EFFECT OF RADIATION-INDUCED ISOMERIZATION ON GASOLINE UPGRADING

Yuriy A Zaikin and Raissa F. Zaikina
PetroBeam, Inc.

212 Powell Drive, Unit 130, Raleigh, NC 27606, USA
yzaikin@petrobeam.com

Effect of radiation-induced isomerization was used for upgrading gasoline fractions and their mixtures with low-grade diesel and furnace oil. Experiments have shown that radiation ozonolysis combined with X-ray irradiation are most favorable for isomerization processes in these types of oil feedstock and, therefore for improvement of gasoline quality.

Considerable radiation-induced isomerization of paraffin molecules was observed when heavy aromatic hydrocarbons were added to relatively lighter feedstock and this mixture was irradiated with high-energy X-rays. In these experiments, heavy residua of bitumen radiation processing were used as an additional agent. Effect of paraffin isomerization became apparent only in presence of heavy aromatic compounds and only as a result of radiation processing; the added aromatics was varied in the range from 5 to 50 mass%.

Radiation processing provoked considerable increase in iso-alkane concentrations in the gasoline fraction (by more than 15 mass %) together with the corresponding rise in the gasoline octane numbers.

I. INTRODUCTION

Isomerization by-effects in conditions of induced cracking were noted in the works on radiolysis and photolysis[1,2] of light oil fractions. The phenomenon of strong radiation-enhanced isomerization in the process of radiation-thermal cracking (RTC) was first observed in the experiments on radiation-thermal processing of high-viscous oil from Karazhanbas field, Kazakhstan[3-5].

Intense isomerization was defined not only by conditions RTC but also by specific hydrocarbon contents of the oil feedstock characterized by heightened concentrations of pitch-aromatic components. The latter are the compounds of high radiation resistance that absorb a considerable part of radiation energy, and thus can lower the rate of radiation-induced chemical conversion and provoke isomerization processes.

High isomerization rate in RTC of hydrocarbon compositions with high concentrations of heavy aromatics was explained by availability of the lower temperature and dose rate limits for noticeable RTC reactions. Transfer of the excess radiation energy to an alkyl radical in the excited paraffin composition assists its disintegration and impedes intromolecular isomerization. On the contrary, the addition of heavy aromatics allows combination of rather high dose rates and temperatures with favorable conditions for isomerization. Aromatic compounds, known for high radiation resistance, can absorb the excess energy of a considerable part of radiation-generated radicals. In this case, many alkyl radicals can have enough time to stabilize their electron structure and to form isomers before their disintegration or recombination.

This interpretation was confirmed by the experiments on bitumen which are characterized by higher concentrations of heavy aromatics and, therefore, still more pronounced effects of enhanced isomerization[6]. In this study, the ability of polyaromatic structures to enhance radiation-induced polymerization of light fractions was used for gasoline upgrading.

In this paper, our previous studies on radiation-thermal processing of mixtures of heavy and light oil fractions in frames of the IAEA Project[7] are supplemented with new results and applied to the problem of gasoline upgrading.

II. RADIATION UPGRADING OF GASOLINE

The favorable conditions for isomerization are lowered dose rates of ionizing irradiation and lowered temperatures. Therefore, the effect of radiation-enhanced isomerization in presence of heavy aromatics should be considerable in the case of low dose-rate electron or gamma-irradiation of aromatic-rich hydrocarbon mixtures at lowered temperatures.

For experimental verification of this conclusion, special experiments were conducted on radiation processing of low-octane gas-condensate gasoline at room temperature (Ref.7). Gasoline was irradiated with the bremsstrahlung X-rays from the 2-MeV electron beam without selection of energy range.

Table 1. Fractional, hydrocarbon contents and octane numbers of gas-condensate gasoline after irradiation with bremsstrahlung X-rays from 2 MeV electrons

Sample	Processing conditions	Hydrocarbon contents					Octane number
		n-alkanes	iso-alkanes	arenes	naphthenes	olefins	
GCG	feedstock	25.7	29.3	12	32.2	0.8	54
GCG	Bremsstrahlung X-rays D=6-8 kGy	24.6	30.5	10.3	29.1	5.5	63
GCG +6 mass% bitumen (mix1)	Bremsstrahlung X-rays D=6-8 kGy	24.5	38.6	11.8	22.4	2.7	67
GGG +15 mass% bitumen (mix2)	Bremsstrahlung X-rays D=6-8 kGy	25.1	39.2	12.3	21.1	2.3	68

GCG – gas-condensate gasoline

In these experiments, heavy residua of bitumen radiation processing were used as additional agents for initiation of isomerization.

Table 1 (Ref.7) summarizes the observed changes in fractional and hydrocarbon contents of gasoline extracted from gas condensate and demonstrates the effect of aromatics addition on radiation-induced isomerization.

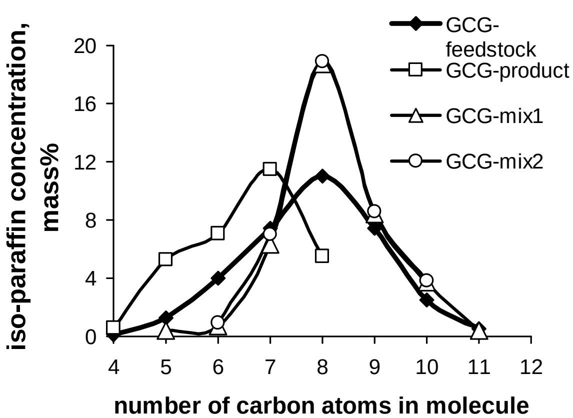

Fig.1. Molecular mass distribution of iso-paraffin concentration in mixtures of gas-condensate gasoline. Designations are the same as in Table 1

Experimental data of Table 1 and Fig.1.show that effect of paraffin isomerization becomes apparent only in presence of heavy aromatic compounds and only as a result of radiation processing. Mixing gas-condensate gasoline with 15 mass% residue of bitumen vacuum distillation and subsequent X-ray irradiation at room temperature provide increase in iso-alkanes concentration by 33.8% and increase in gasoline octane number from 54 to 68 without any chemical additions.

The effect of aromatics on gasoline upgrading comes close to saturation at 5-6 mass % bitumen residue added to low-grade gasoline. Increase of the additive concentration from 6 to 15 mass % leads to additional rise in iso-alkane concentration only by 2 mass % and increase in the gasoline octane number by one point. Molecular mass distribution of iso-paraffins is almost the same in the cases of 6 mass % and 15 mass % added bitumen residue.

III. PRODUCTION OF UPGRADED GASOLINE FROM MIXTURES OF LOW-QUALITY DIESEL AND FURNACE OIL

A promising approach to processing of high-viscous and high-sulfuric oil is application of synergetic action of two types of initiated cracking: radiation-thermal cracking and cracking initiated by ozonolysis[4, 8]. This approach is based on the ability of ozonides and sulphoxides to initiate radical chain reactions that can be effectively used for intensified thermal destruction of heavy, high-sulfuric crude oil, bitumen and different types of oil wastes. An additional advantage of such combination is a possibility to utilize ionized ozone-containing air as a by–product of a radiation facility operation, instead of expensive ozone.

The temperature of ozone-initiated cracking is lower than that of conventional thermal cracking (TC) by $100\text{-}150^0$ K and close to the temperature of radiation-thermal cracking (RTC) (Ref.4, 8). Therefore, the two types of initiated cracking can be combined in a one process.

Experiments (Ref. 8) have shown that the synergetic effect of ionizing radiation and ozonolysis on chemical conversion of oil feedstock near the room temperature strongly depends both on processing conditions and, especially, on the original content of the feedstock processed. In particular, irradiation of furnace oil by bremsstrahlung X-rays from 2 MeV electrons in conditions of continuous feedstock bubbling by ionized air has resulted in the increase of gasoline concentration by 28.4 mass %. The result of combined action of the two factors (X-ray irradiation and continuous ozonolysis) is higher than the sum of the effects of their separate action by 1.7 times, i.e. the synergetic effect has made 170%. The value of the gasoline G-value was 13800 molecules/100eV, that is characteristic for chain cracking reactions.

In Fig.2, yields of the gasoline fraction boiling out below 180^0C are plotted versus the time of bubbling for the tree processing modes characterized by different dose rate, P, of bremsstrahlung X-ray irradiation from 2 MeV electrons, and rate of air bubbling, V. In all the cases, X-ray irradiation at 30^0C was combined with continuous bubbling by ionized air during 2 hours.

Yields of light fractions can be raised by increase in irradiation dose, rate of ionized air bubbling (Fig.2) and process temperature. However, the heavier is feedstock the less considerable is the effect of these parameters.

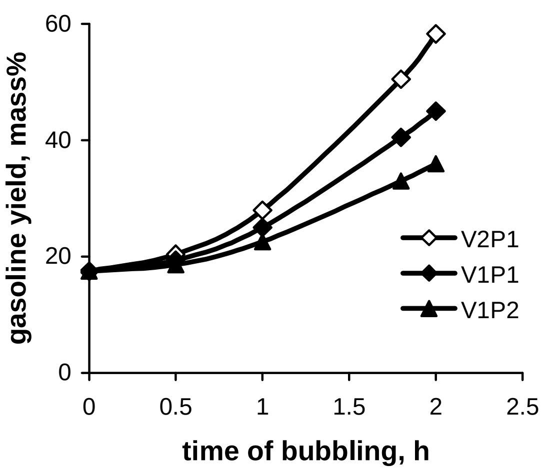

Fig.2. Dependence of gasoline yield after X-ray irradiation of furnace oil combined with radiation ozonolysis.at 30^0C. The dose rates are P1=0.275 Gy/s and P_2 =1.9 Gy/s; the doses are D1=2 kGy and D2=1.4 kGy, the bubbling rates V1= 20 mg/s per 1 kg of feedstock and V_2=40 mg/s per 1 kg of feedstock.

Similar synergetic effects were observed in such wide-spread and cheap feedstock as mixtures of low-quality diesel and furnace fuel. Processing of these types of feedstock in optimal conditions provides considerable changes in their hydrocarbon contents and improvement of their quality (Table 2).

Upgrading of oil feedstock with relatively high contents of light fractions (15-20 mass% gasoline and light diesel) with minimal losses for gas evolution can be achieved by application of low-temperature X-ray or electron irradiation at low dose rates combined with bubbling of ionized-ozone containing air.

In these processing conditions, the main role of ionized air is destabilization of heavy aromatic structures that facilitates detachment of alkyl substituents. Simultaneous gamma or electron irradiation provides destructive chain reactions in which gasoline fraction can be presumably considered as a source of light alkyl radicals that appear as a result of gasoline radiolysis. Thus, the heavy aromatic component enriches gasoline fraction with light aromatic compounds and simultaneously provides a high degree of gasoline isomerization.

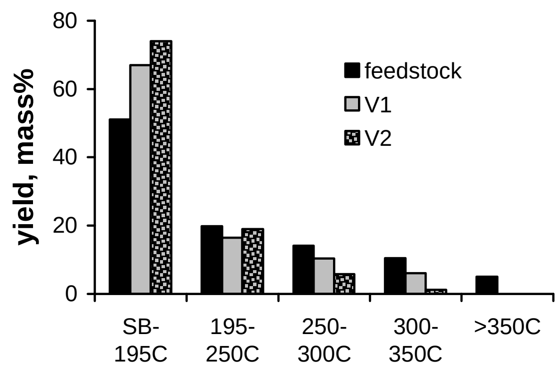

Fig.3. Dependence of distillate fraction yields on the rate of bubbling of diesel and furnace fuel mixture with ionized air in the field of X-ray radiation at 30^0C. The dose rate is 0.275 Gy/s; the doses are D1=2 kGy and D2=1.4 kGy, the bubbling rates V1= 20 mg/s per 1 kg of feedstock and V2=40 mg/s per 1 kg of feedstock.

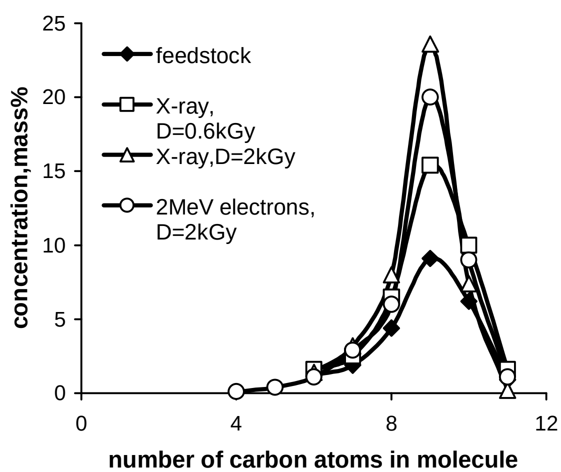

Fig. 4. Isoparaffin concentration in the gasoline fraction of the mixed low-quality diesel and furnace fuel before and after its radiation processing at 30^0C. The dose rate of bremsstrahlung X-ray irradiation is 0.275 Gy/s; the dose rate of electron irradiation is 0.5 kGy/s.

Fig.3 shows that increase in the rate of bubbling leads to the rise in the yields of gasoline and kerosene fractions and, therefore, improvement of hydrocarbon contents of the feedstock processed.

Quality of the gasoline fraction obtained to a great extent depends on concentration of isomers that can be essentially increased and controlled in this type of processing. Fig.4 gives comparison of isoparaffin molecular mass distributions in the gasoline fraction of the original feedstock, in the product of X-ray irradiation combined with ionized air bubbling, and in the liquid product of radiation-thermal cracking.

Radiation processing provokes considerable changes in gasoline hydrocarbon contents with corresponding rise in gasoline octane numbers (Fig.4).

The other essential factors that affect product quality are concentrations and distributions of aromatic compounds. Fig.5 shows that combined X-ray irradiation and radiation ozonolysis of furnace oil and low-grade diesel fuel up to the dose of 2 kGy practically do not change mass distributions of aromatic compounds in the gasoline fraction.

However, processing of furnace oil with higher concentration of heavy aromatics in similar conditions essentially raises concentration of C7-C9 aromatic compounds, even more considerably than high-temperature radiation-thermal cracking (Table 3).

Table 2. Hydrocarbon contents of gasoline produced by radiation processing of mixed low-quality diesel and furnace oil

Type of processing	D, kGy	n-alkanes	iso-alkanes	aromatics	naphtenes	oleffins	Octane number
feedstock	0	48.5	23.7	12.8	13	2	56
Radiation oznolysis	0.6	30.7	37.6	17.6	12.8	1.3	72
Radiation ozonolysis	2	26.5	43.8	15.1	12.9	1.7	72
RTC (2 MeV electrons, 300^0C)	2	26.6	40.6	11.5	18.4	2.9	70
RTC (X-rays, 30^0C,	2	26.5	39.3	10.3	21.9	2	76

RTC (X-Rays, 30^0C) – chain reaction initiated at 30^0C by combined action of irradiation with bremsstrahlung X-rays from 2 MeV electrons and feedstock bubbling with ionized air (Ref.7)

Table 3. Hydrocarbon content of gasoline aromatic part and gasoline octane numbers in the product of low-temperature radiation processing of fuel oil

Aromatic hydrocarbon	feedstock (octane number - 60)	Bubbling by ionized air (octane number – 64)	Bubbling by ionized air + X-ray irradiation (octane number–75)
Benzene	-	0.03	0.19
Toluene	0.23	0.92	1.20
Ethylbenzene	-	-	1.18
n-xylene	-	1.24	0.80
n-xylene	0.86	-	1.42
o -xylene	-	0.11	0.41
1-methyl-2-ethylbenzene	-	-	1.03
1- methyl -3- ethylbenzene	0.3	0.94	0.66
1- methyl -4- ethylbenzene	-	-	0.67
1,3,5 trimethylbenzene	-	-	0.92
1,2,4 trimethylbenzene	-	-	0.40

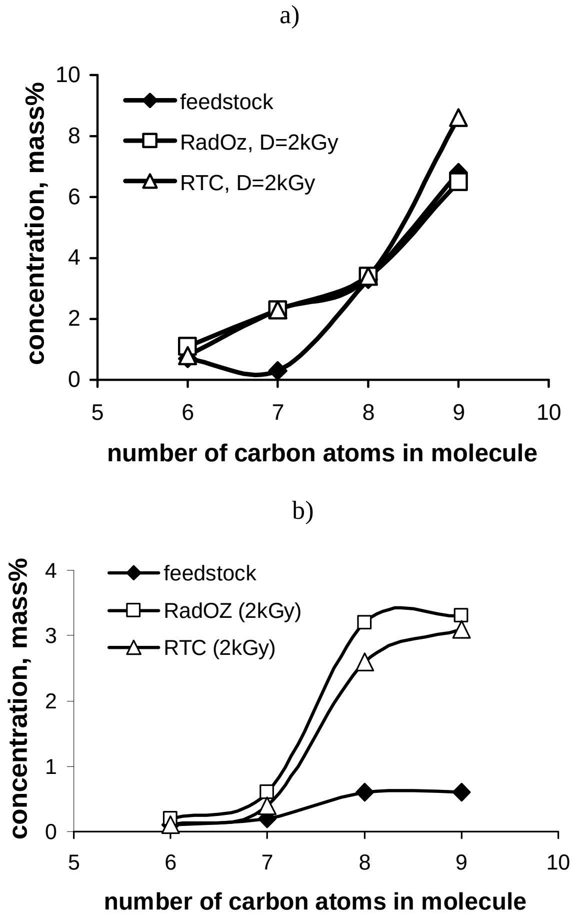

Fig.5. Molecular mass distributions of aromatic compounds in the gasoline fraction extracted from the liquid products after X-ray irradiation of low-grade diesel fuel (a) and furnace oil (b) at 30^0C combined with radiation ozonolysis. RadOZ - rate of air bubbling V=20 mg/s per 1 kg of feedstock at the dose rate of X-ray irradiation P=0.275 Gy/s; RTC – radiation-thermal cracking at 300^0C initiated by 2 MeV electrons at the dose rate of 0.5 kGy/s.

Hydrocarbon contents of gasoline fractions produced as a result of combined action of radiation ozonolysis and X-ray irradiation on low-quality diesel fuels are shown in Fig. 6. Concentrations of n-alkanes (Fig.6a), iso-alkanes (Fig.6b) and aromatic hydrocarbons (Fig.6c) are plotted as a function of the number of hydrocarbon atoms in a molecule. Concentration ratios for these types of hydrocarbons substantially define the gasoline quality. Generally, Fig.6 demonstrates considerable changes in hydrocarbon contents of gasoline fraction.

Therefore, in the heavier feedstock, relatively light alkyl substituents in aromatic rings can be easier torn away from heavy aromatic structures.

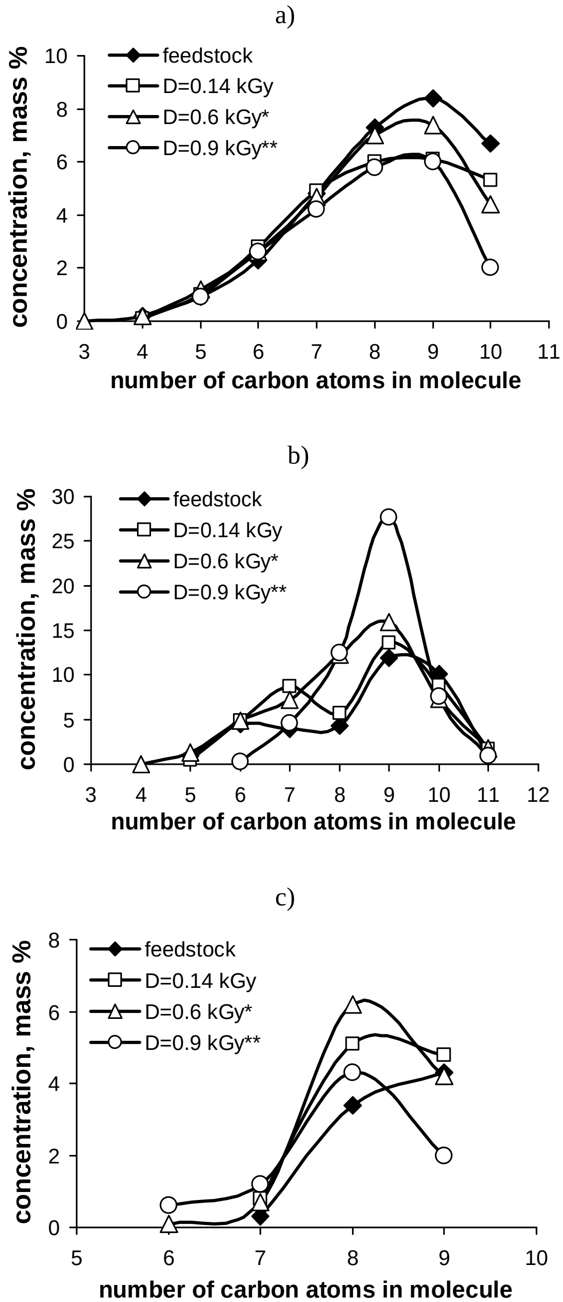

Fig.6. Molecular mass distributions of hydrocarbons after radiation processing of low-grade diesel fractions
a) n-paraffins; b) iso-paraffins; c) aromatic hydrocarbons
All the samples were irradiated with bremsstrahlung X-rays from 2 MeV electrons at 30^0C at the dose rate of 0.275 Gy/s

* Irradiation accompanied by bubbling with ionized air at the rate 20 mg/s per 1 kg of feedstock

** Irradiation accompanied by bubbling with ionized air at the rate 40 mg/s per 1 kg of feedstock

Generally, enrichment of gasoline fraction by light aromatic compounds and isoalkanes during radiation processing raises gasoline octane number by about 15 points.

Hydrocarbon contents of gasoline fractions produced as a result of combined action of radiation ozonolysis and X-ray irradiation on low-quality diesel fuels are shown in Fig. 6. Concentrations of n-alkanes (Fig.6a), iso-alkanes (Fig.6b) and aromatic hydrocarbons (Fig.6c) are plotted as a function of the number of hydrocarbon atoms in a molecule. Concentration ratios for these types of hydrocarbons substantially define the gasoline quality. Generally, Fig.6 demonstrates considerable changes in hydrocarbon contents of gasoline fraction.

Figs. 6b and 6c show that iso-alkanes are concentrated in the gasoline fraction of the hydrocarbon mixture with the maximum at 9 C-atoms. Radiation processing does not shift this maximum but makes it considerably higher. Together with the rise in total iso-alkane concentration, some increase of their average molecular weight is observed, that positively affects the gasoline properties. As evident from Fig.6c, radiation-induced isomerization is accompanied by decomposition of aromatic structures that raises the maximum of aromatic hydrocarbons concentration and shifts it to lower molecular mass values. These changes also contribute to the increase in gasoline octane numbers.

IV. CONCLUSIONS

Effect of radiation-induced isomerization of light fractions in presence of heavy aromatic additives can be effectively used for gasoline upgrading.

Upgrading of oil feedstock with relatively high contents of light fractions (15-20 mass% gasoline and light diesel) with minimal losses for gas evolution can be achieved by application of low-temperature gamma, X-ray or electron irradiation at low dose rates combined with bubbling of ionized ozone-containing air. This type of processing considerably increases the gasoline yield and improves its quality due to combination of intense isomerization and gasoline enrichment with light aromatics.

The process is highly economic as it uses only by-products of accelerator operation (X-ray background and ionized air) and does not require feedstock heating.

REFERENCES

1. A.V.TOPCHIEV. *Radiolysis of Hydrocarbons*, 232 pp., El. Publ., Amst-London-NY (1964).
2. G.DOLIVO, T.GAUMANN and A.RUF, "*Photoinduced Isomerization and Fragmentation of the Pentane Radical Cation in Condensed Phase*", Radiation Physics and Chemistry,.28, 2, 195-200 (1986).
3. R.F.ZAIKINA, Y.A.ZAIKIN, T.B.MAMONOVA and N.K.NADIROV, *"Specificity of Isomerization Processes in Radiation-Thermal Processing of Karazhanbas Oil"*, Oil and Gas (Kazakhstan), 2, 65-70 (2000).
4. Y.A.ZAIKIN, R.F.ZAIKINA, T.B.MAMONOVA and N.K.NADIROV, *"Radiation-Thermal Processing of High-Viscous Oil from Karazhanbas Field"*, Radiat. Phys. Chem., 60, 211-221 (2001).
5. Y.A.ZAIKIN and R.F.ZAIKINA, *"Criteria of Synergetic Effects in Radiation-Induced Transformations of Complex Hydrocarbon Mixtures"*, Oil & Gas (Kazakstan), 2 (22), 64-73 (2004).
6. Y.A.ZAIKIN and R.F.ZAIKINA, "Bitumen Radiation Processing", Radiation Physics and Chemistry, 71, 471-474 (2004).
7. Development of the Methods for Processing of Oil Products Using Complex Radiation-Thermal Treatment and Radiation Oxonolysis. Final Report on IAEA Project (Research Contract # 11837/RO), Almaty, Kazakhstan, 34 pp., (2004).
8. Y.A.ZAIKIN and R.F.ZAIKINA, "*Stimulation of radiation-thermal cracking of oil products by reactive ozone-containing mixtures*",Radiat. Phys. Chem., 71, 475-478 (2004).
9. V.F.KAMYANOV, A.K.LEBEDEV and P.P. SVIRIDOV. *Ozonolysis of Oil Feedstock*, 271 pp., Rasko Publ., Tomsk (1997).