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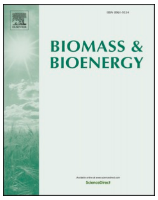

Production of hydrogen by supercritical water reforming of O-containing organic components of plant raw materials

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ABSTRACT

Supercritical water reforming (500–700 °C, 30 MPa) of different alcohols, including ethanol, glycerol and sorbitol as the components of plant raw materials revealed the common features and peculiarities depending on the nature of the substrate. It was found that glycerol and sorbitol demonstrate higher degrees of gasification under equal conditions compared to ethanol. In the case of ethanol, the methanation reaction occurs to a more significant extent than in the case of glycerol and sorbitol. The highest concentration of hydrogen in the gas products (up to 45%) was found for ethanol reforming due to the high H/C ratio in this substrate.

1. Introduction

Hydrogen generation from renewable raw materials is the main trend of the world's innovative alternative energy technologies [1–8]. In comparison with traditional pyrolysis technologies, for processing of non-renewable carbon-containing raw materials, the conversion of biomass components and products of its transformation in supercritical water (SCW) can be considered as an efficient and environmentally friendly process. Hereinafter we will use the terms "reforming" and "gasification" as equivalent terms in the manuscript.

Bioethanol is used as a solvent, a precursor for the production of monomers, an alternative to gasoline fuel. A number of works [1–7] are also devoted to the steam reforming of ethanol into a hydrogen-enriched gas mixture. The reaction of ethanol with water was studied at temperatures of 500–750 °C both without oxidants and catalysts [1–3] and in the presence of heterogeneous catalysts: Mn-doped catalyst CeO_2-MnO_x-SiO_2 [4], mixed oxide systems La–Sr–Mn–Ni–O [5], nanocrystalline catalyst CeO_2 modified with Co. In addition to gaseous products: H_2, CO_2, CO, CH_4, the formation of catalyst-deactivating products, such as ethylene, acetaldehyde, and acetone was observed.

Due to the increasing global production of biodiesel in recent years, there is an excess of glycerol, since it is a by-product of transesterification of triglycerides of fatty acids with methanol. When producing biodiesel, up to 10 wt % of glycerol is formed. Along with the developed technologies for converting glycerol into valuable chemicals, i.e. 1,3-propanediol, acrolein and hydroxyacetone, the production of hydrogen from glycerol is also an important task. Conversion of glycerol in SCW [8] was performed at 500 °C with the formation of acetaldehyde, acrolein and, in the gas phase, H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 as products. It was found [9] that only a dilute solution of glycerol can be completely converted into a gas without a catalyst. In the presence of catalysts such as alkali, metal oxides, the gasification of glycerol is accelerated with a decrease in the yield of tars. Glycerol gasification in SCW was performed in a tubular flow reactor at temperatures of 380–500 °C and a pressure of 25 MPa using Na_2CO_3 as a catalyst [10]. As the temperature increased, the yield of the main gaseous products increased: H_2, CO, and CH_4. Researchers have confirmed that formaldehyde is an intermediate product in the decomposition of glycol and formaldehyde. Catalytic gasification of a 10–25% glycerol solution in SCW was performed at a temperature of 510–550 °C and a pressure of 35 MPa on inert nonporous particles ZrO_2 and Ru/ZrO_2 [11], the main products were acetaldehyde, hydroxyacetone with small amounts of

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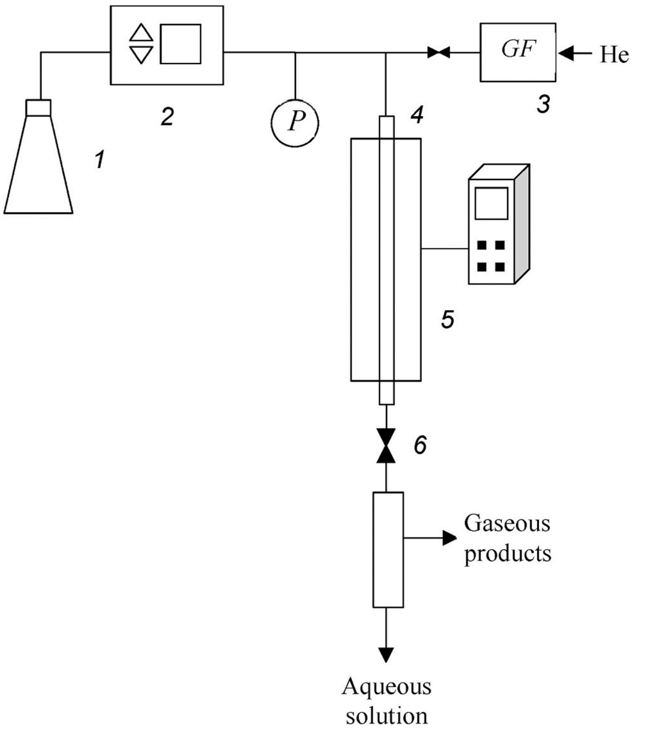

Fig. 1. The scheme of the laboratory setup: (1) aqueous solution of a substrate, (2) high-pressure liquid pump, (3) gas flow controller, (4) reactor, (5) tubular electric furnace with a thermoregulator, (6) valve, (*P*) pressure gauge.

propionaldehyde and acrolein. The gaseous products consisted of hydrogen, carbon oxides, and methane. At 510 °C the conversion of glycerol was complete only at the contact time of 5–8.5 s and at 550 °C and in the presence of a catalyst. It was shown [12] that at temperatures of 445–600 °C, a pressure of 25 MPa and a contact time of 3.9–9.0 s, the degree of gasification and the yield of H_2 and CO_2 significantly decreased with an increase in the concentration of glycerol in the solution from 10 to 25%. These parameters are stabilized at a low conversion level when the concentration of glycerol increased from 25 to 50%. Also a significant increase in the yield of H_2, CO_2 and a decrease in the yield of CO was revealed during the gasification of glycerol on alkaline catalysts (K_2CO_3, KOH, NaOH, Na_2CO_3).

The conversion of the carbohydrate components of renewable raw materials is also of considerable scientific and practical interest. The conversion of glucose, fructose, sorbitol, and cellulose in sub- and supercritical water was studied without and in the presence of heterogeneous catalysts at 225–700 °C [13–23]. The steam reforming of glucose, sorbitol, glycerol, methanol, and ethylene was studied at temperatures of 225 °C on a Pt/Al_2O_3 catalyst [13]. Gasification of aqueous glucose solutions was performed in the presence of catalysts. When studying the conversion of glucose, sorbitol, cellulose [14–17], it was shown that the yield of hydrogen-containing gas was high when ZrO_2, Ni-Mg-Al-O_x [14], as well as Pt-, Ru supported on carbon [15,16] catalysts were used. Na_2CO_3 reduces the decomposition temperature of cellulose and slows down the formation of tars. Glucose and fructose at temperatures above 550 °C are converted by more than 97% to acetylacetone, propionic acid, and acetaldehyde, as well as to gaseous H_2 and CO_2 [17]. Water-soluble components are further gasified into hydrogen, CO, CO_2, and CH_4. It was found that K-containing catalysts prevent the formation of furfurols during glucose gasification in SCW [18,19]. The conversion of fructose as a model compound of biomass was studied [20,21]. The largest amount of hydrogen was obtained by gasification of a 4% aqueous solution of fructose at 700 °C.

Thus, the overwhelming majority of experiments in the available publications on the conversion of ethanol, glycerol and carbohydrates in supercritical water were carried out at temperatures up to 600°C, when oxygenates were the main reaction products. The deep gasification of aqueous solutions of O-containing organic substrates with the formation of CO_2 and H_2 was achieved in the presence of solid basic catalysts and oxidizing agents as additives. The objective of the present study was the search for the optimal conditions of the complete conversion of O-containing components derived from natural renewable raw materials – ethanol, glycerol and sorbitol - in supercritical water with the formation of hydrogen-rich gaseous products without using catalysts and additionally introduced oxidants.

2. Materials and methods

To study the conversion of glucose, a platinum deposited catalyst on the carbon carrier Sibunite (hereinafter Pt/C) with a metal content of 3 wt % was used. The catalyst was prepared by impregnating the carrier with an aqueous solution of H_2PtCl_6. The size of the catalyst granules was 1–2 mm, the bulk density was 0.75 g/cm^3. Before the experiment, the catalyst was activated in a hydrogen flow at 320 °C for 2 h.

The experiments were performed in a flow-type reactor (internal diameter 0.9 cm, length 12 cm) with a fixed catalyst bed (Fig. 1). The temperature was controlled by a thermocouple located in the catalyst layer. The volume of the loaded catalyst was 5 cm^3, the remaining free volume of the reactor was filled with quartz (with a particle size of 1–2 mm).

Glucose conversion was studied at a temperature of 140–240 °C and a pressure of 5 MPa. The concentration of glucose in the initial aqueous solution was 30 g/L (3 wt %). Experiments were performed in the presence of an inert gas - helium. The pressure in the system was created by supplying the reagent solution with a high-pressure liquid pump and regulated by a diaphragm valve. The gas was supplied by a Bronkhorst gas flow controller, with a feed rate of 1.8 L/h. Heating to reach the reaction temperature was carried out when distilled water was supplied (1 ml/min) at a given pressure in the gas flow. After reaching the required temperature, distilled water was replaced with an aqueous glucose solution (1 ml/min). Aliquots were selected for analysis after 1 h.

Glucose conversion products were analyzed by high-performance liquid chromatography (HPLC) on a Waters 600 chromatograph with a refractometric detector and a Rezex RCM-Monosaccharide Ca^{2+} column (mobile phase - water, flow rate - 0.6 ml/min, column temperature 65 °C). The gaseous products were analyzed using a Crystal 5000.2 chromatograph with Porapak Q and CaA packed columns. Additionally, reaction products containing hydroxyl and carbonyl groups dissolved in an aqueous solution were identified using a Focus GC/DSQII chromato-mass-spectrometer (“Thermo Fisher Scientific”, USA) with a Thermo TR-5MS column.

The experimental error in determining the conversion and contents of products in the mixture was below 5 rel. %.

The glucose conversion (1) and product selectivity (2) were calculated using the following formulas:

$$C = (c_o - c)/c_o \times 100, \quad (1)$$

$$S_i = 100 * c_i/(c_o - c) \times 100, \quad (2)$$

where c_0 and c are the initial concentration and the current concentration of glucose in the products, c_i is the concentration of the i-th product (molar concentrations are used). The conversion of glucose is accompanied by the formation of gaseous products, mainly H_2 and CO_2. In this case, the degree of gasification for steam reforming of glucose was evaluated by the amount of CO_2 formed using the formula

$$G = n_{CO2}/6*n_{gl} \times 100, \quad (3)$$

where n_{CO2} is the number of moles of CO_2 formed in 1 h, n_{gl} is the number of moles of glucose supplied in 1 h.

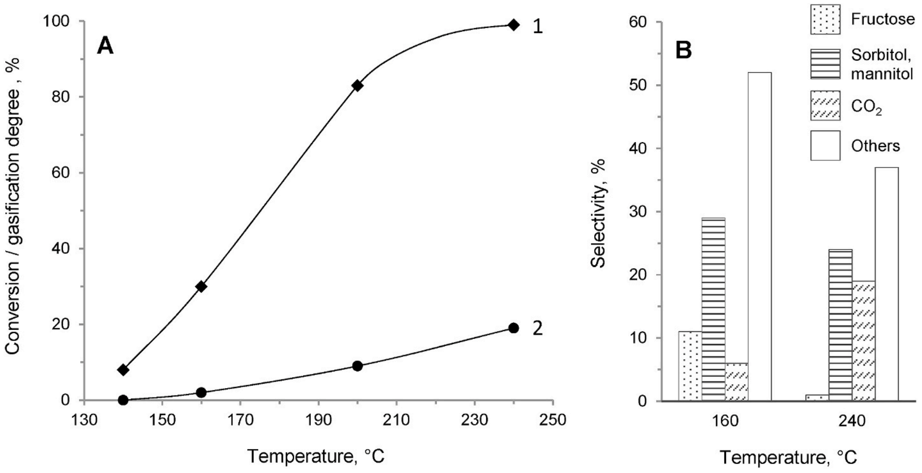

Fig. 2. (A) Glucose conversion (1) and gasification degree (2) in an aqueous solution on a Pt/C catalyst at 140–240 °C and 5 MPa. (B) Selectivity of glucose conversion to the products: fructose, sorbitol/mannitol, carbon dioxide and others (Fig. 3).

Transformations of aqueous solutions (2 wt %) of ethanol, glycerol, and sorbitol were studied in a flow-type reactor, which was a U-shaped tube (316 stainless steel) with an internal diameter of 4.4 mm and a volume of 8.8 cm^3. The aqueous solution of the reagent was supplied by a Gilson high-pressure liquid pump and regulated by a fine adjustment valve (HiP, USA). The flow of the reagent solution was directed into the reactor from bottom up. The reactor was heated in an electric oven using a temperature controller (Thermodat, Russia).

The experiments were performed at temperatures of 500–700 °C and a pressure of 30 MPa. Heating to the reaction temperature was carried out with a supply of distilled water at a pressure of 30 MPa. After reaching the set temperature, the water was replaced with a solution of the reagent. The volume flow rate of the solution V_L, i.e. the ratio of the reagent flow rate (ml/h) to the volume of the heated part of the reactor (ml), was 2.0 h^{-1}. The duration of the experiment was 3 h. The collection of products was started 1.5 h after the start of the supply of an aqueous solution of the reagent. The gaseous products were collected in a gas burette.

Analysis of ethanol, glycerol, and sorbitol gasification products in supercritical water included determination of the concentration of substrates in the water phase by HPLC and gas phase analysis by gas chromatography.

The concentration of ethanol, glycerol, and sorbitol was determined by HPLC using a Waters 600 chromatograph with a refractometric detector and a Rezex RCM-Monosaccharide Ca^{2+} column (mobile phase - water, flow rate - 0.6 ml/min, column temperature 65 °C). Gaseous products from the gas burette were analyzed using a PYE Unicam PU 4550 chromatograph equipped with Porapak Q and CaA (1.5 m × 3 mm) packed columns and a thermal conductivity detector.

The substrate conversion was calculated using the formula:

$$C = \frac{c_o - c}{c_o} \times 100\%, \tag{4}$$

where c_o is the initial concentration of the substrate, mmol/ml; c is the concentration of the substrate in the liquid analyte sample, mmol/ml.

The degree of gasification of the substrates was calculated by the formula:

$$G = \frac{V\sum(c_j n_j)}{V_1(c_0 - c)n_0 \nu t} \times 100\% \tag{5}$$

where c_0 and c are the initial and final concentrations of the substrate, c_j is the concentrations of carbon-containing gases (CO, CO_2, CH_4, C_2H_6, C_2H_4, vol. %), n is the number of carbon atoms in the molecule of the initial compound or product, V and V_1 are the volumes of collected gas and 1 mol of gas, ν, t are the flow rate and duration of the substrate solution supply.

3. Results and discussion

In order to find approaches to generation of hydrogen-rich gas mixtures from components of bioresources, we studied the transformations of ethanol, glycerol, glucose and sorbitol with supercritical water. It was found that ethanol, glycerol, glucose and sorbitol were not converted into hydrogen to any significant extent without catalysts and oxidants at temperatures below 500°C. Also, plugging of the gas pipelines with heavy caramel-like species was observed under supercritical conditions of the transformation of an aqueous solution of glucose at temperatures over 250 °C. Caramelization process of glucose occurs at T > 300°C and involves the degradation of sugar (like glucose, sucrose, etc.) molecules and the polymerization of intermediate reactants [24]. Caramelization product is a mixture of macromolecular colloids, and it consists of oligomers with less than 6 carbohydrate units in the form of dehydration, hydration, and disproportionation materials and aromatic compounds.

It was found that only glucose reacts with water in subcritical conditions at temperatures up to 350°C with a maximum degree of gasification of 20% at 250°C and only in the presence of a catalyst.

The conversion of an aqueous glucose solution on a Pt/C catalyst is characterized by the formation of the products shown in Fig. 2. At 140 °C, the glucose conversion is low (8%) and the main product is fructose. It is also necessary to note the formation of sorbitol, which indicates the occurrence of the glucose hydrogenation reaction. This reaction is possible only if the conversion of glucose produces some amount of hydrogen. Thus, glucose reforming with the formation of hydrogen and CO_2 occurs already at a temperature of 140 °C. This temperature is lower than that found by Dumesic et al. [13] who observed steam reforming of sugars and alcohols at temperatures near 230 °C in a single-reactor aqueous-phase reforming process using a platinum-based catalyst. Reforming of glucose and fructose on a Pt/Al_2O_3 catalyst was also realized at 2.7 MPa in an autoclave at temperatures of 185–220°C, with the rate of hydrogen release at 185°C being about 0.1 ml/min [22]. Aqueous phase reforming of ethanol, glycerol and sorbitol was studied over Pt/Al_2O_3 at 225 °C [23,25,26]. The catalyst demonstrated stable performance and high selectivity towards a variety of organic products and hydrogen. In our study, when the temperature rises to 200 °C, the conversion of the substrate increases to 83%. Along with fructose, mannitol, and sorbitol, which were quantified using liquid chromatography, alcohols and ketones were detected in an aqueous solution by the GC-MS method. The main gaseous

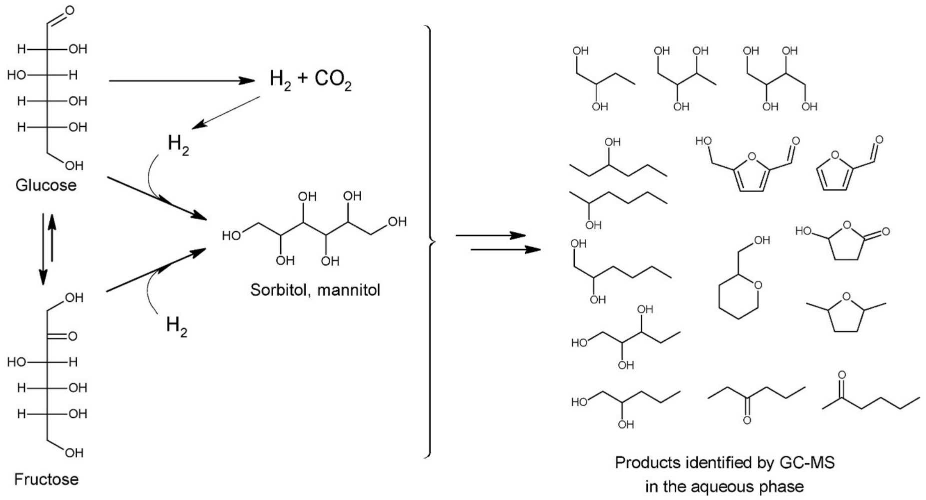

Fig. 3. Scheme of glucose conversion in the aqueous phase on a Pt/C catalyst.

products are hydrogen and carbon dioxide. C_2–C_4 hydrocarbons were also found in trace amounts. The general equation of glucose reforming in the water phase can be presented as follows:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6\ CO_2 + 12H_2. \tag{6}$$

Hydrogen reacts by hydrogenating glucose into sorbitol, and mannitol is obtained by hydrogenation of fructose. A decrease in the yield of sorbitol is possible due to its steam reforming by analogy with glucose. In the process of glucose hydrogenation, a large number of by-products present in the aqueous solution are also formed. The resulting compounds undergo further transformation by dehydration and hydrogenation reactions, which leads to a wide range of products. These compounds have different functional groups and include alcohols, diols, polyols, ketones, tetrahydrofuran derivatives, and other products (Fig. 3). Often, the formation of products with a number of carbon atoms 2–4 is associated with the retro-aldol condensation of glucose with the subsequent transformation of the resulting aldehydes. However, direct hydrogenolysis of the C–C bond in the general process of glucose transformation in the presence of hydrogen cannot be excluded. Reduction of the length of the carbon chain is associated by some researchers with reactions of decarbonylation of aldehydes and decarboxylation of acids. Next, successive dehydration and hydrogenation reactions occur, which are responsible for the formation of alcohols and ketones from polyols.

Fig. 3 shows possible transformations of glucose. Isomerisation of glucose into fructose occurs first in an aqueous solution. The key stage of the proposed scheme is steam reforming of glucose with the formation of hydrogen and carbon dioxide.

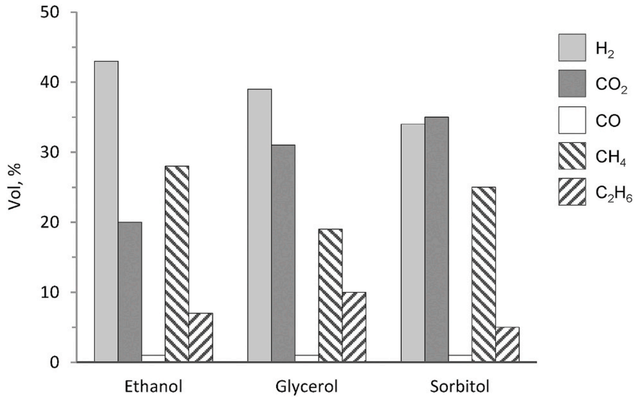

Fig. 4. Distribution of gaseous products of ethanol, glycerol, and sorbitol gasification in supercritical water at 700 °C and 30 MPa.

As follows from the data in Fig. 2, less than 1% of glucose undergoes steam reforming at 140 °C. Increasing the temperature to 200 °C significantly intensifies the gasification of glucose. At a temperature of 240 °C, almost complete glucose conversion is achieved, with a selectivity to gas products of 19%. At higher temperatures, caramelization of glucose occurs, which deactivates the catalyst.

Therefore, it was decided to perform gasification of ethanol, glycerol, and the hydrogenated glucose. i.e. sorbitol in supercritical water without using a catalyst. All the alcohols are subject to significant gasification to a mixture H_2/CO_2 in supercritical water in the absence of any catalyst at temperatures over 600°C. Gasification of organic compounds in supercritical water with the formation of hydrogen and carbon oxides occurs as a result of interaction with water that exhibits strong oxidizing properties in the supercritical state.

According to the reaction of steam reforming 7, the main products of

Table 1
Gasification of ethanol, glycerol, and sorbitol in supercritical water (500–700 °C, 30 MPa).

Substrate	T, °C	Conver-sion, %	Gasification degree, %	Distribution of gas products, vol. %					
				H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6
Ethanol	500	37	0	–	–	–	–	–	–
	600	69	47	45	21	8	16	1	9
	700	100	100	44	28	1	20	0	7
Glycerol	500	60	12	35	7	11	43	1	3
	600	99	61	40	10	17	25	1	7
	700	100	95	39	19	1	31	0	10
Sorbitol	500	97	0	–	–	–	–	–	–
	600	100	73	32	14	18	29	1	6
	700	100	100	34	25	1	35	0	5

the interaction of O-containing organic substrates with supercritical water are hydrogen and carbon dioxide. In addition, methane and C_2 hydrocarbons produced by hydrogenolysis of the substrate, as well as CO formed by the reverse water gas shift reaction are also present:

$$C_xH_yO_x + xH_2O = xCO_2 + (x+1/2y)H_2, \tag{7}$$

$$CO + H_2O = CO_2 + H_2. \tag{8}$$

The results of analysis of gasification products of aqueous solutions of the studied substrates in supercritical water are shown in Table 1 and Fig. 4.

Thus, the studies of the steam reforming of different alcohols, including ethanol, glycerol and sorbitol in supercritical water revealed the common features and peculiarities depending on the nature of the substrate. Glycerol and sorbitol demonstrate higher degrees of gasification under equal conditions compared to ethanol. With polyols, water gas shift reaction is also more clearly pronounced than in ethanol reforming. On the other hand, in the case of ethanol, the methanation reaction occurs to a more significant extent than in the case of glycerol and sorbitol. Also, the highest concentration of hydrogen in the gas products is found in the case of ethanol reforming (up to 45%).

4. Conclusions

Thus, the data obtained provide evidence for the feasibility of conversion of polyols derived from renewable raw materials into hydrogen, which is a valuable energy carrier. The highest concentration of hydrogen in the gas products up to 45 vol % is revealed in ethanol reforming. The interaction of supercritical water with alcohols, including ethanol, glycerol and sorbitol proceeds through the steam reforming and water gas shift reaction.

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