HEAT AND MASS TRANSFER IN DISPERSION MEDIA

HYDROGEN PRODUCTION WITH THE USE OF AN INDIRECT-HEAT-INPUT GASIFICATION SCHEME

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An experimental plant of productivity up to 10 kW for obtaining synthesis gas with a high content of hydrogen has been developed and realized. Experimental studies have been made, and the dependence of the composition of produced synthesis gas on the gasification chamber temperature, the catalyst content, and the moisture content of the raw material has been revealed.

Keywords: gasification, dolomite, experimental plant, synthesis gas.

Introduction. Vegetable, in particular, wood biomass is a valuable hydrocarbon raw material renewable in nature through biosynthesis due to solar energy. It contains a negligibly small quantity of ash (~1%), sulfur (~0.01%), and nitrogen (~0.1%) and serves as a CO_2-neutral energy resource whose rational and effective use under the condition of its equilibrium reproduction opens up the possibility of obtaining regenerated energy (direct or two-stage burning), ennobled high-calorific energy carriers (synthesis gas, hydrogen, semi-coke, granules/pellets, bricks, etc.), promising high-tech (carbon nanomaterials, activated carbons), and building materials (products of ash reclamation). The above directions are based on the thermochemical conversion of biomass, whose end product and efficiency depend on the process conditions [1].

Gasification is an endothermal process requiring heat input for realizing the conversion reactions and making up for the heat loss. The traditional air gasification of a solid fuel with direct heat input by means of partial oxidation of the raw material directly in the gasification reactor leads to a dilution of the synthesis gas with nitrogen. Therefore, we took a scheme with indirect heat input using superheated steam as a fluoridation agent.

To provide a high thermal, economic, and ecological efficiency and reliability of hydrogen production from biomass, it is necessary to use catalysts promoting the destruction (cracking) of resins and the acceleration of conversion processes in temperature regimes optimum as to the conditions for preventing agglomeration of the bed and emission of alkali metals and haloids in aggressive forms.

The aim of the present work is to develop a technology and an experimental plant for obtaining a hydrogen-enriched synthesis gas from biomass on the basis of thermochemical conversion with the use of the fluidization technique.

Use of Belarusian Dolomite as a Catalyst-Adsorber. As the investigations of [2] have shown, the use of Belarusian dolomite as a primary catalyst gives satisfactory results as compared to commercial catalysts. The introduction into the bed of dolomite (20% of the bed volume) leads to a decrease in the content of resins by 60–75% [2]. In the case of using other catalysts at a content of 20%, the yield of resins is much higher. The hydrogen content in the synthesis gas obtained with the use of dolomite is much higher (by 40–55%) than in the case of using an inert fluidized bed. Moreover, the use of dolomite as a catalyst for gasifying a wood biomass permits additional sorption of CO_2 from the obtained synthesis gas, which markedly increases the hydrogen concentration. This explains the noticeable (by 35–40%) decrease in the CO_2 content in the synthesis gas in the results of the described experiments compared to the inert fluidized bed (FB). A more significant decrease can be attained due to continuous removal of adsorption products from the bed and the introduction into it of fresh burnt dolomite.

In the case of continuous introduction of calcium oxide (burnt dolomite) into the reactor of steam conversion (gasification) of the biomass, the following reactions proceed:

a) endothermal net-reaction of steam conversion

$$CH_xO_y + (1-y)\,H_2O = CO + (0.5x + 1 - y)\,H_2 ,$$ (1)
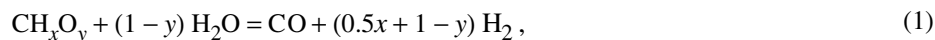
where CH_xO_y is the generalized formula of the mass;

b) exothermal steam-gas substitution (water gas reaction, "shift"-reaction)

$$CO + H_2O = H_2 + CO_2 ,$$ (2)

c) exothermal adsorption of carbon dioxide

$$CO_2 + CaO = CaCO_3 .$$ (3)

Continuous removal of CO_2 from conversion products as a result of absorption (2) shifts the equilibrium of reaction (2) towards an increase in the yield of hydrogen and a decrease in the CO_2 concentration. Likewise, the absorption process affects all concurrent conversion reactions taken into account in Eqs. (1), which leads to an increase in the H_2 concentration and a decrease in the concentrations of CO and CO_2. In the ideal case, the equilibrium gasification process is described by the summary equation of the reaction (the formation of hydrocarbons, coke, and soot, as well of resin due to the absence of equilibrium between the real processes is neglected)

$$CH_xO_y + (2-y)\,H_2O + CaO = CaCO_3 + (0.5x + 2 - y)\,H_2 .$$ (4)
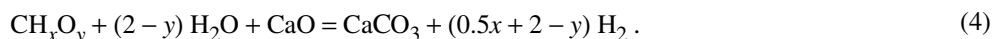
Unlike the reaction of the ideal process, the process of steam gasification of the biomass without CO_2 sorption is described by the equation

$$CH_xO_y + (2-y)\,H_2O = CO_2 + (0.5x + 2 - y)\,H_2 .$$ (5)
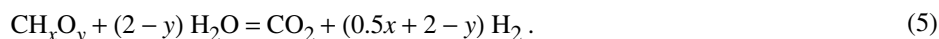
Ideally, the only gas product of process (4) is hydrogen. The solid product of the reaction ($CaCO_3$) should be removed continuously from the reactor and, if possible, regenerated to obtain calcium oxide and CO_2.

To achieve this technological process, we have developed and realized an experimental plant with a paired reactor of the fluidized bed for obtaining from the biomass a synthesis gas enriched with hydrogen by means of steam gasification with indirect heat input. This is realized with the help of organized circulation of a dispersion heat-transfer material between the gasification zones in the fluidized bed and partial oxidation in the circulating fluidized bed. A similar technology of gasification of brown coal and biomass combining two reactors with a fluidized bed was used in [3]. In the first reactor, oxidation carbonization of the fine raw material in the fluidized bed of open-hearth slag is carried out automatically, and in the second reactor gasification of the carbonized fuel by steam takes place.

Flow Diagram of the Experimental Plant. The basic flow diagram of the experimental plant used in our investigations for obtaining a hydrogen-enriched synthesis gas from a biomass is given in Fig. 1.

The basic structural elements are the fluidized bed gasification chamber 1 and the circulating fluidized bed (CFB) oxidation chamber 2 made in the form of columns from high-temperature steel and equipped with surface electric heaters 3, outer heat insulation, and unperforated porous gas distributors located in the lower part of the columns. The gasification chamber is designed for carrying out steam oxygen-free gasification of the biomass in the inert material and dispersion catalyst FB. The chamber diameter is 0.15 m, and its height is 2 m. The temperature in the oxidation chamber is 873–1073 K depending on the kind of raw material and the type of catalyst.

The oxidation chamber is designed for burning in the CFB a part of the raw material and the coke formed in the gasification chamber with the aim of transporting into it the heat needed to carry out the gasification process by circulating the bed material between the chambers as an intermediate heat-transfer material. The chamber diameter is 0.05 m, the height is 2.5 m, and the temperature exceeds the gasification chamber temperature by 50–100 K.

The gasification and oxidation chambers are equipped with screw feeders with a regulated number of rotations for feeding the raw material, the catalyst, and the CO_2 sorbent (dolomite).
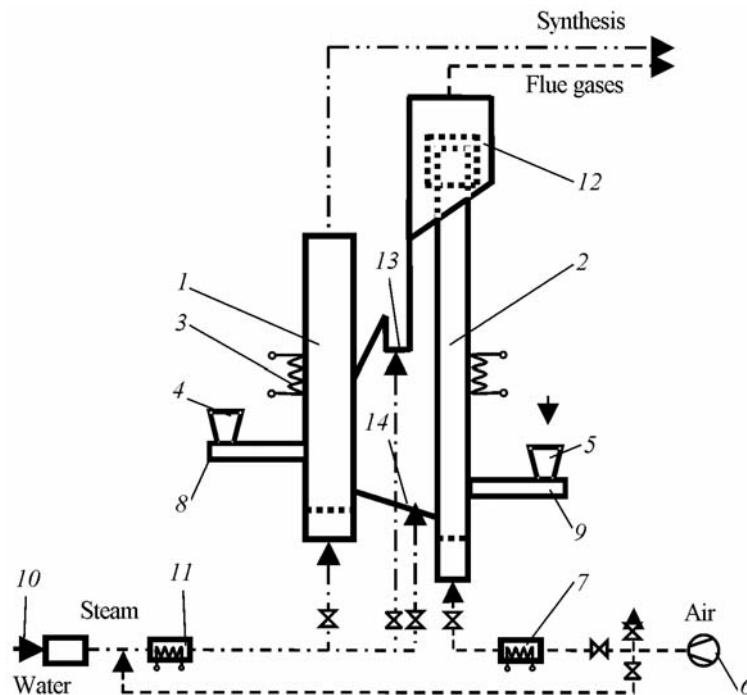
Fig. 1. Flow diagram of the experimental plant of indirect gasification of the biomass: 1) fluidized bed gasification chamber; 2) oxidation chamber of the circulating fluidized bed; 3) surface heaters of the FB and CFB chambers; 4) fuel service bunker; 5) service bunker of the auxiliary fuel and dolomite; 6) compressor; 7) electric air heater; 8) fuel feeder; 9) auxiliary fuel and dolomite feeder; 10) steam generator; 11) steam superheater; 12) cyclone; 13) fluidized bed separator; 14) branch pipe.

In the upper part of the oxidation chamber, an inertial cyclone 8 separating the circulating material of the bed and the oxidation products of the fuel is situated. The cyclone has in its lower part a branch pipe for draining the circulating material into the fluidized bed separator 9 designed for preventing backflow of the gas from the gasification chamber.

In the lower part of the separator, at the level of the fluidized bed height, there is a branch pipe for draining the circulating material into the gasification chamber. In the lower part of the gasification chamber, a steam-aerated branch pipe for recirculating the bed material and coke into the oxidation chamber is located.

The basic elements of the plant are mounted on steel support structures having operating floors. The dimensions of the plant are $2.6 \times 2.2 \times 3.7$ m. The working capacity of the plant has been substantiated by the calculations and experimental investigations carried out as part of the assignment "Vodorod 01" of the State program of applied scientific research "Vodorod."

Before starting the plant, the inert bed material (quartz sand) is poured onto the gas distributors of the gasification and oxidation chambers. The gas-tight bunkers 4 and 5 of the feeders are filled with the raw material (sawdust). The air pumped by the compressor 6 is heated in the electric air heater 7 to a temperature of 573–773 K and passes into the sublattice volumes of both chambers to be fluidized and heated. The surface electric heaters are turned on for external heating of the chamber cases.

The material in the FB and CFB of the gasification and oxidation chambers, respectively, is heated to the temperature of stable inflammation of the biomass (about 623 K). Then the biomass is fed by means of the feeders 8 and 9 into the plant, and when the temperature in the chambers reaches 873–973 K the air draught into the gasification chamber is switched to steam draught. Steam at a pressure of 0.14 MPa is generated by the electric steam generator 10 with a steam superheater 11 where its temperature reaches 573 K.
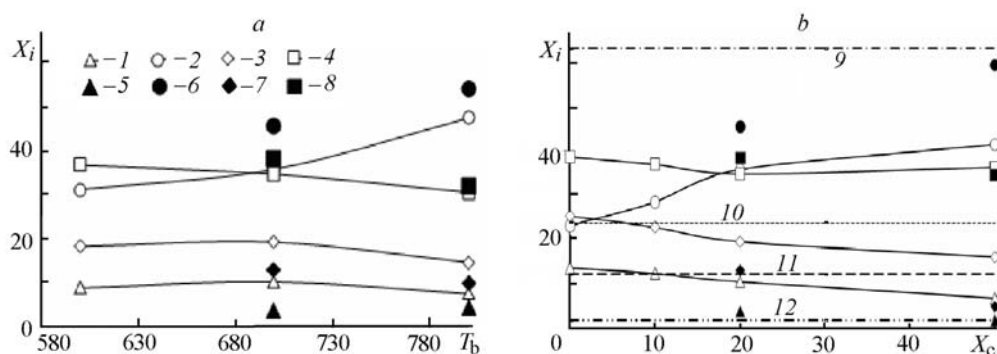
Fig. 2. Composition of the steam gasification products versus the bed temperature (volume content of dolomite 20%) (a) and the catalyst content in the bed (bed temperature 700°C) (b): 1, 5) CH_4; 2, 6) H_2; 3, 7) CO_2; 4, 8) CO; 9) H_{2equil}; 10) CO_{equil}; 11) CO_{2equil}; 12) CH_{4equil}. Bed — sand + dolomite. Solid symbols show the composition of gases obtained on the experimental plant; open symbols show the results obtained on the experimental stand [3]. The raw material is wood with a moisture content of 8%. X_i, X_c, %; T_b, °C.

Steam gasification of the biomass is carried out in the FB at the cost of the heat released due to the burning of a part of the fuel in the CFB of the oxidation chamber and transferred into the gasification chamber by means of continuous circulation of the bed material between the gasification and oxidation chambers.

The hot material of the CFB, whose temperature is 50–100 K higher than in the gasification chamber, is carried out of the upper part of the CFB chamber by the flow of combustion products, is separated from the gases in the inertial cyclone 12, and, through the separator 13 of the fluidized bed, is fed into the FB chamber. Recirculation of the cooled material of the bed (sand, dolomite) with a temperature of no more than 1073 K together with the coke contained in it is realized by the gravity flow from the lower part through the aerated branch pipe 14 set at an angle smaller than the angle of natural slip of the material.

The bed temperature in the gasification and oxidation chambers equipped with a "Sosna" device and chromel-alumel thermocouples is regulated by varying the capacity of the fuel feeders and the steam supply with the aim of influencing the flow rate of the circulating material.

At the exit from the chamber the synthesis gas is sampled for chromatographic analysis. The synthesis gas and the combustion products are subjected to cleaning in the cyclone 12 and discharged into the furnace of the plant of combustible waste heat recovery.

Experimental Investigation of the Wood Biomass Gasification. We carried out adjustment tests of the basic units, made corrections of the design documentation, and additionally rigged the experimental plant with control and automatic equipment for obtaining a hydrogen-enriched synthesis gas from the biomass with the use of the fluidization technique. It has been shown that the operating parameters of the basic units of the plant are in agreement with the calculated values.

We developed the basic regime and design parameters of the process of internal circulation of the intermediate heat-transfer material (bed material). Ground Belarusian dolomite mixed with sand served as the bed materials. The dolomite content in the mixture was 20 and 50%. The size of dolomite particles was 1–2 mm, and that of sand particles was 0.25 mm.

The duration of the experiment was 30 min.

We investigated the influence of the content of the primary catalyst (Belarusian dolomite) mixed with sand, of the gasification chamber temperature, and of the raw material moisture-content on the composition of the synthesis gas obtained from the wood biomass. The experimental results are given in Figs. 2–4. The new compositions of the gases were compared with those obtained by us earlier on the laboratory stand [4], and the results of experiments performed on it are presented in [2].

It is seen that in using high-temperature sorption of CO_2 in the gasification zone the hydrogen yield is much higher (by 15–35%) than in the experiments performed in [2]. The CO_2 content therewith markedly decreases
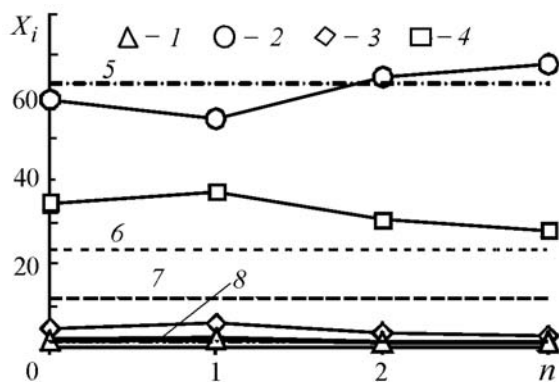
Fig. 3. Composition of the steam gasification products versus the number of secondary catalyst beds: 1) CH_4; 2) H_2; 3) CO_2; 4) CO; 5) H_{2equil}; 6) CO_{equil}; 7) CO_{2equil}; 8) CH_{4equil}. The dolomite content in the bed is 20%. X_i, %.
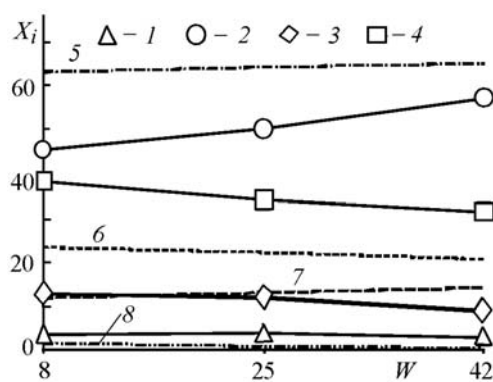
Fig. 4. Composition of the steam gasification products versus the moisture Content of the wood raw material. Designations 1–8 are same as in Fig. 3. The dolomite content in the bed is 20%. X_i, W, %.

(by 35–50%) due to its sorption in the gasification chamber. The methane yield also decreases due to the larger residence time of the synthesis gas in the reactor. The CO content changes insignificantly (within the measurement error of the composition of the gases — by 10%).

It should be noted that in all experiments the synthesis gas contained nitrogen. Its content constituted from 8 to 15%. This is explained by the fact that the air from the oxidation chamber was added to the obtained synthesis gas.

In the next run of experiments, we placed at the exit from the gasification chamber a fixed porous bed from the secondary nickel catalyst. As a result, the synthesis gas obtained in the catalytic circulating bed reacted additionally with the secondary catalyst. In the experiment, we used, as a circulating bed, a mixture of sand and dolomite in a 1:1 ratio. The temperature in the bed was 1073 K. The number of fixed beds of the secondary catalyst was varied from one to three.

The results of the experiments performed with the use of the primary catalyst (dolomite) and the secondary catalyst are given in Fig. 3.

From the graph it is seen that the introduction of the secondary catalyst has a weak effect on the synthesis gas composition.. As the number of catalyst beds increases from zero to three, the hydrogen yield increases by 14%. The yield of the other components of the synthesis gas decreases: the yield of CO decreases by 18.8%, of CO_2 by 39%, and CH_4 by 12.5%. The composition of the synthesis gas obtained with the use of 50% of dolomite and three beds of the secondary nickel catalyst is as follows: H_2 — 67.9%, CO — 27.9%, CO_2 — 2.8%, and CH_4 — 1.4%.

The results of the investigations presented in Figs. 2 and 3 make it possible to draw the following conclusion: The use of dolomite as a primary catalyst increases considerably the hydrogen yield due to the high-temperature sorption of CO_2 with wood gasification in a fluidized bed and exclusion from the obtained synthesis gas of a portion of carbon dioxide. It should also be noted that the use of the secondary catalyst in addition to dolomite is inexpedient since it has a weak effect on the composition of the obtained synthesis gas.

We have investigated the influence of the moisture content of the wood biomass on the composition of obtained gases. For the raw material, we used sawdust with a moisture content of 8.25 and 45%. The temperature in the oxidation chamber was 700°C. We used a mixture of sand and dolomite as a bed material. The content of dolomite was 20%. The results of the experiments are given in Fig. 4.

From Fig. 4 it is seen that as the moisture content of the wood increases from 8 to 45%, the hydrogen yield increased by 18% and the CO yield decreases by 10%. This is explained by the internal conversion of the biomass due tot the fact that the superheated steam coming out a wood particle is mixed with pyrolysis products in the peripheral zone of the high-temperature coke exhibiting catalytic properties. An increase in the moisture content of the biomass weakly influences the CO_2 and CH_4 content.

The foregoing makes it possible to draw the conclusion that the scheme of indirect gasification of the biomass with the use of dolomite permits obtaining producer gas with a high content of hydrogen (~50%), low concentrations of nitrogen (<5%) and resin (<1 g/nm^3), and a medium caloric power (10–15 MJ/nm^3). The obtained gas can serve as a source of pure hydrogen for fuel elements and a raw material for obtaining liquid fuel, or it can be used as a fuel for power plants.

NOTATION

n, number of secondary catalyst beds; T, temperature, $^{\circ}$C; X, volume content of catalyst, %; W, moisture content, %. Subscripts: b, fluidized bed; c, catalyst; i, gas component; equil, equilibrium.

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