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INVESTIGATION OF THE COMPOSITION OF BIOMASS-GASIFICATION PRODUCTS IN A PSEUDOLIQUID LAYER

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Experiments on gasification of the wood biomass in a pseudoliquefied layer are described. The experimental data obtained were compared to the results of calculations of the thermodynamically equilibrium composition of the synthesis gas. The influence of the type of catalyst and moisture of the wood biomass on the composition of the synthesis gas obtained has been investigated.

Gasification of a biomass is a developing technology that can be used for the production of fuel or technological oils with a high concentration of H_2 and CO and, being integrated into combined heat-power cycles, for the generation of electric energy in a gas turbine or a fuel element with a higher efficiency than by direct combustion of biofuel. Conditioning (cleaning from resins and undesirable impurities) and upgrading of the synthesis gas (optimization of the H_2/CO ratio) permit using it as a raw material for the production of methanol or liquid fuel (Fischer–Tropsch process) [1]. Additional processing (maximization of the H_2 content, fine cleaning from impurities) leads to the production of pure hydrogen.

The biomass has such disadvantages as a low content of hydrogen (~6%), a high content of oxygen (~40%), and a low calorific value. Moreover, thermochemical conversion of the biomass causes passage into the composition of the gaseous products of resins — high-molecular organic compounds that condense at a temperature of 60–80^{o}C, alkali metals, primarily potassium, chlorine, and sulfur compounds that are responsible for the failure of conversion catalysts, sulfur cleaners, and ceramic filters, and cause deposition on metal and gunited surfaces of gaseous wastes at the gasifier outlet and their corrosion. When conversion is conducted in a boiling layer (BL) or in a circulating boiling layer (CBL), the resins and potassium, especially in the presence of chlorine, promote agglomeration of the layer material and disruption of the pseudoliquefaction and conversion in general. To provide a high thermal, economic, and ecological efficiency and reliability of the hydrogen production from a biomass, it is necessary to solve the problems connected with the above drawbacks of the raw material. This calls for primary pyrolysis of the biomass in a medium with a water vapor excess in order to shift the equilibrium conditions to the H_2 outlet; the creation of favorable conditions for conducting secondary vapor conversion of the synthesis gas with the aim of increasing the hydrogen content in it as a result of the shift-reaction of water-gas substitution $CO + H_2O = CO_2 + H_2$; oxidation of a part of the raw material to provide autothermality of the process so as to prevent oxidation of hydrogen and dilution of the synthesis gas with inert gases (nitrogen, carbon dioxide, etc.); the application of catalysts promoting the destruction (cracking) of resins and acceleration of conversion processes in temperature regimes that are optimal for the conditions of preventing layer agglomeration and emission of alkali metals and halogens in aggressive forms.

There exists a wide range of commercial nickel-based catalysts used in the processes of oil and natural gas reforming. Their high efficiency has also been confirmed in the case of hot conditioning of biomass gasification products [2]. Apart from their high activity in terms of the destruction of resins, they promote conversion of methane and light hydrocarbons to H_2 and CO (at $T > 700^oC$) and display a certain activity in vapor shift-conversion of CO to CO_2 with increasing concentration of H_2. Some investigations have shown that Ni-catalysts also provide ammonia dissociation into N_2 and H_2 (reverse reaction) in the synthesis gas.

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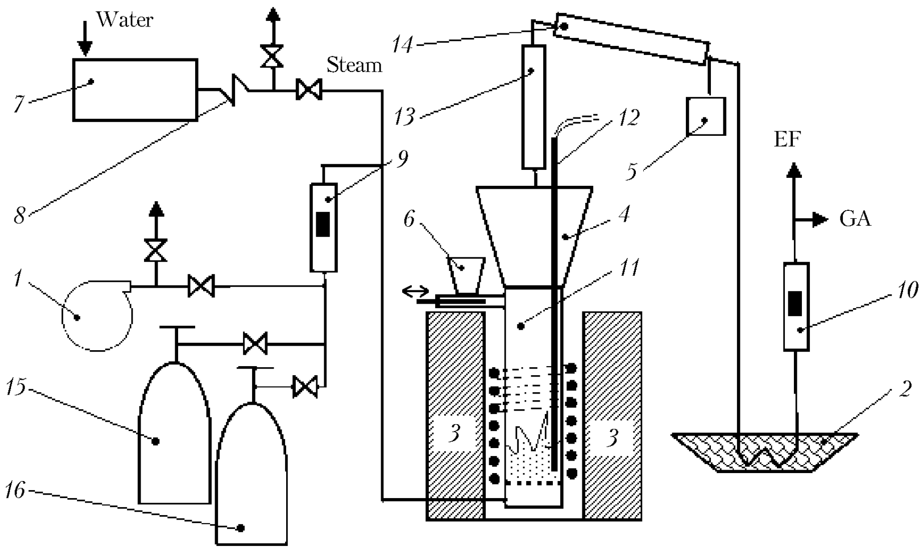

Fig. 1. Scheme of the experimental facility: 1) blower; 2) water-ice tub; 3) heat insulation; 4) confuser; 5) steam trap; 6) biomass feeder; 7) steam generator; 8) steam superheater; 9 and 10) rotameters; 11) boiling-layer reactor; 12) thermocouple; 13) refrigerator; 14) condenser; 15 and 16) vessels with compressed carbon dioxide and nitrogen, respectively.

In modern world practice, gasification of the biomass is carried out, as a rule, upon its preliminary drying in order to decrease the energy expenditure required for the conversion. In so doing, the concurrent processes of outflow of moisture and pyrolysis products from fairly large particles of a high-moisture biomass create favorable conditions for internal conversion of the resin and hydrocarbons capable of upgrading the synthesis gas.

The aim of the present paper is to determine the optimal conditions for introducing model commercial catalysts into a boiling-layer reactor depending on the wood biomass characteristics (in particular, moisture of particles). To estimate the conversion efficiency under different conditions, the experimental data were compared to the results of calculations of thermodynamically equilibrium composition of the synthesis gas.

Experimental Facility and Measurement Procedure. The experiments were performed on a high-temperature facility with a boiling layer with internal circulation of the material (Fig. 1).

The basic component of the facility is an electrically heated boiling-layer reactor (inner diameter of 55 mm) made of stainless steel. The reactor height over the gas-distributing lattice is 0.5 m. The lattice consists of grog crumbs of thickness 1.5 cm clamped between double layers of a heat-resistant net with a 0.5-mm mesh. The layer temperature in the reactor is measured by means of a chromel-alumel thermocouple 12 with an open junction connected through a multichannel interface to a personal computer. The thermocouple can move along the reactor height to measure the vertical temperature profile. The reactor is equipped with an outer electric heater in the form of a Ni-Cr alloy coil providing the necessary temperature regime. The heater power is manually controlled depending on the layer temperature. The reactor and the heater coil are covered with a heat insulator 3 from a mixture of kaolin and grog crumbs and on top of it with a protective metal housing, which guarantees a fairly high thermal inertia of the facility.

The boiling layer of the inert dispersive material (sand, particle diameter $d = 0.25$ mm, apparent density $\rho = 2540$ kg/m^3) was formed due to the pseudoliquefaction by the gaseous agent of gasification, for which superheated steam (pure or mixed with nitrogen) and carbon dioxide were used. The pseudoliquefying agent CO_2 was supplied from a vessel with compressed gas, and as a steam source we used an electric steam generator 7 equipped with a steam superheater 8 to provide a temperature at the reactor inlet higher than the saturation temperature. Provision was also made for air supply to the reactor by means of a fan 1. The flow rates of cold gases before the reactor were measured by a rotameter 9, and the necessary flow rate of steam was given by means of precalibrated regulating fittings. The volumetric rate of flow of the gas in all experiments was equal to 0.3 nliter/sec.

TABLE 1. Characteristics of the Model Catalysts

Catalyst	Shape and size of particles	Apparent density, kg/m^3	Volume fraction of catalyst in BL
K-1 (nickel*)	Cylinders with a 2.5-mm cross section and a length of 5–8 mm	1100	0–0.2
K-2 (magnesium-chromium*)	Spheres with a mean diameter of 1.7 mm	1760	0–0.2
K-3 (copper-chromium*)	Spheres with a mean diameter of 0.7 mm	1800	0–1
K-4 (dolomite)	Crushed stone particles of size 1–1.5 mm	2850–3000	0–0.2

*Aluminum oxide

The conversion products at the confuser outlet go first into a metal water-cooled refrigerator 13 and then into a glass condenser 14, which promotes condensation of pyrolysis resins that settle on the walls of cool gas conduits and steam. The latter's condensate was collected in a steam trap 5. Final drying of conversion products was realized by their deep cooling in a water-ice tub 2. The average content of resins (in the form of deposits on the walls) was determined by weighing cold gaseous wastes before and after an experiment, and the average flow rate of steam — by weighing the condensate. Upon weighing, the deposits on the walls were removed by organic solvents. The content of resins in the condensate was determined by means of low-temperature convective evaporation of moisture at 50^{o}C. As a rule, it constituted 0.4–0.5% of the polluted condensate mass. The flow rate of noncondensable gases at the outlet from the system was measured by a rotameter 10 and then sampling of gases for gas analysis (GA) was carried out, after which they were directed to the exhaust fan (EF).

As a model biomass, we used pine wood of moisture content 7 and 43% in the form of relatively large cylinders with the following characteristics: d = 8 mm, L = 15 mm, q = 0.42 kg/h, ρ = 540 kg/m^3, A^p = 0.9 mass %, C^p = 46.5 mass %, H^p = 5.5 mass %, O^p = 38.5 mass %, N^p = 0.6 mass %, and V^p = 90.0 mass %.

We investigated two basic compositions of the pseudoliquefying gas (gasification agent) — steam (H_2O) and carbon dioxide (CO_2), whose flow rate was 0.3 nliter/sec.

The characteristics of the model catalysts are given in Table 1. Disperse catalysts K-1–K-4 were added directly to the BL, and K-5 (aluminooxide-based nickel catalyst, whose characteristics are not given in the table) having the form of tablets of height 14 mm and diameter 16 mm with seven holes of diameter 3 mm was placed in the secondary stationary layer (one or several horizontal rows with seven tablets in each) in the superlayer volume at the confuser inlet.

Calculation of the Equilibrium Composition. The calculations of thermodynamically equilibrium concentrations of conversion products were performed numerically by the element potential method based on the principle of minimum potential (Gibbs) energy for the equilibrium composition system [3]. The Gibbs energy for a mixture of components is defined by the expression

$$G = \sum_{k=1}^{K} \bar{g}_k N_k \, . \tag{1}$$

For mixtures of ideal gases and ideal solutions, the Gibbs energy of the kth component is

$$\bar{g}_k = g_k (T, P) + RT \ln X_k \, . \tag{2}$$

The equilibrium composition of the system at a given temperature and pressure is calculated by minimizing expression (2) with restrictions imposed by the initial atomic composition of the system and the composition of products chosen according to the analysis of the mechanism of the considered chemical process and (or) the experimental

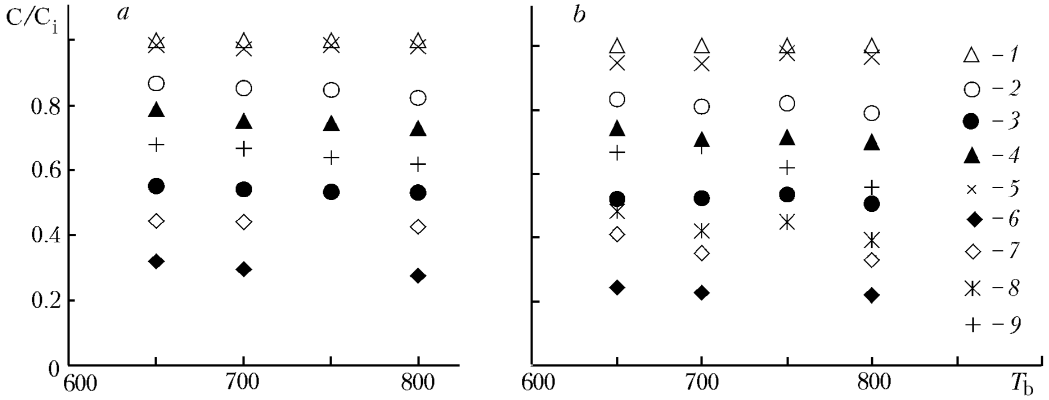

Fig. 2. Mass ratio (resin)/(resin in using an inert layer) at the outlet from the BL reactor depending on the layer temperature and the type of catalyst [a) pseudoliquefaction agent — carbon monoxide, b) steam]: 1) without a catalyst (W = 7%); 2) K-2 (X_c = 20%, W = 7%); 3) K-2 (X_c = 20%, W = 43%); 4) without a catalyst (W = 43%); 5) K-1 (X_c = 20%, W = 7%); 6) K-4 (X_c = 20%, W = 43%); 7) K-4 (X_c = 20%, W = 7%); 8) K-3 (X_c = 100%, W = 7%); 9) K-5 (X_c = 20%, W = 7%).

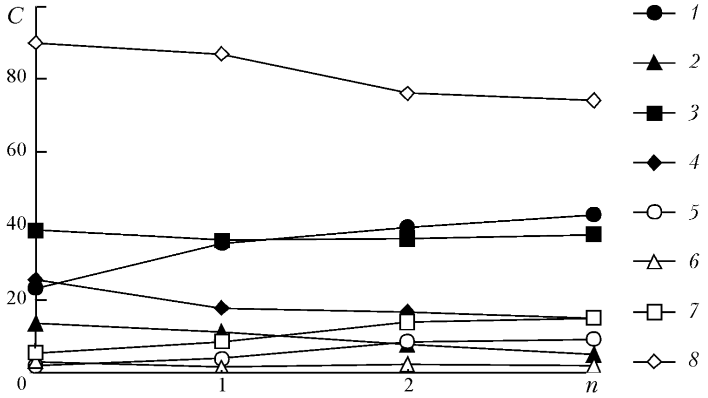

Fig. 3. Composition of gaseous products of the dry biomass gasification (W = 7%, T_b = 700°C) depending on the number of sections of the secondary catalyst K-5 resulting from the pseudoliquefaction by different gases [1–4) steam; 5–8) CO_2]: 1 and 5) H_2; 2 and 6) CH_4; 3 and 7) CO; 4 and 8) CO_2.

data. On the basis of the analysis of literature sources, in the present paper we considered the following composition of admissible mixture components: H_2, O_2, N_2, CO, CO_2, H_2O, CH_4, CH_2, C_2H_2, C_2H_4, C_2H_6, C_3H_8, and C_6H_6. The coke residue resulting from the pyrolysis of the wood, with account for its small ash content, was considered as hard carbon (graphite). Special experiments have shown that under the experimental conditions at a BL temperature of 700°K the yield of coke and volatile matter from pyrolysis of a large wood particle is, respectively, 10 and 90% (of dry mass).

Results and Discussion. Figure 2 shows the experimental dependences of the mass ratio of the average content of resins to the content of resins in the case of using an inert layer (C/C$_i$) on the layer temperature T_b when large wood particles are converted. As a pseudoliquefaction agent, we used: (a) carbon dioxide (the CO_2/biomass mass ratio is 5) and (b) steam (the steam/biomass mass ratio is 1.6). The composition of the layer included inert sand and sand with additives of primary catalysts K-1 (mass fraction X_c = 0.2); K-3 ($X_c \leq 1.0$), and K-4 (X_c = 0.2), as well as with the secondary stationary layer of catalyst K-5 placed over it.

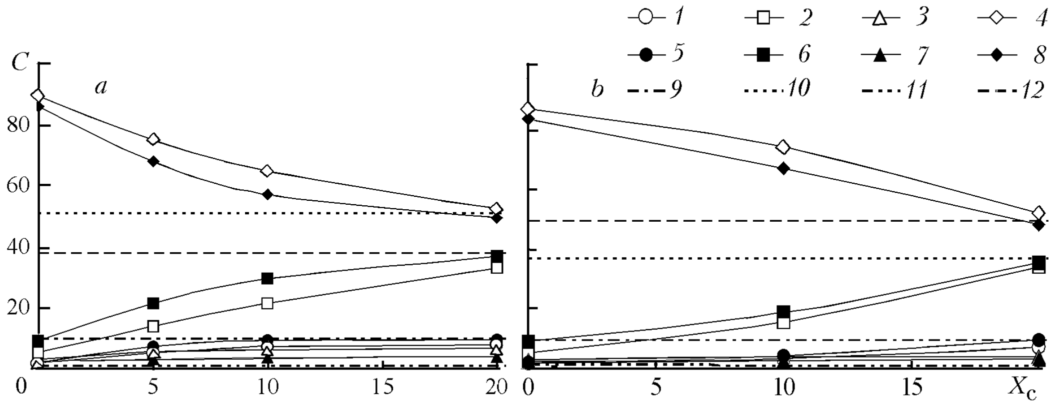

Fig. 4. Influence of wood moisture on the composition of the CO_2-gasification products at T_b = 700°C: 1) H_2 (W = 7%); 2) CO (W = 7%); 3) CH_4 (W = 7%); 4) CO_2 (W = 7%); 5) H_2 (W = 43%); 6) CO (W = 43%); 7) CH_4 (W = 43%); 8) CO_2 (W = 43%); 9–12) equilibrium ones: 9) H_2; 10) CO; 11) CH_4; 12) CO_2; catalysts: K-2 (a) and K-4 (b).

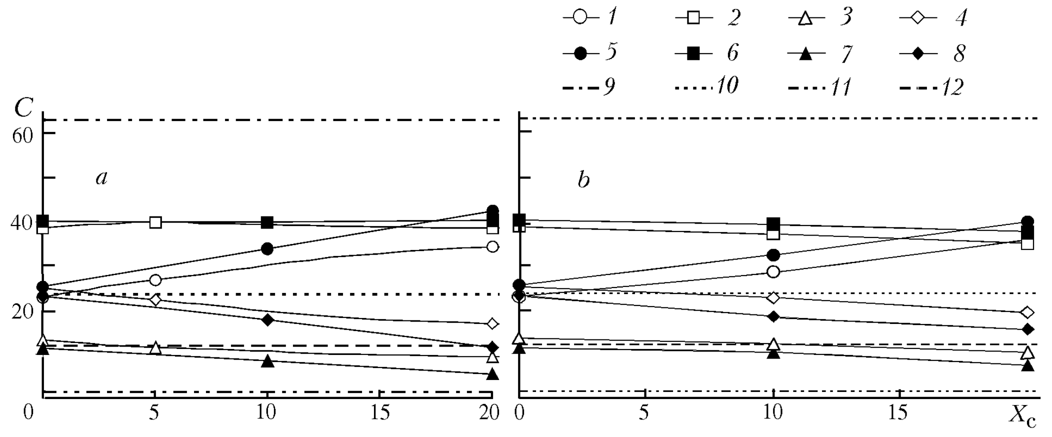

Fig. 5. Influence of wood moisture on the composition of the steam-gasification products at T_b = 700°C. Designations 1–12 same as in Fig. 4.

The experiments have shown that the yield of resins decreases with increasing T_b, and in the case of pseudoliquefaction by steam it is lower than when CO_2 is used. It should be noted, however, that in the case of gasification by an inert BL the type of gasification agent is insignificant.

Upon introduction into the layer of the K-1 catalyst, the yield of resins decreases: insignificantly when gasification occurs in CO_2 and to a greater extent (by 2–6%) in the case of steam, especially at lower temperatures of the layer. At $T_b \geq 700$°C, the ratio C/C_i stabilizes in steam conversion at a level of 10%. In the absence of a catalyst in the layer, the same content of resins is attained at T_b = 750°C. In the case of conversion in CO_2, this level is 0.5% higher. The primary catalyst K-2 ($MgO{\cdot}Cr_2O_4/\gamma\text{-}Al_2O_3$) compared to K-1 displayed a higher activity in CO_2 and steam gasification.

A higher efficiency of catalytic destruction of resin (over 93% at 750°C, Fig. 2) is attained with the use of the secondary catalyst K-5 in the process of CO_2-gasification. However, the lowest yield of resins is observed when the primary catalysts K-3 ($CuO{\cdot}Cr_2O_4/\gamma\text{-}Al_2O_3$) and K-4 (dolomite) are introduced into the layer. From Fig. 2 it is also seen that in gasification of wood with a higher moisture content the yield of resins markedly decreases.

Figure 3 shows the influence of the number of sections of the secondary catalyst K-5 on the composition of dry products of gasification of large wood cylinders in the layer pseudoliquefied by carbon dioxide CO_2 and steam.

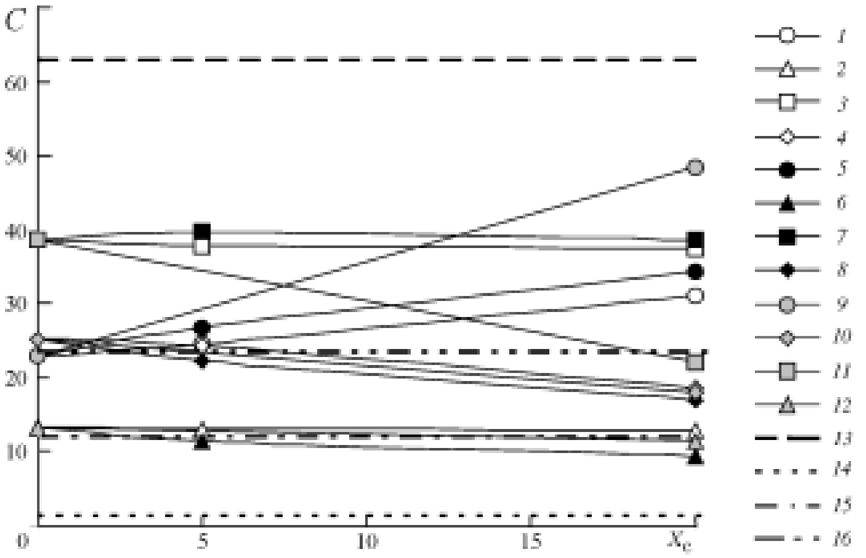

Fig. 6. Influence of the type and concentration of the catalyst on the composition of products of the steam gasification of dry wood cylinders (W = 7%) at T_b = 700°C [catalysts: 1–4) K-1; 5–8) K-2; 9–12) K-3]: 1, 5, 9) H_2; 2) 6, 10) CH_4; 3, 7, 11) CO; 4, 8, 12) CO_2; 13–16) equilibrium ones: 13) H_2; 14) CH_4; 15) CO; 16) CO_2.

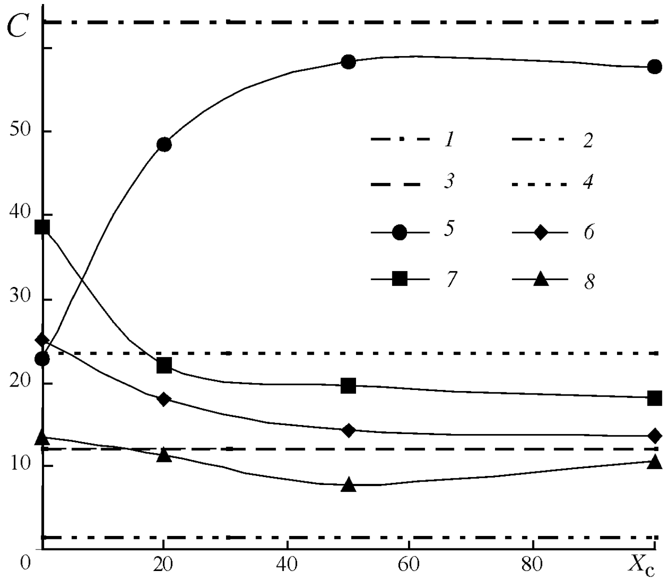

Fig. 7. Influence of the concentration of the catalyst K-3 ($CuO{\cdot}Cr_2O_4/\gamma{\cdot}Al_2O_3$) on the composition of steam-gasification products at T_b = 700°C and W = 7%: 1) H_2 equilibrium; 2) CO_2 equilibrium; 3) CO equilibrium; 4) CH_4 equilibrium; 5) H_2; 6) CO_2; 7) CO; 8) CH_4.

The experimental data for CO_2-gasification with the use of the primary catalysts K-2 ($MgO{\cdot}Cr_2O_4/\gamma\text{-}Al_2O_3$) and K-4 (dolomite) presented in Fig. 4 point to their higher efficiency compared to the traditional Ni-catalysts. The same conclusion follows from the data on conversion of resins (Fig. 2). This agrees indirectly with the results of [4, 5] pointing to the efficiency of modification of nickel catalysts by means of chrome additives. As a raw material, dry (W = 7%) and moist (W = 43%) wood was used. The yield of H_2 and CO is higher and that of CO_2 and CH_4 is lower for moist wood than for dry wood.

Figure 5 presents the experimental data for steam gasification with introduction into the layer of the primary catalysts K-2 ($MgO \cdot Cr_2O_4/\gamma$-Al_2O_3) (a) and K-4 (dolomite) (b) with the use of dry ($W = 7\%$) and moist ($W = 43\%$) wood. From the graph it is seen that the yield of H_2 and CO is higher and that of CO_2 and CH_4 is lower for moist wood than for dry wood (as in the case of CO_2-conversion, Fig. 4).

Figure 6 shows the dependence of the composition obtained by steam gasification of the synthesis gas from wood on the content of the primary catalysts (K-1, K-2, and K-3) in the layer at $T_b = 700^oC$.

The content of hydrogen in using steam and catalyst K-2 is much higher than in using CO_2 (see Fig. 4a). The same trend is characteristic of carbon monoxide and methane (at small concentrations of catalysts). And the content of carbon dioxide thereby is much lower than in using CO_2 as a gasification agent.

From Figs. 6 and 7 it is seen that the highest hydrogen yield (and the lowest CO_2 yield) is provided by using the primary catalyst K-3 ($CuO \cdot Cr_2O_4/\gamma$-Al_2O_3). The content of methane and carbon monoxide is approximately the same as in using catalysts K-1 and K-2.

Thus, gasification of a moist, coarse-dispersion biomass opens up the possibility of increasing the hydrogen yield due to the preliminary stage of internal conversion of the resin and light hydrocarbons.

CONCLUSIONS

1. The experiments performed have revealed the possibility of obtaining a synthesis gas with a relatively high content of hydrogen by means of catalytic steam gasification of the biomass.

2. The efficiency of the process can be upgraded by increasing the catalyst concentration in the layer and the moisture of the wood raw material. Gasification of a moist coarse-dispersion biomass opens up the possibility of increasing the hydrogen yield due to the preliminary stage of internal conversion of the resin and light hydrocarbons.

3. In gasifying the biomass in CO_2, it has been established that the application of the primary copper-chrome catalyst is promising, as evidenced by the closeness of the synthesis-gas composition to the equilibrium one.

NOTATION

A^p, ash content of wood, mass %; C, concentration, %; C^p, content of carbon, mass %; d, particle diameter, mm; G, Gibbs energy for a mixture of components, kJ; $\bar{g}_k$, Gibbs energy of the kth component; kJ/mole; $g_k(T, P)$, Gibbs energy of a pure component determined at a given temperature and pressure, kJ/mole; H^p, hydrogen content, mass %; K, number of chemical components in the system; L, particle length, mm; N_k, number of moles of the kth component in the system; N^p, nitrogen component, mass %; n, number of sections of the secondary catalyst K-5; O^p, oxygen content, mass %; P, pressure, Pa; q, consumption of the raw material, kg/h; $R = 8.314$, universal gas constant, J/(mole·K); T, temperature, °C; V^p, volatile content, mass %; W^p, moisture of wood, mass %; X_c, volume content of the catalyst, %; X_k, molar fraction of the kth component, %; ρ, apparent density, kg/m^3. Subscripts: b, layer; p, pyrolysis; c, catalyst; i, inert.

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