KINETIC REGULARITIES OF THE FORMATION OF GAS PRODUCTS UNDER THE INFLUENCE OF IONIZING RADIATION ON BIOMASS

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The kinetic dependence of molecular hydrogen and other gases emergence out of biomass (oak, beech, pine) by a radiation-thermal method has been studied at the temperature $T = 673$ K. It has been determined that at the rate of $D < 10$ kGy of the absorbed dose the amount of hydrogen and light hydrocarbon gases in the composition of the gas products emerged out of biomass is slightly higher. At the subsequent rates of continuous radiation ($D \geq 10$ kGy) the increase in the amount of hydrocarbons with heavy molecular mass contained in gas occurs as a result of dimerization or trimerization of the emerged radicals. It was presented short mechanism of biomass conversion under ioni-zing radiation.

INTRODUCTION

Affordable and easily-derived biomass energy is very wide spread among renewable energy sources for the use and has big natural resources. So, this type of fuel is widespread on the Earth and there is a great potential to increase them. They have been traditionally used and is currently being used to get energy. The vast majority of the wastes generated by agricultural products used in food, fodder and in other areas of economy are not fully effectively used at an appropriate level [1–3].

Recently the main essence of the biggest environmental problems performed and intended in developed and developing countries is the efficient use of natural resources, protection and extension of greenery and water reservoirs, reducing to the minimum threshold level the amount of the wastes thrown to the environment, increasing to the maximum extent the efficiency of the use of products and energy sources [4–8].

A number of projects are being carried out to search for alternatively new energy sources, to ensure a continuous and sustainable energy supply. In the main concepts of these projects in accordance with the terms and conditions required to select biomass as an alternative renewable energy the following things have to be put forward: a) such a type of biomass should be selected that it would be suitable for use as a food product, and with a maximum productivity; b) the wastes generated out of this type of biomass should be suitable for use as a power source.

There is a high amount of potassium and chlorine compounds in all types of biomass, they create a number of technical problems at technological devices during a direct combustion process; corrosion of a reactor surface, the access roads congestion, slag forming etc.

In order to avoid these kinds of problems initially the investigation of the development of biomass by radiation and physicochemical methods, and its conversion into other types of gaseous and liquid energy types is important and urgent.

For this purpose, in order to study the feasibility of the use of the trees and plants grown in the forestry and fields of the Republic of Azerbaijan as energy sources that would be of a great interest to investigate the products emerged out of a thermal and thermo-radiolysis processes conversion of them together with their power generation and their ability to create energy and all these issues have been considered in this article [7, 8].

EXPERIMENTAL PART

The purpose of the article is to study to obtain molecular hydrogen and other combustible hydrocarbon gases out of biomass (oak, beech, pine) by a thermo and thermo-radiolysis method. Thermo (TP) and thermo-radiolysis (TRP) processes have been conducted under the influence of gamma-rays at different temperatures. The composition of the gas mixture emerged out of the decomposition of biomass has been analyzed at gas analyzers. The samples prepared for carrying out the experiment are filled into ampoules and locked at a vacuum unit. The samples were irradiated by gamma-rays at an isotope ^{60}Co with a dose rate $P = 1.73$ kGy/h in the range of 0…20 hours.

Hydrogen carbon monooxide, carbon dioxide and hydrocarbon gases (C_1–C_7) have been analyzed at "Gazochrome 3101" and "Agilent Technologies 7890A GC" device at J&W 113-4332, Analysis at FID detector. $T = 260$ °C, $l = 30$ m x 320 µm x 0 µm column. Temperature of detector and injector are 230 °C.

The coefficients of sensitivity of chromatographs to the analyzed gases are shown in Tab. 1.

Table 1

Coefficients of sensitivity of devices to gases

Gas products	K, molec./(cm$^3 \cdot$mm)
Hydrogen	$6.3 \cdot 10^{13}$
Carbon monooxide	$9.0 \cdot 10^{14}$
Carbon dioxide	$1.0 \cdot 10^{16}$
Methane	$1.4 \cdot 10^{15}$
Ethane	$2.2 \cdot 10^{15}$
Ethylene	$1.4 \cdot 10^{15}$
Propane	$5.2 \cdot 10^{15}$
Propylene	$4.8 \cdot 10^{15}$
Butane	$13.2 \cdot 10^{15}$

RESULTS AND DISCUSSION

In the recent years, interest has been increased to obtain liquid and gaseous products out of biomass pyrolysis. According to the structure there are three main components of biomass; hemicellulose, cellulose and lignin which are subjected to thermal decomposition in the range of temperature correspondingly hemicellulose 170…260 °C, cellulose 280…500 °C, and lignin 240…350 °C. This article is dedicated to the RTR transformation of small woods of coniferous pine and broad-leaf oak and beech trees; this process is complicated for the decomposition mechanism and multi-stage.

As a result of the studies carried out at different temperature and absorbed dose ranges it has been determined that during the decomposition of biomass in RTP and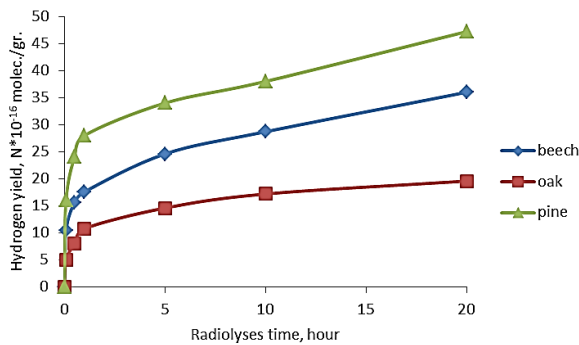 TP accordingly H_2, CO, CO_2, and hydrocarbon C_1–C_7 gases emerge. The analysis of the composition of the gases emerged out of biomass shows that in dependence with the type of biomass and the conditions of conducting a process the amount of interest of CO+CO_2 gases contained in gas composition is changeable and varies as follows: oak wood TRP = 85…95, TP = 76…93; pine wood TRP = 85…97, TP = 87…89; beech wood TRP = 83…96, TP = 92…98. This is explained by the fact that the amount of functional groups making up the structure of hemicellulose $[C_5H_{10}O_5]_n$, cellulose $[C_6H_7O_3(OH)_3]_n$ and lignin is a lot.

To obtain synthetic fuels out of biomass is considered the most perspective fields nowadays and in Figs. 1 and 2 the total amount of molecular hydrogen, hydrocarbon, and CO, CO_2 gases emerged out of biomass is given.
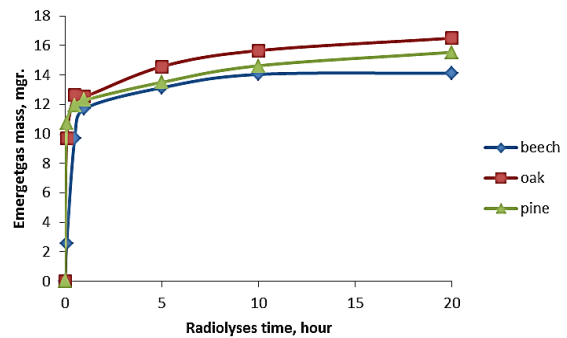

Fig. 1. Kinetic dependence (T = 673 K, P = 1.73 kGy/hour, m = 1 g) of molecular hydrogen generated out of biomass (pine, oak, beech) decomposition under ionizing radiation

Fig. 2. Kinetic dependence (T = 673K, P = 1.73 kGy/hour, m = 1 g) of total hydrocarbon gases generated out of biomass (pine, oak, beech) decomposition under ionizing radiation

According to the kinetic dependences given in Figs. 1 and 2 we can say that in both cases at the rates of absorbed dose as $D < 10$ кGy ($D = 0.48$ Gy/s, $T = 673$ K, $\tau \leq 5$ hour) the generation processes of hydrogen and hydrocarbon gases out of biomass speed up.

The share of radiation in the processes conducted at high temperatures is calculated as a difference of reaction speeds $W_R = W_{RT} - W_T$. Here for hydrogen reaction speed with beech has been $W(H_2) = 0.03 \cdot 10^{17}$ molec./(g·s), radiation-chemical yield $G = 93$ molec./100 eV, for oak $W(H_2) = 0.03 \cdot 10^{17}$ molec./(g·s), $G = 87$ molec./100 eV and for pine $W(H_2) = 0.03 \cdot 10^{17}$ molec./(g·s), $G = 100$ molec./100 eV. The total gas amount generated in this kinetic area makes up 1.27% for beech, 1.46% for oak and 1.25% for pine out of used initial biomass. To contionue subsequent processes shows that starting from the rate of absorbed dose $D > 10$ kGy a saturation state begins, which makes equal the generation and consumption speeds of the generated active particles under the impact of radiation and stabilization process occurs.

Table 2

The comparison of the gases generated out of biomass under the same conditions and at different times

Biomass	Generated gas mass M, mkg							
	5 hours				20 hours			
	H_2	CH_4	ΣC_3	ΣC_4	H_2	CH_4	ΣC_3	ΣC_4
Pine	3.85	608.16	271.44	242.39	6.50	618.77	361.92	269.32
Beech	7.16	570.56	280.20	268.06	11.94	695.19	375.22	278.81
Oak	9.29	533.86	359.00	315.49	15.66	794.96	461.16	338.57

According to the analysis of the gas composition it has been determined that although the amount of hydrogen and light hydrocarbons is high in the composition of the gases hydrogen at low absorbed doses $D < 10$ kGy, under the impact of steady and long-term radiation the amount of hydrocarbons with a heavier molecule weight increase. Tabl. 2 illustrates the comparison of gas masses generated out of biomass

under the same conditions during 5 and 20 hours ($T = 673$ K, $P = 1.73$ kGy/h). As you can see the amount of the weight of ΣC_3 and ΣC_4 fraction of hydrocarbon gases at higher doses increases depending on the absorbed dose.

This causes a sharp increase in the concentration of the light hydrocarbon radicals affected in the radiation zone in the end quadratic collision process of the radicals i.e. dimerization or trimerization processes take place.

At $D > 10$ kGy rate of the absorbed dose the change in the physicochemical characteristics of biomass in solid and liquid phases causes some internal transformations in their structure which could be indirectly explained by the generation of gas mass at the result of RTR decomposition of oak woods with a relatively higher concentration (see Fig. 2).

Under the influence of ionizing radiation the radiolytic transformation processes in biomass (RH) initially happens in the following stages; ionization (1), neutralization of ion-electron pairs (2) and the disposal of the state of excitement (3) and formation process of new radicals takes place [4, 5].

$$RH \rightarrow RH^+ + e^-; \quad (1)$$
$$RH^+ + e^- \rightarrow RH^*; \quad (2)$$
$$RH^* \rightarrow R^\circ + H^\circ. \quad (3)$$

In most states of excitement C (1)-H and C (4)-H bonds being at about the same energy levels break in glucopyranosyl rings and create R°- and H°-radicals. The generated hydrogen radical with a higher mobility breaks one hydrogen atom from the main glucopyranosyl and gives to molecular hydrogen (formula (4)) which again results in the formation of R°-radical. Initially, this process constantly continues under the influence of ionizing radiation.

$$RH + H^\circ \rightarrow R^\circ + H_2. \quad (4)$$

The concentration of the formed radicals $R^\circ \approx \sqrt{I}$ is directly proportional to the square root of the absorbed radiation intensity R°-radicals formed in the kinetic area speed up the process of hydrocarbon generation in gas phase.

By the increase of the amount of absorbed dose as you can see from (3) and (4) reactions R° concentration increases and reaches saturation state and as a result of interaction of these radicals they merge with each other which causes formation of hydrocarbons having a heavier molecular weight in the form of dimerization or trimerization.

CONCLUSIONS

Under the influence of gamma-radiation initially small size oak, pine and beech chippings have undergone a TRR decomposition at the temperature $T = 673$ K and the kinetics of the generation of gas products has been studied. It has been established that though at low doses the amount of molecular hydrogen and light hydrocarbons is a lot in the gas composition the more is rradiolysis time the more becomes the amount of hydrocarbons having a heavier molecular weight at relatively higher rates of absorbed dose $D \geq 10$ kGy, accordingly this happens at the result of dimerization or trimerization of the generated radicals.

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КИНЕТИЧЕСКИЕ ЗАКОНОМЕРНОСТИ ОБРАЗОВАНИЯ ГАЗОВЫХ ПРОДУКТОВ ПОД ВОЗДЕЙСТВИЕМ ИОНИЗИРУЮЩЕГО ИЗЛУЧЕНИЯ НА БИОМАССУ

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Исследована кинетическая зависимость получения молекулярного водорода и других газов из биомассы (дуба, бука и сосны) при температуре $T = 673$ К радиационно-термическим путем. Несмотря на то, что количество газообразного водорода и легких углеводородов в биомассе было высоким при поглощенной дозе $D < 10$ кГр и непрерывном облучении, в высоких оценках поглощенной дозы $D \geq 10$ кГр количество тяжелых молекулярных углеводородов увеличивается в результате димеризации или тримеризации радикалов.

КІНЕТИЧНІ ЗАКОНОМІРНОСТІ УТВОРЕННЯ ГАЗОВИХ ПРОДУКТІВ ПІД ВПЛИВОМ ІОНІЗУЮЧОГО ВИПРОМІНЮВАННЯ НА БІОМАСУ

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Досліджено кінетичну залежність отримання молекулярного водню та інших газів з біомаси (дуба, бука і сосни) при температурі $T = 673$ К радіаційно-термічним шляхом. Незважаючи на те, що кількість газоподібного водню і легких вуглеводнів була високою в біомасі при поглиненій дозі $D < 10$ кГр і безперервному опроміненні, у високих оцінках поглиненої дози $D \geq 10$ кГр кількість важких молекулярних вуглеводнів збільшується за рахунок димеризації або тримеризації радикалів.