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CONVERSION OF ETHANOL INTO WATER SUPERCRITICAL CONVECTION LOOP UNDER ELECTRON IRRADIATION

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To conduct experiments to study the effect of supercritical water on structural materials, a convection loop with a welded irradiation chamber was used. The loop was installed at the output of the electron accelerator. Water decomposes under supercritical conditions and gives a certain amount of hydrogen and oxygen atoms, which exist simultaneously, as well as radicals and hydrogen peroxide. Moreover, water is both a reagent and a medium, in supercritical conditions it acts as an organic solvent. The effect of irradiation enhances the effect of the formation of active particles. In the process of irradiation and ethanol entering the loop, it turned out that in water under supercritical conditions, processes of both the destruction of ethanol and the synthesis of various substances based on it can occur.

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INTRODUCTION

It is appeared many works used the properties of supercritical water (SCW) for obtaining hydrogen from sewage sludge, household waste, straw, etc. SCW is both a medium for chemical reactions and a reagent. Radicals, oxygen and hydrogen in an active state are formed from water in the supercritical state. In the first studies, active additives were used, For example, hydrogen peroxide to enhance the destructive ability of the medium, but even without additives, the oxidizing ability of SCW is quite high. In addition to SCW, subcritical water can also be used for the destruction and synthesis of substances. Some of their characteristics are given in Table [1].

Physicochemical properties of water in different states

Indicators	Liquid, 25°C 0.1 MPa	Subcritical, 250°C, 5 MPa	SCW, 400°C, 25 MPa	Superheated steam, 400°C, 0.1 MPa
Density, kg/m^3	997	800	170	0.3
Dielectric constant	78,5	27.1	5.9	1
Viscosity, µP·s	890	110	30	20

The ionic product of water has a value of 10^{-14} at room temperature regardless of pressure, but at a pressure of 25 MPa and with increasing temperature it increases to about 10^{-12}. At the critical temperature it drops sharply to a value of 10^{-20}, with further increase in temperature it decreases to a minimum value of 10^{-24}, i.e. in supercritical conditions water becomes similar to an organic solvent [1].

Recently, more attention has been focused on obtaining combustible gases from organic waste using SCW. In the article [2], the behaviour of organic substances in water of the subcritical and supercritical states is considered in detail. It was found that more coke, as well as a very wide range of organic substances are formed in the subcritical state. More gases are formed in SCW, that is, simpler substances are synthesized under harsh conditions.

CONVERSION OF SUBSTANCES IN SUPERCRITICAL AND SUBCRITICAL WATER

In water at high temperature, a large number of other organic substances with a small molecular weight (acids, aldehydes, etc.) and some tar are formed from complex organic substances. 5-hydroxymethylfurfural-2 (furfural) was chosen as a model substance for treatment in superheated water, which was done quite arbitrarily, the final model substance was 1,2,4-benzenetriol (trihydroxybenzene or hydroxyhydroquinone) and sometimes 1,4-benzenediol (hydroquinone) [2]. It seems that the choice of model substances is simply related to their availability, which simplifies further studies. In SCW, the amount of formed tar was insignificant, almost all model substances were converted into gaseous substances. Sometimes it is believed that to study the action of SCW, it is necessary to introduce some individual substances whose structure determines the final products, but in fact SCW is such a powerful tool for the formation of substances that the difference in the structure of the input organic substances does not make a significant difference. As a result of the processing of organic substances, including various wastes, hydrogen, hydrocarbons with a low molecular weight and solid particles containing benzene and furan rings are obtained. It often leads to clogging of the reactor. Solid particles were formed mainly in subcritical water, and the formed carbon particles were almost not subject to gasification in SCW. If necessary, the reactor is washed with a mixture of methanol and acetone. Apparently, if it is necessary to synthesize substances in SCW, some balance must be found between the subcritical and critical states. SCW can also be used for the synthesis of mineral substances, what takes millions of years in nature (synthesis of minerals) can be obtained in SCW in a few seconds [1]. When water enters the supercritical state, the dielectric permittivity drops rapidly and at the same time the dissolved metal salt precipitates, most often in the form of hydroxide, which immediately turns into oxide. Since the deposition process is very fast (0.1 s), the particles do not have time to agglomerate. Most of the resulting particles have a size of 5 nm. Some hydroxides do not dehydrate (Al, La) and do not give oxides in SCW [3]. The density of SCW with increasing pressure from 27 to 50 MPa also increases by about 1.5 times [4] and the specific heat capacity drops by about 6 times at 50 MPa than at 27 MPa, and its peak falls at a temperature of about 470°C at 50 MPa. Thus, with increasing pressure, the heat capacity drops significantly. The fact that under supercritical conditions water becomes a non-polar solvent makes it possible to obtain hybrid metal-organic particles that can find application in medicine.

PROCESSING OF ORGANIC WASTES TO OBTAIN GAS FUEL

It is promising to use SCW for processing (utilization) of wet biomass. In this case it is get rid of hazardous waste and obtain hydrogen and other combustible gases [5]. Heteroatoms present in organic compounds (such as chlorine, sulfur, nitrogen, and phosphorus) form anions of their corresponding acids and ammonium ions, whose salts precipitate. Schematically, the transformation of substances can be presented as follows: biomass + $H_2O \rightarrow H_2 + CO + CO_2 + CH_4$ + HCOOH + other small molecules. In the process of destruction, a certain amount of coke may be formed, which is not desirable, hydrolysis and hydrogenation reactions may also occur. In the article [6] is stated that the SCW is suitable for the destruction of dyes, but sometimes it is not convenient to use it because when water passes into a supercritical state, inorganic substances precipitate and clog the equipment. The disposal of food waste in the SCW is considered in the work [7]. Some basic regularities of the destruction of organic substances and the formation of hydrogen have been established and confirmed. An increase in the temperature of the water contributes to a more complete destruction of waste. To obtain energy, the gases from the SCW reactor were partially oxidized with liquid oxygen. A plant for processing 10 tons per hour of manure with a 50% concentration has been proposed. When processing municipal solid waste in the SCW with the aim of obtaining hydrogen, potash and silicon dioxide were used as catalysts [8], although nickel-based catalysts were previously known. Increasing the temperature from 450 to 650°C gives a hydrogen yield of 63.7 mol/kg and reduces the amount of carbon in the residue by 1.5 times.

EXPERIMENTAL DATA ON THE CONVERSION OF ETHANOL INTO SCW

To conduct experiments to study the effect of SCW on structural materials, a convection loop (CL) with a welded irradiation chamber was used, the design is described in more detail in an early publications [9,10]. The loop was installed at the output of the LPE-10 electron accelerator with an average beam energy of 10 MeV and a current of 0.71 mA. Water decomposes under supercritical conditions and gives a certain amount of hydrogen and oxygen atoms, which exist simultaneously, as well as radicals and hydrogen peroxide [11]. The action of irradiation enhances the effect of the formation of active particles. During the irradiation process, it was revealed that processes of synthesis of various substances can take place in the SCW. Moreover, SCW is both a reagent and a medium, and in supercritical conditions acts as an organic solvent. When ethanol was fed into the loop with SCW, tar formation and an unpleasant odour of water were observed. Further analysis of the water, along with ethanol, revealed the presence of acetone, hexane, methyl ethyl ketone, methyl isopropyl ketone, and propyl cellosolve. It is not exclusive that the unpleasant odor was formed due to the synthesis of unidentified sulfur-containing organic substances. Sulfur passed into the water during corrosion of the structural stainless steel of the CL, where its content was 0.033% by weight.

CONCLUSIONS

The effect of ethanol conversion that we observed opens up possible prospects for processing organic waste in SCW, both for the purpose of their neutralization and for obtaining liquid or gaseous fuel. Waste of both natural and artificial origin is suitable for this. Examples of household waste processing give hope for using SCW for processing plastic waste on various bases. When processing household wastewater sludge, attention should be paid to a fairly significant concentration of heavy metals that can be valuable raw materials. When changing the status of water from subcritical to supercritical, it is possible to organize both the release of inorganic salts and the synthesis, destruction and oxidation of organic substances.

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ПЕРЕТВОРЕННЯ ЕТАНОЛУ У ВОДЯНІЙ НАДКРИТИЧНІЙ КОНВЕКЦІЙНІЙ ПЕТЛІ ПІД ОПРОМІНЕННЯМ ЕЛЕКТРОНАМИ

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Для проведення експериментів по дослідженню дії надкритичної води на конструкційні матеріали була використана конвекційна петля з ввареною камерою опромінення. Петля була встановлена на виході прискорювача електронів. Вода в надкритичних умовах розкладається і дає деяку кількість атомів водню і кисню, які існують одночасно, а також радикали і пероксид водню, причому вода є одночасно і реагент, і середовище, в надкритичних умовах діє як органічний розчинник. Дія опромінення посилює ефект утворення активних часток. У процесі опромінювання і попадання в петлю етанолу виявилося, що у воді в надкритичних умовах можуть проходити процеси як деструкції етанолу, так і синтезу на його основі різних речовин.