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Petrochemistry**AEROBIC OXIDATION OF NAPHTHENE-PARAFFIN HYDROCARBONS
MIXTURE OF BAKU OILS UNDER THE INFLUENCE
OF VARIOUS CATALYTIC SYSTEMS****Academician of ANAS V.M.Abbasov, M.C.Ibrahimova, L.M.Afandiyeva,
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This paper presents the results of liquid phase oxidation of naphthenic-paraffinic hydrocarbons obtained from 217-349°C fractions of Baku oils in the presence of Cr-Mn salts of natural petroleum acids, and catalysts based on the precipitation of Cr,Mn salts on a copolymer consist of styrene and butoksimetilemetakrilate at a temperature 135-140°C. Synthetic petroleum acids have been isolated from these oxidate and was proved that using catalytic composites with minimal amount of metals (0.3% for raw materials) increased the catalytic activity, acid number and yield synthetic petroleum acids.

Keywords: diesel fraction, extraction, oxidation, catalysts, synthetic petroleum acids

Currently organic acids are one of the most widely used product as raw materials in the chemical and petrochemical synthesis [1]. Moreover, there is a great need for acids contain naphthenic ring in its radicals, as they make possible to obtain products with a higher exploitation properties. Thus, it is possible to synthesize additives to improve the quality of diesel fuel, high effective corrosion inhibitors, bactericides, conservation fluids, siccatives to lacquer-dye substances and surfactants on the bases of metal salts, oxygen, nitrogen derivatives of the synthetic petroleum acids (SPA) [2-6]. Baku oils are their main source since synthesis processes of such acids were not developed. However, amount of natural petroleum acids (NPA) separated from these oils are limited and contain phenol derivatives as ballast [7]. Therefore, the growing demand for oil acids and as well as lack of natural resources and being in the form of complex mixtures makes actual the researches on synthesis of oil acids in synthetic way. In this regard, synthesis of SPA on the basis of diesel distillate of Baku oils and creation of high quality and industrially important products on the basis of SPA is scientifically important and practically significant.

One of the prospective methods for obtaining SPA is aerobic oxidation of naphthene-paraffinic hydrocarbons of oil fractions with mo-

lecular oxygen [8-11]. For this purpose, Azerbaijan oil's fraction boiled at 217-349°C temperature was dearomatized and oxidized in the presence of various catalytic systems as a research object. Dearomatization process was carried out by extraction method. N-methyl pyrrolidone (NMP) was used as extractant and extraction process was carried out at room temperature in 4 stage. It has been determined that, after the fourth stage of extraction process the residual amount of aromatic hydrocarbons in the fraction is ~ 1%.

Some physical-chemical indicators of fraction were determined before and after dearomatization, UV spectrum was taken at Jenway 6850 UV / VIS spectrophotometer. UV spectrum of the samples are given in figure 1.

Naphthene-paraffinic hydrocarbons obtained after dearomatization diesel fraction was oxidized 5 hours with air oxygen at a 135-140°C temperature, at sparging type reactor in the presence of various catalysts. In the oxidizing process Cr and Mn salts of natural oil acids (NPA Cr, NPA Mn) [13] and metal composites, first, obtained by precipitated Mn and Cr salts of NPA to purified structure block copolymer synthesized with "live" radical mechanism by a 90: 10% mass ratio of butoxymethyl styrene ester of methacrylic acid with other components, was used as catalysts.

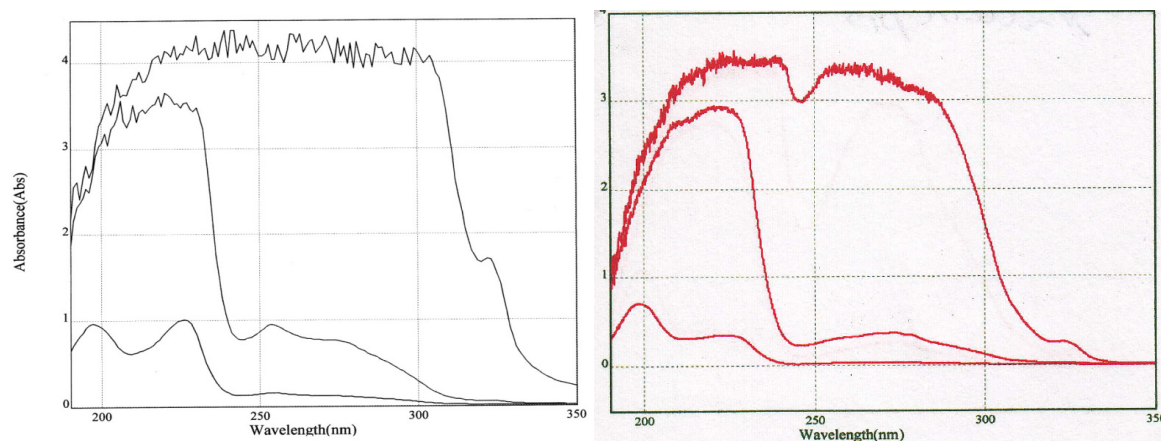


Fig. 1. UV spectrum of diesel faction before and after the dearomatization

Table 1

The oxidation results of salt of NPA compounds of naphthenic-paraffin hydrocarbons mixture in the presence of catalytic component

Composition of the catalyst	Acid number of oxide, mg KOH/g	SPA		NPA	
		Yield, % mas	acid number, mg KOH/g	Yield, wt. %	acid number, mg KOH/g
The concentration of catalyst, 0,2% mas					
NPA Cr	59,2	22.1	132	4.1	115.8
NPA Mn	36	10.1	130.7	3	117.6
The concentration of catalyst, 0,3% mas					
NPA Cr	53,8	17.8	134.2	8.7	116.2
NPA Mn	36,7	12.8	131.1	3.5	110

Stabil free radical-4-carboxamide-2,2,5,5-tetramethylpyrroline-1-oxsil and radical initiator of mentioned block copolymer styrene in the presence of cumene hydroperoxide with butoximethyle ester of metacryle acids of styrene macromonomeres obtained from mass polymerizations were synthesized at the inert environment in the presence of radical initiator in "live" radical mechanism with block copolymerizations.

Catalytic metal composites developed on the basis of Mn, Cr salts of NPA and synthesized block copolymer are obtained by precipi-

tating the Mn or Cr salts of natural petroleum acids and benzene solutions of block copolymer in alcohol.

Samples prepared in 4:1 və 10:1 mass ratio according to Mn NPA or Cr NPA salts of block copolymer were used as a catalyst. In addition to this, metal composite sample that prepared by mixtures of Cr and Mn salts of NPA with 3:1 mass ratios block copolymer with 4:1 mass ratios used as catalysts. The results of oxidation processes are given in table 1 and 2.

Table 2

**The oxidation results of metal composite compounds of naphthenic-paraffin hydrocarbons mixture
in the presence of catalytic component**

Composition of the catalyst (0.3% for raw materials)	Acid number of oxidate, mg KOH/g	SPA		NPA	
		Yield, %mas	acid number, mg KOH/g	Yield, %mas	acid number, mg KOH/g
Block copolymer : NPA Mn =10:1	60	14	153	11	121.3
Block copolymer: NPA Mn = 4:1	62	18.8	126.4	8	110.2
Block copolymer : NPA Cr=10:1,	58	16.7	149.5	7.8	112,1
Block copolymer : (NPA Cr:Mn=3:1)=4:1	49	14.5	128	7.2	109.8

As seen from table 1 and 2, in comparison to Cr and Mn salts of NPA as catalytic system higher acidic number mixture were obtained in the presence of metal composite compounds. It is known from literature, acid formation in the oxidation process of petroleum hydrocarbons occurs only as a result of the decomposition hydroperoxides. Variable-valency metal salts and complexes accelerates the decomposition of hydroperoxides [15].

Free radicals are produced as a result of decomposition of hydroperoxides and they activate oxidation process of hydrocarbons in the presence of oxygen. Catalysts by generating intermediate complexes with hydroperoxides provide transfer of electronic charge. As a result salt's metal oxidizes and reaches higher valence state and hydroperoxides easily decomposed by forming active centers. In the next stage, metal is restored by contacting once more with hydroperoxides in a high oxidation state and leads to create a new active centers from hydroperoxides. Catalyst in the oxidation process as the transition metal salts, metal ions plays catalytic center role also in Cr and Mn composite components obtained on the basis of block copolymer. In this case, formation of the free radicals occur more rapidly as a results of active centers dispensed through the surface in a catalytic system obtained on the basis of Cr

and Mn salts and block co-polymer regulated structures of styrene with butoximethylmetacrylate. For this purpose to obtain (~3-4 time) higher acidic number SPA and OPA even very small concentration of metal ions amounts in composite content developed compared with NPA salts.

Structure of SPA obtained by oxidization of naphthene-paraffinic hydrocarbons in the presence of investigated catalysts was studied by IR spectral analysis and appropriate functional groups has been determined.

Thus, metal composite compounds, used as a catalyst for aerobic oxidation of naphthene-paraffinic hydrocarbons separated from Baku oils in liquid phase, completely reflect the regularity of the oxidation reaction and make possible to obtain of synthetic petroleum and oxyacids with high yield.

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BAKİ NEFTLƏRİNİN NAFTEN-PARAFİN KARBOHİDROGENLƏRİ QARIŞIĞININ MÜXTƏLİF KATALİTİK SİSTEMLƏRİN TƏSİRİLƏ AEROB OKSİDLƏŞMƏSİ

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Təqdim edilmiş məqalədə Bakı neftlərinin 217-349°C fraksiyasından ayrılmış naften-parafin karbohidrogenləri qarışığının təbii neft turşularının Cr, Mn duzları və bu duzların stiroulun metakril turşusunun butoksimetil efiri ilə blok birgə-polimerlərinə çökdürülməsi ilə alınmış katalizatorlar iştirakında, 135-140°C temperaturda maye fazada oksidləşmə prosesinin tədqiqindən alınmış nəticələr verilmişdir. Oksidləşmə məhsulu olan oksidatdan sintetik neft turşuları ayrılmış və sübut edilmişdir ki, tərkibində minimum miqdarda metal ionları saxlayan katalitik kompozitlər iştirakında sintetik neft turşularının çıxımı və turşu ədədi yüksək olur.

Açar sözlər: dizel fraksiyası, ekstraksiya, oksidləşmə, oksidləşmə katalizatorları, sintetik neft turşuları

АЭРОБНОЕ ОКИСЛЕНИЕ СМЕСИ НАФТЕНО-ПАРАФИНОВЫХ УГЛЕВОДОРОДОВ БАКИНСКИХ НЕФТЕЙ В ПРИСУТСТВИИ РАЗЛИЧНЫХ КАТАЛИТИЧЕСКИХ СИСТЕМ

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В данной статье представлены результаты жидкофазного окисления нафтено-парафиновых углеводородов, выделенных из фракции 217-349°C Бакинских нефтей при температуре 135-140°C в присутствии солей природных нефтяных кислот Cr, Mn и металл композитных каталитических систем на основе солей Cr, Mn и блок сополимера стирола с бутоксиметилметакрилатом синтезированного по механизму «живой» радикальной полимеризации. Из полученных оксидатов выделены синтетические нефтяные кислоты (СНК) и доказано, что с использованием каталитических композитов с минимальным содержанием количество металлов, (0,3% к сы-рю), каталитическая активность, кислотное число и выход СНК увеличивается.

Ключевые слова: дизельная фракция, экстракция, окисление, катализаторы, синтетические нефтяные кислоты