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FORMATION OF GAS PRODUCTS DURING γ-RADIOLYSIS OF PLASTIC WASTES

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Abstract: This study explores the gas formation patterns dependent on the dose of various plastic wastes (PET, PP, PS, MS-1009). The primary gas phase products identified are hydrogen and methane. The other hydrocarbons are formed in low concentration. Radiation chemical yields for H_2, CH_4, C_2H_6, ΣC_3, ΣC_4, ΣX_6, and ΣC_7 during radiolysis processes in the specified plastic wastes were calculated from kinetic curves. The radiation chemical yields for hydrogen range from 10^{-1}-10^{-3} mol/100eV. The radiation stability of the examined plastic wastes is decreasing as PP-5>PET-1>PS-6>MS-1009.

Keywords: polymer wastes**,** gas products, radiation-chemical yields, γ-irradiation.

1. Introduction

Continued growth in plastic demand and the short lifespan of many of them lead to their accumulation in landfills, in the sea, and in the environment in general [1-3]. The low rate of processing plastic waste using existing methods makes it possible to look for new ways of recycling and improving existing methods. In this regard, radiation chemistry opens up wide possibilities for the modification of plastics [5, 9].

At the irradiation of the polymers, in addition to cross-linking and destruction processes, chemical transformations occur, such as the release of gases, changes in unsaturation, isomerization, and other processes that are interrelated with each other. Gas evolution during the radiolysis of plastic wastes has been widely studied, particularly in polyethylene radiolysis [6]. It has been established that hydrogen is the primary gas product, and other products such as CH_4, C_2H_6, ΣC_3, ΣC_4, ΣX_6, and ΣC_7 are formed in low radiation chemical yields. Notably, in the radiolysis of propylene, lower radiation-chemical yields of hydrogen and other hydrocarbon gases are observed. In the radiolysis of polystyrene and polyethylene terephthalate, radiation-chemical yields of hydrogen are below 0.1 mol/100 eV, attributed to the presence of benzene rings.

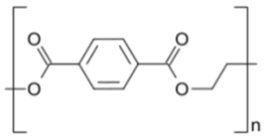
In this study, we investigated the kinetics of gaseous product formation during γ-radiolysis of polymer wastes, such as polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) and MS- 1009 (methyl octadecanoate).

The study aimed to assess the impact of the polymer waste structure on gaseous product formation during the radiolysis of this waste under the influence of γ-irradiation.

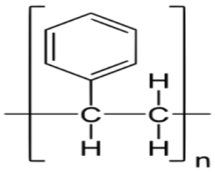
2. Materials and methods

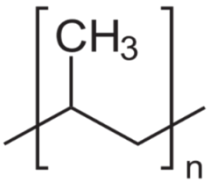
Samples for irradiation consisted of polymer waste derived from packaging materials utilized in the food industry and other household applications. The structural formulas and characteristics of the samples are provided below:

PET

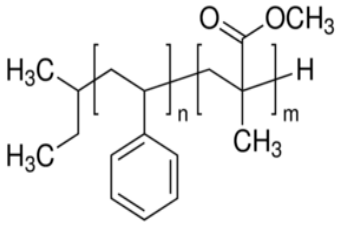


PS





PP



MS-1009

Table 1

Physico-chemical characteristics of polymer wastes [1]

Parameters	PET-1	PS	PP	MS-1009
Molar mass, g/mol	192	104.15	42.08	298.5
Density, g/cm³	1.38, 20 °C	1.069-1.125	0.855	0.8498
Melting point, °C	>250°C-260	~160-170	130 to 171	39.1
Boiling point, °C	> 350	430	−47.7	215
Glass transition temperature, Tg	73-78 °C	90°C	-20°C	-

Waste samples (S=3-4mm^2) were exposed to γ-radiation from the Co^{60} isotope under static conditions in glass ampoules with a volume of 10 cm^3 at room temperature and in vacuum conditions. The dose rate was 1.6 Gy/sec. The study was conducted at a dose range of 5-750 kGy. Gas chromatography analysis using Agilent chromatography (7820 GC system) was employed to analyze the gaseous products.

3. Results and discussion

H_2, CH_4, C_2H_6, ΣC_3, ΣC_4, ΣX_6, and ΣC_7 were identified as gas products, and the kinetics of their formation was studied up to a dose of 750 kGy. The following are the kinetics of the formation of the identified gas products depending on the absorbed dose during the radiolysis of wastes PET, PP, MS-1009, and PS.

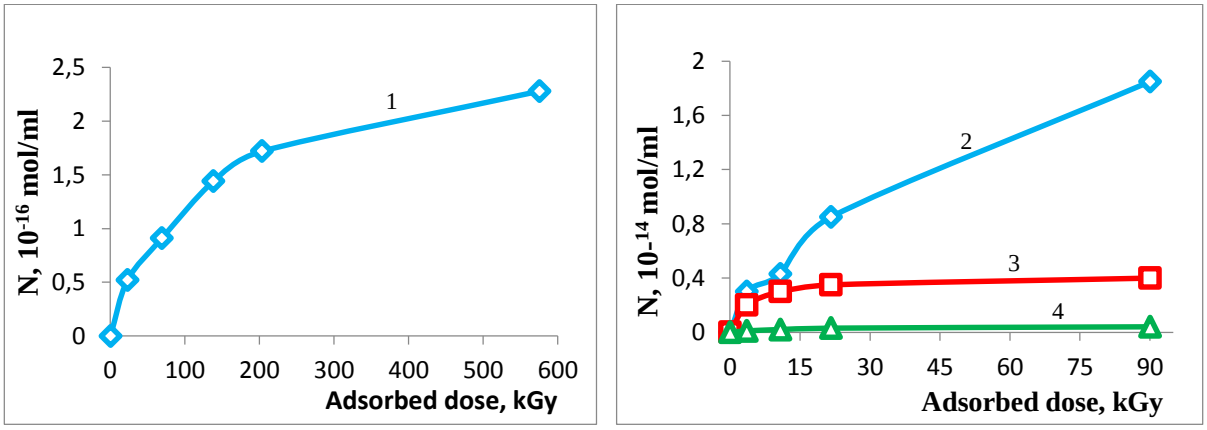


Fig.1. Kinetics of hydrogen formation (1), CH_4 (2), C_2H_6 (3), ΣX_6 (4) during PET radiolysis

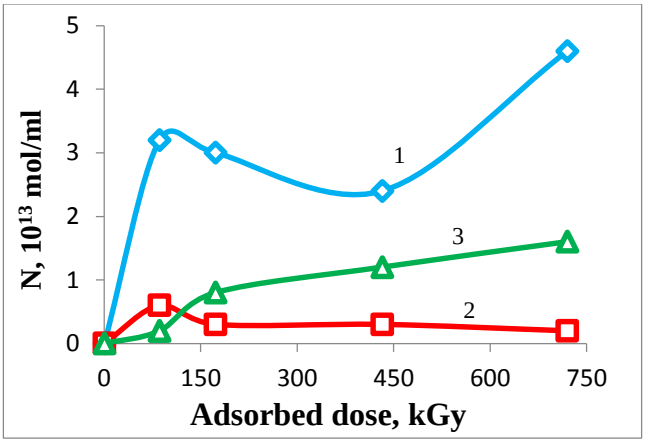


Fig. 2. Kinetics of formation of CH_4 (1), C_2H_6 (2), ΣC_7 (3) during radiolysis of MS-1009

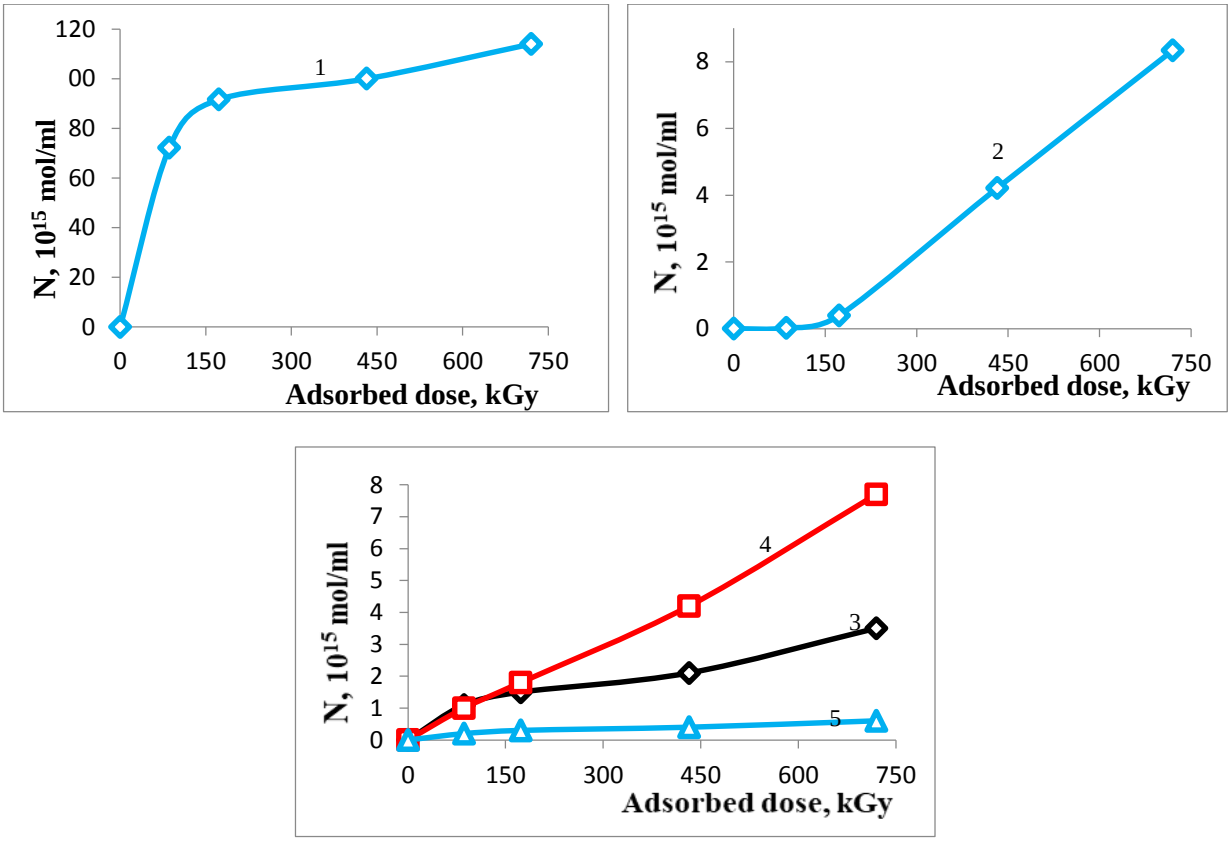


Fig. 3. Kinetics of hydrogen formation (1), CH_4 (2), ΣC_3 (3), ΣC_4 (4) and ΣC_7 (5) during radiolysis of PP

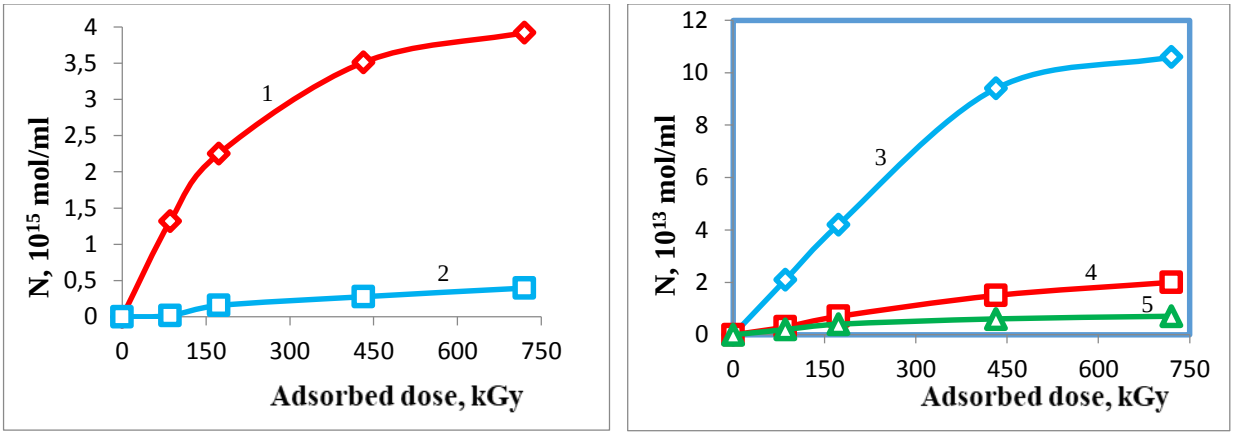


Fig. 4. Kinetics of hydrogen (1), CH_4 (2), C_2H_6 (3), ΣC_3 (4), and ΣC_7 (5) formation during PS radiolysis

As can be seen from Figure 1-4, all kinetic curves are characterized by a saturation region, which is associated with secondary reactions of the formed products. The formation of hydrogen occurs in two ways: the abstraction of atomic hydrogen from molecules and a further reaction of abstraction or recombination; in addition, part of the atomic hydrogen can be formed during the recombination of ions and electrons, which can lead to the formation of an excited molecule and its further decay with the formation of molecular hydrogen. During the radiolysis of polymer molecules, radicals such as CH_3, C_2H_5, and other types are also formed. As a result of the reaction of these active particles, heavier hydrocarbon gases are formed. Of course, these radical particles can lead to cross-linking and increase the mass of polymer molecules[7, 8]. If the excitation of the molecule is sufficient to break stronger bonds, it can lead to degradation (destruction) of the polymer molecules.

From the kinetic curves of the formation of gas products, the radiation-chemical yields of their formation were calculated and are presented in Table 2.

Table 2

Radiation-chemical yields of gas products during the radiolysis of plastic wastes PET-1, PP-5, MS-1009, PS-6

Radiation-chemical yields, mol/100 eV	**Wastes**			
	PET-1	**PP-5**	**MS-1009**	**PS-6**
H_2	$6 \cdot 10^{-2}$	$1 \cdot 10^{-1}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
CH_4	$1 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$6 \cdot 10^{-5}$	$3 \cdot 10^{-5}$
C_2H_6	$9 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$4 \cdot 10^{-6}$	$4 \cdot 10^{-5}$
ΣC_3	$5 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$6 \cdot 10^{-6}$
ΣC_4	$4 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$5 \cdot 10^{-6}$
$\Sigma X6$	$3.3 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$3 \cdot 10^{-6}$
ΣC_7	$8 \cdot 10^{-5}$	$4 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$4 \cdot 10^{-6}$

The data on radiation chemical yields indicates that the radiation stability of the investigated polymer wastes decreases in the order PP-5>PET-1>PS-6>MS-1009. The radiation

chemical yields of hard hydrocarbons are very low, attributed to the low efficiency of reactions of hydrocarbon ions.

The mechanism of hydrogen formation involves the following reactions:

$[M]_n \rightarrow [\dot{M}] + H$ $\quad\quad$ $[\dot{M}] + H_2 \rightarrow [M] + H$

$H + H \rightarrow H_2$ $\quad\quad$ $[M]_n \rightarrow [M]_n^+ + e$

$H + [M]_n \rightarrow H_2 + [\dot{M}]$ $\quad\quad$ $[M]_n^+ + e \rightarrow [N]_n + H_2$

The radiation stability of PET, PS, and MS-1009 wastes is associated with the presence of aromatic nuclei in the polymer molecules.

Acknowledgment

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ОБРАЗОВАНИЕ ГАЗОВЫХ ПРОДУКТОВ ПРИ γ-РАДИОЛИЗЕ ПЛАСТИКОВЫХ ОТХОДОВ

М.А. Гурбанов, Э.В. Мирзазаде, У.А. Гулиева, С.М. Алиев

Резюме: В работе выявлены закономерности газообразования в зависимости от дозы и различных пластиковых отходов (ПЭТ, ПП, ПС, МС-1009). Показано, что основными продуктами газовой фазы являются водород и метан. Остальные углеводороды образуются в низких концентрациях. По кинетическим кривым рассчитаны радиационно-химические выходы образования H_2, CH_4, C_2H_6, ΣС3, ΣС4, ΣХ6, ΣС7 для процессов радиолиза в данных пластиковых отходах. Радиационно-химические выходы водорода находятся в пределах 10^{-1}-10^{-3} моль/100эВ. Радиационная устойчивость данных пластиковых отходов снижается по мере ПП-5>ПЭТ-1>ПС-6>МС-1009.

Ключевые слова: полимерные отходы, газо продукты, радиационно-химические выходы, γ-облучение.

PLASTİK TULLANTILARIN γ-RADİOLİZİ ZAMANI QAZ MƏHSULLARININ ƏMƏLƏ GƏLMƏSİ

M.Ə. Qurbanov, E.V. Mirzəzadə, Ü.A. Quliyeva, S.M. Əliyev

Xülasə: Bu tədqiqatda dozadan asılı olaraq qazın əmələ gəlməsi qanunauyğunluqları və müxtəlif plastik tullantılar (PET, PP, PS, MS-1009) tədqiq edilmişdir. Göstərilmişdir ki, qaz fazasının əsas məhsulları hidrogen və metandır. Digər hidrokarbonlar aşağı konsentrasiyada əmələ gəlir. Kinetik əyrilərdən plastik tullantının radiolizi zamanı H_2, CH_4, C_2H_6, ΣC3, ΣC4, ΣX6, ΣC7 əmələ gəlməsinin radiasiya- kimyəvi çıxımı hesablanmışdır. Hidrogen üçün radiasiya- kimyəvi çıxım 10^{-1}-10^{-3} mol/100eV intervalındadır. Verilmiş plastik tullantıların radiasiya davamlılığı PP-5>PET-1>PS-6>MS-1009 sırası ilə dəyişir.

Açar sözlər: polimer tullantıları, qaz məhsulları, radiasiya-kimyəvi çıxım, γ-şüalanma.