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LOW-CARBON RADIATION-THERMAL PYROLYSIS OF LIGNITES

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Abstract: The article lists the necessity of transition to low-carbon technologies and the main provisions of international policy documents in this field. It is noted that the transition to low-carbon technologies should be ensured both in the production and consumption of energy. Ways to use renewable energy sources and energy from nuclear reactors for low-carbon energy production are shown. The main content is devoted to the use of ionizing radiation and thermal energy for low-carbon reactions in the chemical industry. It has been shown that when high-intensity accelerated electrons are used, it is possible to provide both high-temperature and ionizing components with a low-carbon effect to carry out radiation-thermal processes. For example, the regularities of obtaining H_2 and CO gases in the radiation-thermal pyrolysis of lignite were studied, and the possibility of carrying out the process with zero emissions was proven.

Keywords: Low-carbon, accelerated electrons, pyrolysis, hydrogen

1. Introduction

The basis for the transition to low-carbon technologies is related to climate change. Since the rapid development of industry in the 1850s, the average global temperature has risen by 0.8-1.2°C (1). Many years of research show that such an increase in global temperature is directly related to greenhouse gas emissions. Calculations of different scenarios based on climate models show that a likely temperature increase in the 21st century could be 0.3-4.8 degrees. The change in this range is determined by the amount of carbon emissions. The amount of emissions of CO_2, CH_4, and other greenhouse gases will determine the likely increase in temperature. Therefore, the introduction of low-carbon technologies in the world has become essential. Countries that have joined the UNCCC and the Paris Agreement, as well as the Green Deal priorities of the European Union for 2019-2024 and the decisions of the 2019 Dawos World Economic Forum, are currently implementing policies to reduce carbon emissions. Zero carbon emissions are targeted in 2050 (2). Although the introduction of low-carbon renewable energy sources plays a key role in achieving these goals, reducing carbon emissions in energy use is also important. As part of this policy, it covers legislation, economic, international cooperation, scientific research, Project implementation activities in this field, etc.

It should be noted that the annual emission of greenhouse gases worldwide is 50 billion tons (3). The chemical industry produces 2.9 billion tons of carbon emissions. These emissions are generated during the implementation of energy-intensive chemical processes. In the world, 257 million tons of oil, 114 million tons of natural gas, and 47 million tons of biomass are used in chemical technology to meet their energy and heat needs.

For example, 450 million tons of carbon emissions occur in the synthesis of ammonia, and 300 million tons in petrochemical processes. Stimulating these types of processes through physical methods can limit carbon emissions. In this article, energy-intensive chemical processes stimulated by ionizing rays and electrical and thermal energy from renewable energy sources are studied.

2. Methods

Among the physical methods, various types of radiation from atomic reactors (gamma, neutron-gamma, fission fragments), and electron accelerators working with electricity from solar wind and nuclear reactors in principle were used. Pyrolysis and gasification of coal, which are energy-intensive processes, as well as the reactions of obtaining gases and olefins from oil fractions, were studied in the facilities designed to work according to the following scheme (4-6).

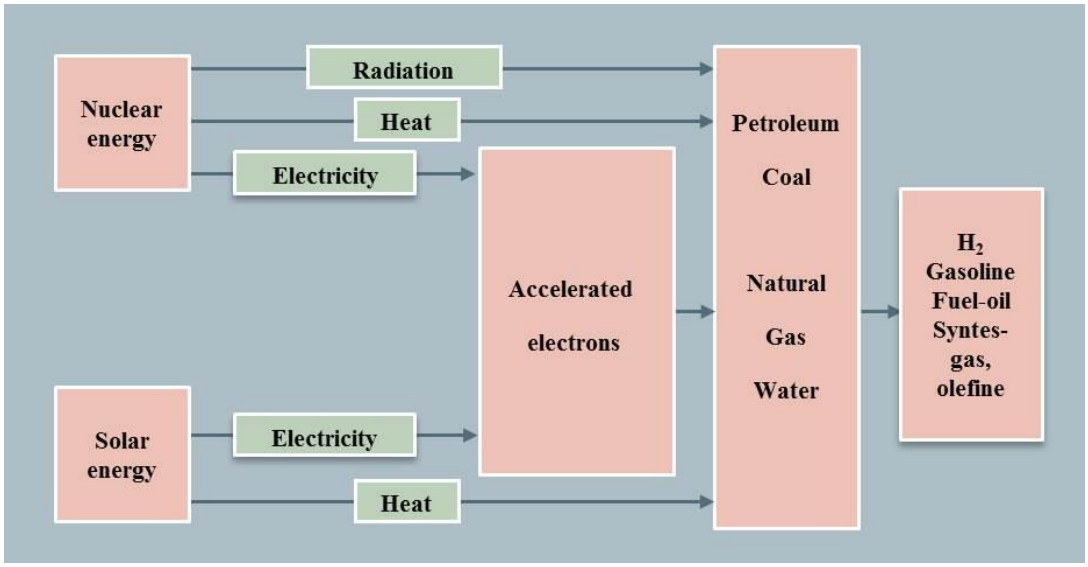

Fig. 1. Use of Nuclear and Solar energy in low Carbon radiation-chemical technology for processing of fossil fuels.

A summary of conducted Researches in the Laboratory of Energy-saving processes of IRP addused in the Table 1.

Table 1

Summary of conducted research of low-carbon Radiation-thermal processes

Primary compounds	Petroleum and its fractions, coals, oil-bituminous rocks, natural gas
Radiation sources	Accelerated electrons, Nuclear energy, gamma-radiation, Solar energy
Processes	Dehidrogenisation - Olefin production, Refining, Gasification, Pyrolysis, Co-processing,
Parameters	P= 1.15 – 500 kW, T=20-500C
Products	H_2, Olefines, H_2-CO, Gasoline, Fuel-oil,

This article deals only with the pyrolysis of lignites under the influence of electron beam.

Radiation-thermal pyrolysis of lignite under the influence of electron beam

Experiments on RT pyrolysis of lignite were carried out using an accelerated electron beam under flow conditions. The use of an accelerated electron beam as a source of ionizing radiation made it possible to significantly expand the range of parameters of the studied processes. Kinetic regularities of gas formation during pyrolysis of lignite under the influence of electron beam were studied in the temperature range of $\Delta T = 150 \div 600^{o}C$, the radiation dose rate of $\Delta P = (0.5 \div 15) \cdot 10^3$ kGy/h and absorbed doses of radiation $\Delta D = 0 \div 4000$ kGy.

Figure 2 shows the dependencies of the formation rates of H_2 and CO on $T = 150^{o}C$ and radiation dose rate P=1250 kGy/h. As can be seen from the figure, after a certain time (ι = 8-10 min), a stationary mode of gas formation rate in the system is established. However, such dependencies are characteristic only at relatively low radiation dose rates ($P \leq 1250$kGy/h) and low temperatures ($T \leq 350^{o}C$).

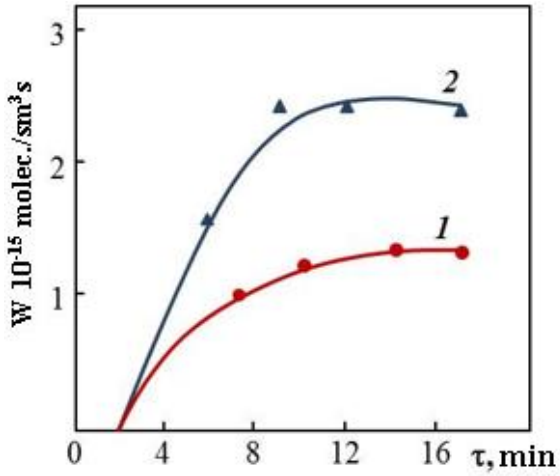

Fig. 2. Dependence of H_2 (1) and CO (2) formation rates on $T = 150^{0}C$ and irradiation time P=1250 kGy/h.

Figures 3, and 4 show temperature dependences of formation rates of H_2, CO, and CH_4 at irradiation doses rate P=500 and 1250 kGy/h.

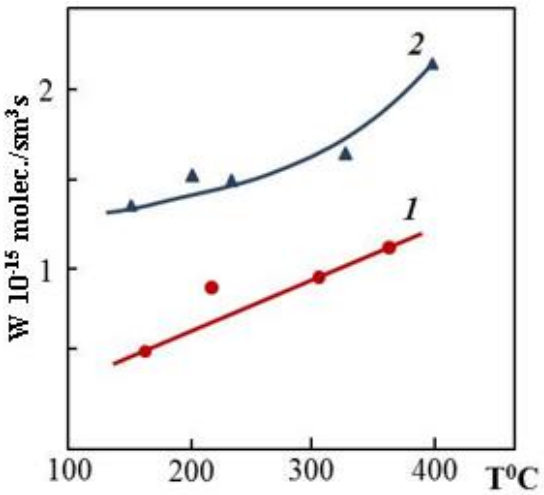

Fig. 3. Temperature dependence of the formation rate of H_2 at the dose rate of the electron beam P=500 kGy/h (1) and 1250 kGy/h (2).

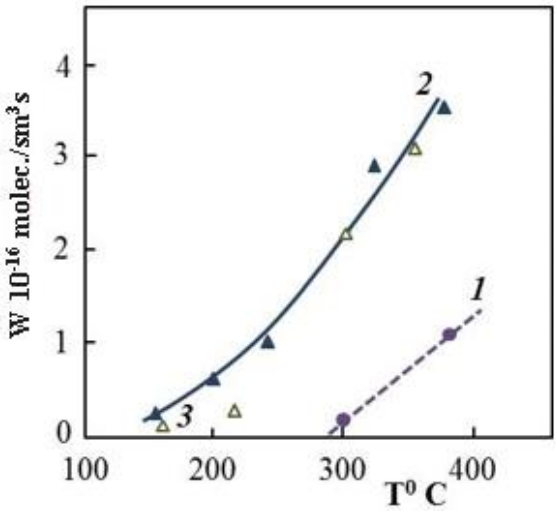

Fig. 4. Temperature dependence of the formation rate of CO (Δ,▲) and CH_4 (●) at P=500 (Δ) and 1250 kGy/h (▲,●).

The increase in temperature from 150 to 375ºC causes a slight increase in the formation rate of hydrogen. A practically proportional increase in the formation rate of H_2 is observed when the irradiation dose rate increases from 500 to 1250 kGy/h. In this temperature range, the values of radiation-chemical yields of hydrogen vary in the range $G(H_2)$=0.1-1.2. There is no such dependence in the case of CO. Formation rate of CO increases from $1.3 \cdot 10^{15}$ to $3.52 \cdot 10^{16}$ molec/cm^3·s at given values of process parameters and, accordingly, radiation-chemical yields of CO vary in the range of G=0.2÷5. The methane formation is only observed at the radiation dose rate of P = 1250 kGy/h.

It should be noted that when higher irradiation doses are used, the accelerated electrons serve as a source of heat and ionizing radiation. This feature of irradiation of samples with an accelerated electron beam eliminates the need for external heat sources and allows experiments to be carried out at high T and P. These experiments are characterized by a fairly good isothermality within the mass of the irradiated material.

Figure 5 shows the kinetic curves of formation rates of H_2 and CO at high dose rates in RT and T reactions ($P=10^4$kGy/h and T=460ºC) as an example.

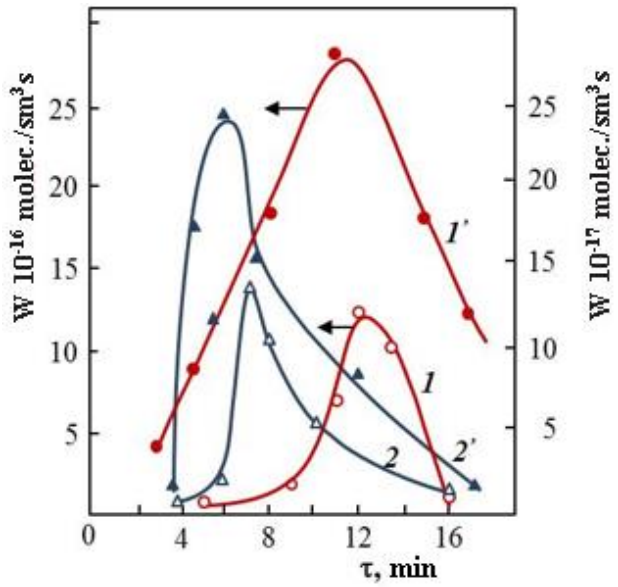

Fig. 5. Dependence of formation rates of H_2 (1, 1') and CO (2, 2') on irradiation time in RT(1', 2') and T(1, 2) processes; $T=10^4$kGy/h and T=460ºC.

Under the influence of an electron beam, a stationary temperature is established after 3-4 minutes (T=460°C). In contrast to low-temperature pyrolysis processes, the curves of the formation rate of H_2 and CO pass through a peak at both the radiation-thermal and thermal processes. In both cases, the formation rates of the product observed in the radiation-thermal process are higher than in the thermal process. Such a "bell-type" of curves leads to the multi-stage process of lignite pyrolysis. As a result of the stabilization of the condensated residue, there is a rapid loss of mass with each new and higher heat load, which stops during the destruction. Thermal conversion helps the development of a combination system, which increases the structural stiffness and the thermal stability of the condensed phase, as a result, sources of OML that provide gas-like products are depleted. Radiation thermal of gases and thermal processes of gases (Table 2) and thermal processes were carried out using the maximum speeds of gas.

The radiation-chemical yields of gases were determined (Table 2) using maximum rates of RT gas formation at thermal processes.

Table 2

Values of radiation-chemical yield G(molec/100eV) of gases from dose rate, electron beam dose, and temperature in the radiation-thermal process of lignite pyrolysis

P, 10^{-3} kGy/h	kGy	T, °C	H_2	CO	CH_4
5.0	830	330	0.2	4.5	0.4
7.5	1250	390	0.64	5.6	1.0
10.0	1670	460	0.9	5.9	1.2
12.5	2080	530	1.0	5.4	4.2
15.0	2500	590	0.8	5.0	6.4

Table 2 shows the results of the study of the radiation-initiator effect of lignites at different dose rates. ΔD=830-2500 kGy, ΔT= 330 ÷ 590ºC and P=5-15·10^3 kGy/h. As it can be seen from the table, the radiation-chemical yield of gases in the range of parameters of the studied process varies in the following limits: G(H_2)=0.2÷1, G(CO)=4.5÷5.9, G(CH_4)=0.4÷6.4. The total value of combustible products, which account for more than 90% of all gas production, is $\sum \cong 10 \div 12$

Figure 6 shows the dependence of the total rate of gas extraction from coal in the radiation process on the radiation dose rate.

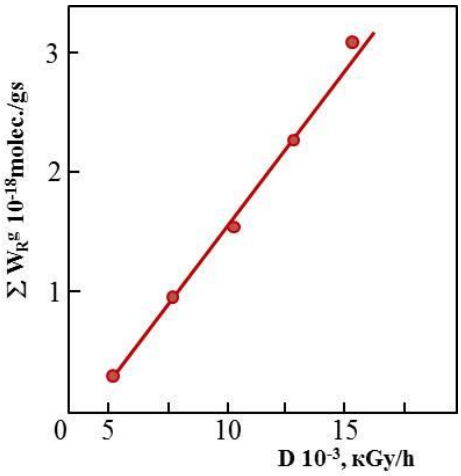

Fig. 6. The dependence of the total rate of gas extraction from lignite in the radiation process on the electron beam dose rate.

A practically linear increase in the total gas formation rate is observed with an increasing radiation dose rate. A radiation rate limit of ~1 W/g can clearly be seen. The gas extraction rates are very low below this value of radiation dose, and when the threshold is increased, they increase rapidly with the increase of the beam rate. As expected, the changes in W_{RT}/W_T ratio with increasing irradiation dose and temperature correspond to the competition of thermal and RT processes, indicating that both develop independently. For example (see Fig. 7) with the increase of W_{RT}/W_T dose rate from $5\cdot10^3$ to $15\cdot10^3$kGy/h, it falls from 10 to 1.1 for hydrogen and from 3.7 to 1.3 for CO. It should also be noted that high lignite conversions can be achieved using high radiation rate.

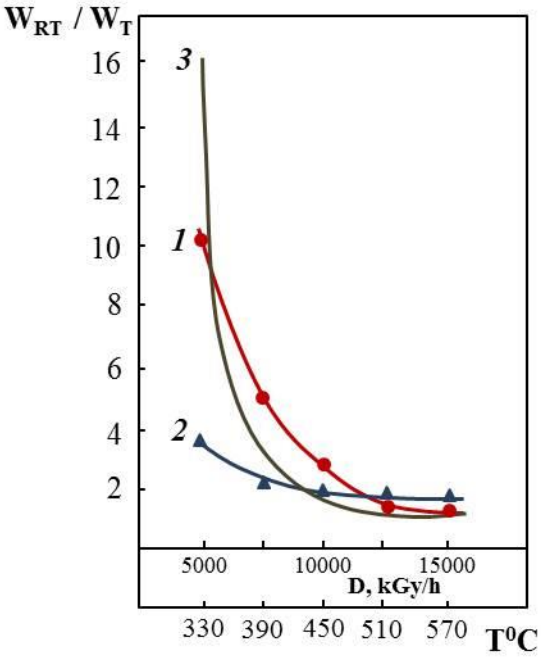

Fig. 7. Dependence of the ratio of formation rates of H_2 (1) and CO(2) in radiation-thermal and thermal processes on the electron beam dose rate. $W_{RT}/W_T = f(D,T)$ curve 3 - calculation dependence.

Thus, an increase of beam rate from 10^4 to $15\cdot10^3$kGy/h results in an increase of the total conversion rate from 8 to 20% in the RT processes within 10 min. At the same time, the conversion rate increases from 4.5 to 12%, respectively, when the temperature range corresponding to a given level of energy release rate in the thermal process is changed.

As can be seen from the presented data, the effects of heat, i.e. $W_R=W_{RT} - W_T$ comparable temperature ranges (ΔT=150-400ºC) are a little different for H_2 and CO in the case of irradiation of coal by gamma radiation and by accelerated electrons. The final values of radiation-chemical yields of gases in studied parameter ranges are as follows: - $G(H_2)=0.03\div1.3$; $G(CO)=0.02\div10.4$; $G(CH_4)=10^{-3}\div43.3$ in case of γ-irradiation and $G(H_2)=0.06\div0.64$; $G(CO)=0.2\text{-}5.6$; $G(CH_4)=0.1\text{-}1.1$ in case of accelerated electron irradiation

The observed difference in the values of product G during radiation-stimulated pyrolysis of lignites under the influence of γ-irradiation and accelerated electrons is apparently connected with the depth of lignite conversion, which depends on the irradiation parameters.0.4-1.5% of lignite is converted into gaseous products by γ-irradiation and 6-10% by accelerated electron irradiation at comparable temperatures (≤400ºC). This case also suggests that the deepening of lignite conversion changes the composition of unstable components and the radiation-chemical yield of gases determined by these components decreases.

There are some other cases that can make a significant difference in the gas yields under the influence of electron beam and γ-radiation. These cases can be the specificity of the influence of γ-radiation and accelerated electrons on coal, as well as methods of heating coal with an electric furnace and braking electrons. During the irradiation of coal with γ-radiation and accelerated electrons of low beam rate (P≤1250kGy/h), the temperature of the lignites is regulated by the electric furnace's surface heating. When irradiating lignite with electrons of high beam rate (P≥$5\cdot10^3$ kGy/h), the temperature is regulated by the beam rate.

Kinetic regularities of gas formation during pyrolysis of lignite under the influence of electron beam in temperature range ΔT= (150÷600)ºC, radiation dose rate D=(0.5÷15)10^3 kGy/h and absorbed radiation doses D=(0-400º) kGy were studied. Irradiation under static conditions was carried out in D=2088kGy/h ampoules in the temperature range T=(300÷500)ºC. The ratio of total gas extraction rates was W_{RT}/W_T=(16.2÷38.4) in the radiation-thermal (RT) and thermal (T) processes. As the temperature increases from 300 to 500ºC, the W_{RT}/W_T value decreases from 38.4 to 16.2. A detailed study of gas formation regularity during radiation pyrolysis was carried out under flow conditions.

The dependences of H_2 and CO formation rates on irradiation time and radiation dose rate of accelerated electrons D=1250 kGy/h at T=150ºC were investigated. After a certain period (ι=8-10 min), a stationary mode of gas formation rates is established in the system. However such dependencies are characteristic only at relatively low radiation dose rates (D≤1250 kGy/h) and low temperatures (T≤350ºC).

Increasing the temperature from 150 to 375°C causes a slight increase in the hydrogen generation rate. Increasing the irradiation dose from 500 to 1250 kGy/h shows an almost proportional increase in the formation rate of H_2. In this temperature range, the values of the radiation-chemical yield of hydrogen fluctuate in the range G(H_2)=0.1-0.2. In the case of CO, this dependence is not observed. At given values of process parameters, the rate of formation of CO in the air increases from $2\cdot10^{15}$ to $6\cdot10^{16}$ molec/g·s, and respectively, the radiation-chemical yield of CO varies in the range of G = 0.2-5. Methane formation is observed only at an irradiation dose of D=1250 kGy/h.

Stationary temperature is established after 3-4 minutes (T=460ºC) under the influence of an electron beam. In contrast to low-temperature pyrolysis processes, the curves of formation rates of H_2 and CO at both radiation thermal and thermal processes pass through the peaks. In both cases, the rates of formation of products observed in the RT process exceed the rates of the thermal process. Such "bell-type" curves lead to a multi-stage process of lignite pyrolysis. As a result of the stabilization of the condensed residue, a rapid loss of mass occurs with each new and higher heat load, which is interrupted during destruction. Thermal conversion promotes the development of a combination system, which increases the stiffness of the structure and the thermal stability of the condensed phase, resulting in the depletion of the organic mass of lignite (OML) sources that yield gaseous products. Determination of the radiation-chemical yield of gases was carried out using the maximum rates of RT gas formation in thermal processes.

Experiments on the pyrolysis study of the radiation initiator effect of coals at a different dose rate of radiation ΔD=830-2500 kGy, ΔT=330-590ºC, and D=5-15·10^3 kGy/h are presented. As can be seen from the table, the radiation-chemical yield of gases in the range of parameters of the studied process varies in a range: G(H_2)=0.37-1, G(CO)=2.5-5.9, G(CH_4)=0.4- 6.4. The total G value of combustible products, which accounts for more than 90% of gas extraction, is G=10-12.

A practically linear increase in the total rate of gas formation is observed with increasing radiation dose. The radiation rate limit of 4MGy/h is clearly visible. The gas extraction rate is very low below this value of the radiation dose, and when the threshold is increased, they

increase rapidly with the increase of the beam rate. As expected, changes in the W_{RT}/W_T ratio with increasing radiation dose and temperature correspond to the competition of thermal and radiation thermal processes, indicating that both develop independently. With an increase of W_{RT}/W_T dose rate from $5\cdot10^3$ to $15\cdot10^3$kGy/h, it decreases from 10 to 1.1 for hydrogen and from 3.7 to 1.3 for CO. It should also be noted that high conversions of lignites can be achieved when using high radiation rates.

Thus, an increase of beam rate from 10^4 to $15\cdot10^3$kGy/h results in an increase of the overall conversion rate from 8 to 20% in the RT processes within 10 min. At the same time, the conversion rate increases from 4.5% to 12%, respectively, when the temperature range corresponding to a given level of energy release rate at the thermal process is changed.

As can be seen from the presented data, the effects of heat, i.e. $W_R=W_{RT} - W_T$ comparable temperature ranges (ΔT=150-400ºC) do not deviate much in the case of irradiation of coal with γ-irradiation and accelerated electrons. The final values of radiation-chemical yields of gases in studied parameter ranges are as follows: - $G(H_2)=0.03\div1.3$; $G(CO)=0.02\div10.4$; $G(CH_4)=10^{-3}\div43.3$ in case of γ-irradiation and $G(H_2)=0.06\div0.64$; G(CO)=0.2-5.6; $G(CH_4)$=0.1-1.1 in case of accelerated electron irradiation.

There are some other cases that can make a significant difference in the gas yields under the influence of electron beam and γ-radiation. These cases can be the specificity of the influence of γ-radiation and accelerated electrons on coal, as well as methods of heating coal with an electric furnace and braking electrons. During the irradiation of coal with γ-radiation and accelerated electrons of low beam rate (D≤1250kGy/h), the temperature of the coal is regulated by the electric furnace's surface heating. When irradiating coal with electrons of a high beam rate (~$5\cdot10^3$kGy/h), the coal temperature is regulated by the beam rate.

3. Conclusion

It is possible to produce H_2 and CO gas in the lignite pyrolysis process by applying a radiation dose rate of more than $5\cdot10^3$kGy/h through electron accelerators running on electricity obtained from carbon-free nuclear reactors or renewable energies.

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НИЗКОУГЛЕРОДНЫЙ РАДИАЦИОННО-ТЕРМИЧЕСКИЙ ПИРОЛИЗ ЛИГНИТОВ

И.И. Мустафаев, Х.М. Гаджиев

Резюме: В статье перечисляется необходимость перехода на низкоуглеродные технологии и основные положения международных политических документов в этой области. Отмечается, что переход на низкоуглеродные технологии должен быть обеспечен как в производстве, так и в потреблении энергии. Показаны пути использования возобновляемых источников энергии и энергии ядерных реакторов для производства энергии с низким содержанием углерода. Основное содержание посвящено использованию ионизирующих излучений и тепловой энергии для проведения низкоуглеродных реакций в химической промышленности. Было показано, что при использовании ускоренных электронов высокой интенсивности для проведения радиационно-тепловых процессов возможно обеспечение как высокой температуры, так и ионизирующего компонента низкоуглеродным эффектом. В качестве примера исследованы закономерности получения газов H_2 и CO при радиационно-термическом пиролизе лигнитов, доказана возможность проведения процесса с нулевой эмиссией.

Ключевые слова: низкоуглеродный, ускоренные электроны, пиролиз, водород.

LİQNİTLƏRİN AZKARBONLU RADİASİYA-TERMİK PİROLİZİ

İ.İ. Mustafayev, H.M. Hacıyev

Xülasə: Məqalədə azkarbonlu texnologiyalara keçidin zərurəti və bu sahədə beynəlxalq siyasət sənədlərinin əsas müddəaları sadalanır. Qeyd olunur ki, azkarbonlu texnologiyalara keçid həm enerjinin istehsalında, həm də istehlakında təmin olunmalıdır. Enerji istehsalının azkarbonlu olması üçün bərpa olunan enerji mənbələrindən və nüvə reaktorlarının enerjisindən istifadə olunmasının yolları göstərilir. Əsas məzmun kimya sənayesində azkarbonlu reaksiyaların aparılması üçün ionlaşdırıcı şüalar və istilik enerjisindən istifadə olunmasına həsr olunmuşdur. Göstərilmişdir ki, yüksək intensivlikli sürətləndirilmiş elektronlardan istifadə edildikdə radiasiya-termiki prosesləri aparmaq üçün həm yüksək temperaturu, həm ionlaşdırıcı komponenti azkarbonlu təsirlə təmin etmək mümkündür. Örnək olaraq liqnitlərin radiasiya-termiki pirolizində H_2 və CO qazlarının alınması qanunauyğunluqları tədqiq olunmuş, prosesin sıfır emissiya ilə aparılmasının mümkünlüyü sübut edilmişdir.

Açar sözlər: azkarbonlu, sürətlənmiş elektronlar, piroliz, hidrogen