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EFFECT OF HIGH MOLECULAR PARAFFINS ON THE EXPLOITATION PROPERTIES OF MOTOR FUELS

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Abstract

The isomerization of paraffin with different molecular mass has been studied and the reaction products have been tested as components for motor gasoline and diesel fuels. It has been shown that the isomerization reaction carried out at lower temperatures (300-400K) results in the formation of isomers, which has a greater impact on the performance characteristics of motor fuels.

Keywords: isomerization, paraffin, motor fuels, octane number, diesel fuels, low temperature characteristics, diesel fuels.

1. Introduction

The isomerization of paraffins can be regarded as one of the most modern and promising process, which in the last years occupies a basic place in the petrochemical and petrorefining industry $^{[1]}$. At first, this process was used for rising the octane number of light petroleum fraction, which is obtained from straight-run petroleum distillation and boiling up to 70°C . Since this fraction consists mainly pentane and hexane hydrocarbons, the isomers obtained are used predominantly for the preparation of high-octane lead-free gasoline $^{[2]}$. In addition, isobutane obtained from the isomerization can be used as a component in the alkylation process. The isomerization reaction of higher paraffins with molecular chain length from C_{10} to C_{20} carbon atoms makes possible the obtaining of components with good low temperature properties (pour point) required for the production of jet fuels, winter grade diesel fuels and lubricating oils. The isomerization is a catalytic process $^{[3]}$ and as catalysts are employed aluminium chloride, aluminium-platinum catalysts promoted by fluorine and chlorine, metal-zeolite catalysts and fluorides of metals from V and VII group of the periodic table, which have not yet found wide industrial application.

K. Nentusso and A.Dragan discovered the isomerization reaction of paraffins catalysed by aluminium chloride in 1933. The process has gained an industrial significance after the reported by B.I.Moldovski possibility for promotion of the reaction by hydrogen chloride ^[4]. The "Shell" Company in England built the first industrial installation. The process was carried out in liquid phase and the isomerization of *n*-butane took place in the presence of aluminium chloride dissolved in antimony chloride at temperature of 65-100°C and pressure - 2 MPa ^[5]. Further progress in the process has been achieved in the 50-es of the last century when technologies for conducting the process in vapour phase and temperature 350-500°C in the presence of hydrogen have been developed. Some oxide and sulphide catalysts of the metals from the VIII group of the periodic table on acid supports – aluminium oxide or alumni-silicates promoted by fluorine ^[6] have been also applied. Regardless of the high temperature at which the reaction is carried out (over 227°C) the use of bi-functional catalysts and hydrogen makes possible the rise of the reaction selectivity. The process was further improved by implementation of recycling of the non-reacted paraffins, which results in increasing the isoparaffins yield. The development of higher effective aluminium-platinum catalysts by the UOP (USA) and British Petroleum (England) Companies makes possible the process to be carried out at lower temperatures

of 120-200°C which in its turn results in improvement of the thermodynamic equilibrium of the isomerization reactions $^{[7]}$. The "Shell" Company enhances the rate and selectivity of paraffin isomerization in the presence of metal zeolite catalysts used. The process is carried out at temperature 260-370°C and pressure 1.5 – 2.5 MPa $^{[8]}$.

Individual paraffins and narrow petroleum fractions rich in these hydrocarbons may be used as feedstock for the isomerization process.

2. Experimental and discussion

The aim of the present study is to establish the possibility for widening the feedstock basis for isomerization of normal paraffins and their employment for improving the performance behaviour of lubricants.

The concentration of individual paraffins with chain length of from 4 to 9 carbon atoms in the crude petroleum of "Export" type (Russia), which is processed in the installation units of the Petrochemical Refinery – Bourgas (Bulgaria), is about 16%. The content of isoparaffins is not higher than 2.3%. The total distribution of normal paraffins according to the length of the hydrocarbon chain to 22 carbon atoms is given in table 1.

Table 1. Distribution of normal paraffin in the fraction boiling to 360°C from "Export" type crude

petroleum	(Russia).	
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 $\boldsymbol{\Sigma}$ di-substituted

Hydrocarbon chain length	Content per crude petroleum (%)	Hydrocarbon chain length	Content per crude petroleum (%)
C ₄	2.9	C ₁₄	0.4
C ₅	3.1	C ₁₅	0.4
C ₆	3.0	C ₁₆	0.3
C ₇	2.6	C ₁₆ C ₁₇ C ₁₈	0.3
C ₈	2.8	C ₁₈	0.3
C ₉	1.5	C ₁₉	0.3
C ₁₀	1.4	C ₂₀	0.2
C ₁₁	0.9	C ₂₁	0.3
C ₁₂	0.8	C ₂₂	0.1
C ₁₃	0.5		Σ 21.3

Although the crude petroleum under study consists mainly of normal paraffins, among the isomers with branched chain the monomethyl substituted structures are prevailing while the content of dimethyl-substituted derivatives is very low. The relative distribution of C_6 - C_9 paraffin with various topology of the hydrocarbon chain in the investigated crude petroleum is demonstrated in table 2.

Table 2. Distribution of paraffin hydrocarbons with hydrocarbon chain length from C_6 to C_9 in the "Export" type crude petroleum (Russia)

Export type crude petr	oleum (Russia).		
Hydrocarbon	Content relative to crude	Hydrocarbon	Content relative to crude
	petroleum (%)		petroleum (%)
<i>n</i> -hexane	2.830	<i>n</i> -octane	2.511
2-methylpentane	0.035	Σ mono substituted	0.192
3-methylpentane	0.075	Σ di-substituted	0.097
1,2-dimethylbutane	0.030		
2,3-dimethylbutane	0.030	<i>n</i> -nonane	1.277
Σ mono substituted	0.110	Σ mono substituted	0.117
Σ di-substituted	0.060	Σ di-substituted	0.106
<i>n</i> -heptane	2.352		
Σ mono substituted	0.171		

The individual paraffin C_4 , C_5 or fractions of C_4 and C_5 paraffin isomers of sufficiently high purity are obtained from the gas fractionating installation (GFI) within the "Petroleum refining" unit in the Petrorefining Company in Bourgas. The feedstock for this installation is coming from the units for petroleum atmospheric distillation and catalytic reforming and their composition is presented in table 3.

0.077

	Hydrocarbon concentration (%)		
Hydrocarbon	In the gas from the	In the gas gasoline from	In the gas gasoline
	atmospheric	the atmospheric	from the catalytic
	distillation unit	distillation unit	reforming
Methane	1.1	-	-
Ethane	3.9	0.6	3.2
Propane	40.2	22.1	54.8
Isobutane	9.8	12.1	19.6
<i>n-</i> Butane	22.6	40.0	20.1
Pentanes and higher	22.4	25.2	2.3

Table 3. Basic composition of the feedstock employed in the gas fractionating installation.

In many cases the fraction with a boiling point 62°C, removed from the unit for the secondary rectification for the stabilization of the gasoline fraction, can be used as feedstock for isomerization. In this case the separation of the butane, pentane and hexane fraction is carried out in the rectification column, which is within the complex isomerization installation.

The paraffins with chain length ranging from C_{10} to C_{22} can be isolated from the diesel fraction via complexion with urea (for *n*-paraffins), by adsorption using zeolites or by low temperature deparaffinization ^[9]. In this regard a number of new methods for removal of arene hydrocarbons from the liquid paraffins have been advanced ^[10].

In our investigations paraffins with hydrocarbon chain ranging from C_4 to C_{22} were isolated via complex formation. They were further subject to isomerization to yield products for various practical application ^[10]. Isobutane can be used in the alkylation process for the preparation of isobutylene, which is applied in the synthesis of the high-octane product methyl-*tert*-butyl ether (MTBE) and for isoprene production, too. Isopentane can be used as a component for motor gasoline and for widening the feedstock for isoprene production. The higher paraffins C_7 - C_9 have not yet found an independent application except as high-octane components for motor fuels. They can be also used as feedstock for catalytic reforming. The alkylation of *n*-butylene with isobutane may result in the formation of isooctane, which is a standard for determining the octane number of gasoline. Isoparaffinic hydrocarbons C_{10} - C_{18} boiling in the range of 200-320°C are proprietary components for compounding winter grade diesel fuels. Isoparaffinic hydrocarbons with hydrocarbon chain length from C_{18} to C_{20} are used for the preparation of trade lubricants with very good viscosity-temperature characteristics.

The up-to-date research shows that the isomerization reaction of paraffins with different molecular mass takes place with different rate constant. For this reason, the paraffins used in our experiments have been preliminary concentrated to individual compounds after which they were isomerised under the corresponding technological conditions and catalysts ^[10]. It should be noted that the various types of crude petroleum processed during the last years as well as the "Export" type petroleum used for our investigations show a tendency of reduced content of paraffin hydrocarbons. This means that isomerization should be carried out with high selectivity, and high isoalkane yield considering also the fact that the process is equilibrium. Since the process takes place practically without volume change, the thermodynamically equilibrium depends mainly on the temperature. Low temperatures shift the equilibrium to the formation of isoparaffins. The thermal effect for the isomerization reactions is ranging from 2 to 20 kJ/mol ^[9]. The data for the equilibrium constants, enthalpy and the entropy change during the isomerization of C_4 - C_6 paraffins on platinum catalyst supported on fluorine promoted aluminium oxide are shown in table 4. The content of platinum in the catalyst is 0.6% and that of fluorine – 4%.

The values were obtained on the basis of the calculations from the spectral data for the end products and the data for the free energy of the isomerization reaction carried out at temperatures 300, 500 and 700K. The equilibrium constant of the isomerization reaction was calculated using the difference in the free energy of the isomers [12].

The composition of the isomers mixtures (table 5) was calculated on the basis of the equilibrium constant of isomerization for the individual hydrocarbons according to the following formulae:

Mass composition =
$$\frac{1/K_r 100}{\sum (1/K_r 100) + 1}$$
 [1]

Table 4. Enthalpy (ΔH), entropy change (ΔS_T) and the equilibrium constant (K_R) at the isomerization of

C₄ - C₆ paraffin at temperatures 300, 500 and 700 K.

Isomerization of	-ΔH,	-ΔS,	K_R		
C ₄ - C ₆ hydrocarbons	/J/mol/	/J/mol.K/	''K		
C4- C6 Hydrocarbons	At 300 K				
n hutana () 2 mathylprapana	8.3	15.1	4.7		
n-butane ↔ 2-methylpropane			13.1		
<i>n</i> -pentane ↔ 2-methylbutane	7.9	5.5			
n -pentane \leftrightarrow 2,2-dimethylpropane	19.6	42.3	15.4		
n -hexane \leftrightarrow 2-methylpentane	7.2	8.1	6.6		
n -hexane \leftrightarrow 3-methylpentane	4.5	8.8	2.0		
<i>n</i> -hexane ↔ 2,2-dimethylbutane	18.2	30.2	14.4		
n -hexane \leftrightarrow 2,3-dimethylbutane	10.3	22.6	4.7		
	At 500 K				
<i>n</i> -butane ↔ 2-methylpropane	8.1	15.2	1.1		
n -pentane \leftrightarrow 2-methylbutane	8.0	5.4	3.7		
n -pentane \leftrightarrow 2,2-dimethylpropane	18.5	40.6	0.8		
<i>n</i> -hexane ↔ 2-methylpentane	6.5	6.7	2.1		
n -hexane \leftrightarrow 3-methylpentane	4.2	8.5	1.0		
n -hexane \leftrightarrow 2,2-dimethylbutane	18.1	29.7	2.1		
n -hexane \leftrightarrow 2,3-dimethylbutane	10.5	23.0	1.1		
	At 700 K				
n-butane ↔ 2-methylpropane	7.9	14.5	0.6		
<i>n</i> -pentane ↔ 2-methylbutane	7.7	5.1	2.0		
<i>n</i> -pentane ↔ 2,2-dimethylpropane	17.5	38.2	0.3		
n -hexane \leftrightarrow 2-methylpentane	6.0	6.0	1.3		
n -hexane \leftrightarrow 3-methylpentane	4.3	8.5	0.7		
n -hexane \leftrightarrow 2,2-dimethylbutane	17.2	28.4	0.5		
n -hexane \leftrightarrow 2,3-dimethylbutane	10.4	22.8	0.4		

Table 5. Composition of the equilibrium mixture (%) of C_4 - C_6 paraffin isomers obtained at temperatures 300, 500 and 700K.

Hydrocarbon type	Is	omerization temperature	(K)
	300	500	700
<i>n</i> -butane	17	44	58
2-methylpropane	83	56	42
<i>n</i> -pentane	2	18	29
2-methylbutane	47	69	63
2,2-dimethylpropane	51	13	8
<i>n</i> -hexane	2	13	23
2-methylpentane	24	30	34
3-methylpentane	6	13	18
2,2-dimethylbutane	50	28	13
2,3-dimethylbutane	18	16	12

It has been proved that the isomerization process is equilibrium and at low temperatures it is shifted to isomers formation. It is obvious that rising the hydrocarbon chain length, the number of the isomers increases. This fact complicates their separation and in the case of higher paraffins over C_6 it is more appropriate to use the isomerization mixture to be used as a whole component for improving the petroproducts quality, i.e. without its separation to individual hydrocarbons. The investigations carried out in the last years on the development of supersonic aviation and the dieselization of the automotive transport indicate that the paraffins fractions are very suitable as components for improving a number of characteristics of jet, diesel and motor lubricants. The studies show that the introduction of additives and urea deparaffinization not always can guarantee the required quality of these fuels and lubricants [11]. In addition, the urea deparaffinization of the diesel fraction limits the feedstock for this fuel by 15-20%. The paraffin content in these fuels is usually 20 % with prevalence

n-paraffins. The distribution of paraffins in the diesel fraction 215-360°C obtained from the "Export" type crude petroleum (Russia) is presented in table 6.

Table 6. Distribution of paraffin hydrocarbons in the diesel fraction (215-360°C).

Hydrocarbon chain	Content (%)	Hydrocarbon chain	Content (%)
length		length	
C ₈	0.10	C ₁₈	1.32
C_9	0.11		1.11
C ₁₀	0.35	C ₂₀	1.06
C ₁₁	0.82	$egin{array}{c} C_{19} \\ C_{20} \\ C_{21} \\ C_{22} \\ C_{23} \\ C_{24} \\ C_{25} \\ \end{array}$	0.89
C ₁₂ C ₁₃	1.22	C ₂₂	0.61
C ₁₃	1.71	C ₂₃	0.42
C ₁₄	1.82	C ₂₄	0.31
C ₁₅	1.59	C ₂₅	0.22
C ₁₆	1.50	C ₂₆	0.12
C ₁₇	1.31		

It is seen that the hydrocarbons with chain length from C_{13} to C_{16} carbon atoms are dominant in the diesel fraction.

Using urea deparaffinization in a stationary layer, individual hydrocarbons with normal chain were isolated, which were further subjected to isomerization under conditions already defined [10].

The concentration of paraffin hydrocarbons in the mixtures obtained after isomerization and the compositions of the equilibrium mixtures were determined on the basis of the thermodynamic characteristics and are given in tables 7 and 8.

Table 7. Concentration of higher paraffin hydrocarbons after isomerization at 300, 500 and 700K.

	Concentration (%)		
Hydrocarbon	<i>n</i> -paraffin	Monomethyl	Dimethyl substituted
-	-	substituted	and more
	At 7	00K	
C ₈	10	51	37
C ₉ C ₁₀	9 7	55	38
C ₁₀	7	41	54
C ₁₁	6	38	56
C ₁₂	5	35	60
C ₁₃	5 4 3 2	27	69
C ₁₄	3	21	76
C ₁₅	2	17	81
C ₁₆	1	15	84
C ₁₇	1	12	87
C ₁₈	-	10	90
C ₁₉	-	8	92
C_{20}	-	7	93
		00K	
C ₈	12	59	29
C_9	11	58	31
C ₁₀	9 7	46	45
C ₁₁	7	40	53
C_{12}	6	31	63
C ₁₁ C ₁₂ C ₁₃	6 5	25	70
C ₁₄	4	23	73
C ₁₄ C ₁₅	3 2	20	77
C ₁₆	2	17	81
C ₁₇ C ₁₈	1	14	85
C ₁₈	1	11	88
C_{19}	-	10	90
C_{20}	-	9	91

	Concentration (%)		
Hydrocarbon	<i>n</i> -paraffin	Monomethyl	Dimethyl substituted
	-	substituted	and more
	At 3	800K	
C ₈	16	60	24
C ₉ C ₁₀	14	59	27
C ₁₀	11	47	42
	8	36	56
C ₁₂	7	30	63
C ₁₃	6	24	70
C ₁₄	5	22	73
C ₁₅	4	20	76
C ₁₆	2	18	80
C ₁₇	1	16	83
C ₁₁ C ₁₂ C ₁₃ C ₁₄ C ₁₅ C ₁₆ C ₁₇ C ₁₈ C ₁₉ C ₂₀	1	13	86
C ₁₉	1	11	88
C ₂₀	1	10	89

Table 8. Composition of the equilibrium mixtures at isomerization of C_8 , C_{10} , C_{15} and C_{20} paraffin.

Isomers	Temperature (K)		
	700	500	300
<i>n</i> - C ₈	0.10	0.12	0.16
2-methyl substituted	0.23	0.26	0.20
3-methylsubstituted	0.30	0.33	0.40
2,2-dimethyl substituted	0.04	0.04	0.03
2,3-dimethyl substituted	0.09	0.07	0.06
2,4-dimethyl substituted	0.07	0.05	0.04
3-ethyl substituted	0.08	0.06	0.05
2,2,4-trimethyl substituted	0.09	0.07	0.06
n- C ₁₀	0.07	0.09	0.11
2-methyl substituted	0.23	0.25	0.26
3-methylsubstituted	0.18	0.21	0.21
2,2-dimethyl substituted	0.15	0.23	0.20
2,3-dimethyl substituted	0.10	0.09	0.09
2,4-dimethyl substituted	0.10	0.08	0.07
3-ethyl substituted	0.06	0.04	0.04
2,2,4-trimethyl substituted	0.03	0.02	0.04
<i>n</i> - C ₁₅	0.02	0.03	0.04
2-methyl substituted	0.07	0.14	0.11
3-methylsubstituted	0.10	0.06	0.09
2,2-dimethyl substituted	0.31	0.30	0.29
2,3-dimethyl substituted	0.25	0.24	0.24
2,4-dimethyl substituted	0.22	0.21	0.21
3-ethyl substituted	0.02	0.01	0.01
2,2,4-trimethyl substituted	0.01	0.01	0.01
<i>n</i> - C ₂₀	0.00	0.00	0.01
2-methyl substituted	0.04	0.05	0.06
3-methylsubstituted	0.03	0.04	0.04
2,2-dimethyl substituted	0.35	0.34	0.33
2,3-dimethyl substituted	0.30	0.29	0.28
2,4-dimethyl substituted	0.20	0.20	0.20
3-ethyl substituted	0.05	0.05	0.05
2,2,4-trimethyl substituted	0.03	0.03	0.03

A tendency of decrease in the fraction of the non-reacted hydrocarbons, particularly those with higher molecular mass, with the temperature have been observed. The number of the isomers

increases with the rise of the hydrocarbon chain length. Dimethyl substutituted isoparaffins are dominant in the mixtures and their amount increases with the increase in the hydrocarbon molecular mass. The decrease in temperature leads to increase in the content of mono substituted isoparaffins in the mixtures.

In our further investigations we will analyze some other possibilities for the use of the hydrocarbons obtained from isomerization with the purpose of improving some exploitation indices of petroproducts. Usually the isomers of C_4 - C_6 paraffins are used for increasing the octane number of motor gasoline. In table 9 are shown the antiknocking properties of isoparaffin hydrocarbons with C_5 - C_6 carbon atoms in the hydrocarbon chain.

Table 9. Antiknocking properties of C₅ - C₆ isoparaffins.

Hydrocarbon	Octane number		
	Motor method	Research method	
<i>n</i> -pentane	61.0	61.7	
2-methylbutane	89.0	92.3	
2,2-dimethylpropane	83.4	85.5	
<i>n</i> -hexane	25.2	24.8	
2-methylpentane	73.5	73.4	
3-methylpentane	75.3	74.5	
2,2-dimethylbutane	93.4	96.8	
2,3-dimethylbutane	94.3	101.7	

The antiknocking properties of the mixtures containing the isomers pointed in table 9 and the gasoline produced from the atmospheric distillation of the "Export" type crude petroleum in "Luckoil-Neftokhim"AD – Bourgas have been determined. The results are presented in table 10. Obviously, isoparaffin hydrocarbons can be used as proprietary components for mixing with gasoline fractions. It has been found that the octane number of the isomers mixtures is higher than that of the individual components [12].

Table 10. Antiknocking properties of mixtures of gasolines and C₅ - C₆ isoparaffins.

Mixtures composition	Mixtures composition Octane number	
·	Motor method	Research method
Gasoline from atmospheric distillation	57.5	62.2
+ 10% 2-methylbutane	60.1	68.5
+ 20% 2-methylbutane	74.3	80.3
+ 30% 2-methylbutane	84.4	94.2
+ 10% 2,2-dimethylpropane	59.3	64.1
+ 20% 2,2-dimethylpropane	70.1	73.7
+ 30% 2,2-dimethylpropane	79.6	86.4
+ 10% 2-methylpentane	62.6	70.1
+ 20% 2-methylpentane	66.4	75.3
+ 30% 2-methylpentane	69.5	78.2
+ 10% 3-methylpentane	62.8	70.1
+ 20% 3-methylpentane	66.6	75.3
+ 30% 3-methylpentane	70.1	78.2
+ 10% 2,2-dimethylbutane	69.7	75.4
+ 20% 2,2-dimethylbutane	84.1	95.7
+ 30% 2,2-dimethylbutane	98.3	103.5
+ 10% 2,3-dimethylbutane	75.2	85.4
+ 20% 2,3-dimethylbutane	90.1	99.7
+ 30% 2,3-dimethylbutane	98.7	108.8

The effect of higher isoparrafin on the low temperature characteristics of diesel and oil fractions has been investigated and the results are presented in tables 11 and 12.

Table 11. Low temperature properties of diesel fraction containing isoparaffins with hydrocarbon chain

length ranging from C₈ to C₁₀.

Composition of the	Low temperature properties, temperature (°C)			
model fraction	Cloud point	Cold filter plugging point	Pour point	
Diesel fraction 215-360°C	-1	-4	-11	
+ 10% 2-methyloctane	-1	-6	-14	
+ 20% 2-methyloctane	-1	-9	-18	
+ 10% 3-methyloctane	-1	-6	-14	
+ 20% 3-methyloctane	-1	-9	-18	
+ 10% 2,3-dimethyloctane	-1	-9	-18	
+ 20% 2,3-dimethyloctane	-1	-12	-20	
+ 10% 2,4-dimethyloctane	-1	-9	-18	
+ 20% 2,4-dimethyloctane	-1	-12	-20	
+ 10% 3-ethyloctane		-5	-14	
+ 20% 3-ethyloctane	-1	-9	-18	
+ 10% 2,2,4-trimethyloctane	-1	-12	-22	
+ 20% 2,2,4-trimethyloctane	-1	-19	-27	
+ 10% 2-methyldecane	-1	-4	-11	
+ 20% 2-methyldecane	-1	-6	-14	
+ 10% 3-methyldecane	-1	-4	-11	
+ 20% 3-methyldecane	-1	-6	-14	
+ 10% 2,2-dimethyldecane	-1	-6	-14	
+ 20% 2,2-dimethyldecane	-1	-9	-14	
+ 10% 2,3-dimethyldecane	-1	-6	-14	
+ 20% 2,3-dimethyldecane	-1	-9	-19	
+ 10% 2,4-dimethyldecane	-1	-6	-14	
+ 20% 2,4-dimethyldecane	-1	-9	-19	
+ 10% 3-ethyldecane	-1	-4	-11	
+ 20% 3-ethyldecane	-1	-5	-13	
+ 10% 2,2,4-trimethyldecane	-1	-9	-19	
+ 20% 2,2,4-trimethyldecane	-1	-13	-24	

It has been established that the isoparaffin hydrocarbons do not affect the temperature of the cloud point of the diesel fuel. At the same time they have an essential depressant effect on the temperature as suggested by the data on the cold filter plugging point and particularly on the pour point. Thus it can be concluded that the low temperature characteristics of the petroproducts can be improved by the presence of higher content of paraffin hydrocarbons with branched chains. This tendency gains more significance at the modern petroleum refining along with the wide implementation of the isocracking process. In this way the structural-group hydrocarbon composition of trade petroleum products can be regulated towards improving their low temperature performance.

Table 12. Low temperature properties of oil fractions containing isoparaffins with hydrocarbon chain

length ranging from C₁₅ to C₂₀.

Composition of the	Low temperature properties, temperature (°C)		
oil fraction	Cloud point	Cold filter plugging point	Pour point
Initial fraction	-10	-7	-5
+ 10% 2-methylpentadecane	-18	-15	-17
+ 20% 2-methylpentadecane	-20	-17	-16
+ 10% 3-methylpentadecane	-18	-15	-13
+ 20% 3-methylpentadecane	-20	-18	-17
+ 10% 2,2-dimethylpentadecane	-20	-18	-16
+ 20% 2,2-dimethylpentadecane	-22	-20	-18
+ 10% 2,3-dimethylpentadecane	-20	-18	-15
+ 20% 2,3-dimethylpentadecane	-22	-20	-18
+ 10% 2,4-dimethylpentadecane	-20	-18	-15
+ 20% 2,4-dimethylpentadecane	-22	-20	-18
+ 10% ethylpentadecane	-17	-16	-13

Composition of the	Low temperature properties, temperature (°C)		
oil fraction	Cloud point	Cold filter plugging point	Pour point
+ 20% ethylpentadecane	-19	-17	-15
+ 10% 2,2,4-trimethylpentadecane	-24	-22	-18
+ 20% 2,2,4-trimethylpentadecane	-28	-26	-20
+ 10% 2-methylicosane	-15	-11	-10
+ 20% 2-methylicosane	-18	-15	-13
+ 10% 3-methylicosane	-15	-11	-10
+ 20% 3-methylicosane	-18	-15	-13
+ 10% 2,2-dimethylicosane	-17	-15	-13
+ 20% 2,2-dimethylicosane	-20	-18	-15
+ 10% 2,3-dimethylicosane	-17	-15	-13
+ 20% 2,3-dimethylicosane	-20	-18	-15
+ 10% 2,4-dimethylicosane	-17	-15	-13
+ 20% 2,4-dimethylicosane	-20	-18	-15
+ 10% 3-ethylicosane	-15	-11	-9
+ 20% 3-ethylicosane	-17	-15	-12
+ 10% 2,2,4-trimethylicosane	-20	-18	-15
+ 20% 2,2,4-trimethylicosane	-24	-20	-17

3. Conclusions

The isomerization at low temperatures has greater advantages from the point view of the thermodynamic equilibrium. These conditions are more favourable for the formation of isoparaffin hydrocarbons with highly branched chain, which exert a positive impact on some important exploitation indices of the lubricants. It has been found that the use of mixtures of isoparaffin hydrocarbons without their separation to individual compounds is more beneficial. The technical characteristics of the components and their cost, the production capacity and the level of the development of the petroleum refining industry must be also taken into consideration.

References

- [1] Azinger, F. Die Petrochemische Industrie, Academie Verlag Berlin, 1971, p. 911.
- [2] Bursmann, N. R. Technology for the Isomerization of Paraffin Hydrocarbons, Chemistry, Leningrad, 1955, p. 189.
- [3] Pains, G. Kataliz in Organchemie, 1995, 54, 7.
- [4] Novikov, S.S.; Timofeeva, E.A. Chemistry, 1995, 21, 17.
- [5] Haensel, V.; Bloch, H.S. Plat. Met. Rev., 1994, 7, 2.
- [6] Sinfelt, J.H. Adv. Chem. Eng., 1994, 27, 6.
- [7] Giapetta, F.G.; Dobres, R.M. Catalysis, 1998, 8, p. 477.
- [8] Petkov, P. St.; Ivanov, S. K.; Minkov, D. M. Chimmotology of the Oil Products, Sofia, Bulgarian-English Academic Publishing House, 1995, p. 55.
- [9] Stal, D.; Vestram, E.; Zinke, T. Chemical Thermodynamics of Organic Compounds, Peace, Moscow, 2001, p. 810.
- [10] Petkov, P.; Minkov, D. Separation of Normal Paraffin Hydrocarbons by Applying Carbamide Deparaffinisation in Stationary Phase, Chemistry and Industry, 1984, 5, p. 203.
- [11] Postrov, V.V.; Lukova, P.I.; Mihailov, I.A. Chem. and Techn. of Oil, 2003, 12, p. 40.
- [12] Gureev, A.A.; Azev, V.S. Automobile Gasolines Properties and Application, Moscow, 1996, p. 442.