rate of propane and propylene into yield liquid reaction products, depending on the concentration of propane and propylene in the feedstock.

Table 6. Change of conversion rate of C_3H_8 и C_3H_6 and the liquid yield of reaction depending on concentration of C_3H_8 and C_3H_6 in raw material ($t=280^\circ C$)

Indicators	Ед.из м.	Concentration of components in raw material, wt%			
		C_3H_6	40	50	60
		C_3H_8	60	50	40
Conversion rate of $\Sigma C_3H_6 \cdot 10^{-4}$	mole/l \cdot sec		4.16	10.2	0.045
Conversion of ΣC_3H_6	mole/h		0.045	0.11	0.045
Conversion of C_3H_8	g/mole		0.00745	0.0375	0.014
Conversion rate of $\Sigma C_3H_8 \cdot 10^{-4}$	mole/l \cdot sec		0.69	3.47	1.3
Quantity of liquid product	g/h		1.908	4.65	1.923
Yield of liquid product per unit weight of the catalyst	g/h \cdot sec		0.105	0.257	0.1
Yield of liquid raw product	wt%		33.02	80.87	34.6
Yield of liquid original propylene	wt%		84.8	152.46	58.5


Table 7. Change of technological parameters of process of conversion of C₃H₆ and C₃H₈ into the liquid yield of reaction (t=280°C)

Indicators	Composition of raw material, l/h			
	C ₃ H ₆	2,4	3,0	3,6
	C ₃ H ₈	3,6	3,0	2,4
V _{overall velocity} , h ⁻¹	200			
V _{steam volume} , l/h	6			
V _{steam volume(t)} , l/h	12.15			
V _{overall velocity (t)} , h ⁻¹	405			
V _{linear velocity} sm/sec	1.075			
τ _k , SEC	5.58			

Table 8. Change of conversion of C₃H₈ and C₃H₆ depending on their concentration in raw material composition (t=280°C)

Indicators	Units of meas.	Concentration of components in raw material, wt%			
		C ₃ H ₆	40	50	60
		C ₃ H ₈	60	50	40
C ₃ H ₈ init.	g/h		6.43	5.7	4.56
C ₃ H ₈ prom.	g/h		5.747	5.31	4.36
C ₃ H ₆ init.	g/h		5.1	5.8	6.89
C ₃ H ₆ from dehyd.C ₃ H ₈	g/h		0.652	0.37	0.191
C ₃ H ₆ prom.	g/h		4.12	3.87	6.037
Conversion of Σ C ₃ H ₆	g/h		1.632	2.3	1.044
Conversion of C ₃ H ₈	g/h		0.683	0.39	0.2
Conversion of C ₃ H ₈	wt%		10.62	6.8	4.4
Conversion of C ₃ H ₆	wt%		28.3	37.27	14.7

Table 9. Change of conversion rate of C₃H₈ и C₃H₆ and the liquid yield of reaction depending on concentration of C₃H₈ and C₃H₆ in raw material (t=280°C)

Indicators	Units of meas.	Concentration of components in raw material, wt%			
		C ₃ H ₆	40	50	60
		C ₃ H ₈	60	50	40
Conversion rate of Σ C ₃ H ₆ ·10 ⁻⁴	mole/l _k ·sec		3.52	5	2.3
Conversion of Σ C ₃ H ₆	mole/h		0.038	0.054	0.025
Conversion of C ₃ H ₈	g/mole		0.015	0.009	0.0045
Conversion rate of Σ C ₃ H ₈ ·10 ⁻⁴	mole/l _k ·sec		1.43	0.83	0,42
Quantity of liquid product	g/h		1.663	2.32	1.053
Yield of liquid product per unit weight of the catalyst	g/h·sec		0.09	0.128	0.058
Yield of liquid raw product	wt%		14.42	20.17	9.19
Yield of liquid original propylene	wt%		32.6	40	15.3



CONCLUSION

Changes in the concentration of propylene in the PPF (propane propylene fraction) to the yield of liquid products are described in the proposed article:

With the increase of space velocity (50-200 h⁻¹ at a temperature of 280⁰C), conversion of C₃H₈ increases from 28.7% to 61.1% and with a further increase in the space velocity decreases to 6.8%. At the same conditions C₃H₆ reduces from 100% to 99.2% and, at higher space velocity with concentration of the components in the initial mixture (50/50 of C₃H₈ и C₃H₆), conversion decreases to 37.27%.

As it can be seen from Table 2, C₃H₆ is fully involved in the reaction but C₃H₈ is subjected to alkylation.

It is established that the yield of liquid products at the initial propylene (V_{overall velocity}, 50-200 h⁻¹) increases from 124.37% to 152.46% and at higher feed space velocity reduces to 40%. The best option of experiment is τ=11.2sec, V_{overall velocity}=100 h⁻¹.

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