

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Hydrogen generation by gasification of phenol and alcohols in supercritical water



HYDRÓGEN

Viktor I. Bogdan ^{a,b,**}, Aleksey E. Koklin ^a, Tatiana V. Bogdan ^{a,b}, Igor I. Mishanin ^a, Alexander N. Kalenchuk ^{a,b}, Tatiana V. Laptinskaya ^c, Leonid M. Kustov ^{a,b,*}

^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp., 119991, Moscow, Russian Federation

^b Lomonosov Moscow State University, Department of Chemistry, 3 Leninskie Gory, 119991, Moscow, Russian Federation

^c Lomonosov Moscow State University, Department of Physics, 2 Leninskie Gory, 119991, Moscow, Russian Federation

HIGHLIGHTS

 \bullet Gasification of phenol and alcohols in supercritical water occurs at 500–700 $^\circ C.$

• Complete gasification of ethanol is achieved at 650 °C.

• Maximum phenol conversion is 96% at 750 °C with gasification degree 30%.

• Phenol gasification is possible via hydrogenation of phenol into cyclohexanol.

• Complete conversion of cyclohexanol occurs at 700 °C with 70% gasification.

ARTICLE INFO

Article history: Received 18 July 2020 Received in revised form 8 August 2020 Accepted 11 August 2020 Available online 10 September 2020

Keywords: Phenols Supercritical water Hydrogen Gasification

ABSTRACT

The conversion of phenol, cyclohexanol (a hydrogenated analog of phenol for comparison with phenol), and ethanol into gas products in supercritical water (SCW) was studied with the goal to compare the reactivity of their aqueous solutions with the structural features obtained by the method of classical molecular dynamics. Transformation of phenol and alcohols occurs in different ways. In the case of alcohols, the conversion of 75–100% is achieved at 600 °C with noticeable gasification. At the same time, the conversion of phenol is only 47% and no gas products are formed at all. The complete conversion of phenol is achieved at a temperature of 750 °C, while the degree of gasification does not exceed 30%. It is shown that an increase in the phenol gasification degree is possible by pre-catalytic hydrogenation of phenol into cyclohexanol.

© 2020 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

E-mail address: lmk@ioc.ac.ru (L.M. Kustov).

https://doi.org/10.1016/j.ijhydene.2020.08.086

^{*} Corresponding author. N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991, Moscow, Russian Federation.

^{**} Corresponding author. N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991, Moscow, Russian Federation.

^{0360-3199/© 2020} Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Contents

Introduction	
Experimental	
Results and discussion	
Conclusion	
Declaration of competing interest	
Acknowledgements	
References	

Introduction

Hydrogen being considered as the alternative clean chemical energy source is produced mainly from natural fossil fuels, i.e. gas and oil. Electrolytic and hydrolytic hydrogen generation are well-established techniques for large-scale hydrogen production [1–3]. However, some of these methods are lacking for sustainability and are energy-expensive. The current research focus is the production of hydrogen from renewable resources, like products of processing of lignocellulose materials. Phenols and lignin oligomers from protolignin, furfurols, ethanol and butanol produced from cellulose and hemicellulose carbohydrates are by-products of industrial paper industry, and recently bioethanol and biobutanol became the mass products of biotechnologies.

The main reason for the growing interest in research of processes in supercritical water is its unique physical and chemical properties. In sub- and supercritical states (T_{cr}-= 374 $^{\circ}$ C and P_{cr} = 22.1 MPa), water parameters such as density, viscosity, permittivity, and solubility product vary greatly, which significantly affects the processes of heat and mass transfer, solvation, and chemical interaction of organic molecules with water molecules. Dissociation of water molecules into a proton and a hydroxyl anion in the subcritical region causes the processes of dehydration of oxygencontaining organic substances. When moving to the supercritical region, water becomes "organic-like". Water molecules in the supercritical state can be partially homolytically dissociated into radicals H. and OH., this leads to the oxidation of organic molecules to form, eventually, hydrogen and carbon dioxide. The reaction of ethanol with degassed supercritical water in a quartz tube reactor at a temperature of 500 °C results in the formation of hydrogen and acetaldehyde without using any oxidizing agents and catalysts [4]. In the gas phase, hydrogen, methane, carbon oxides, as well as small amounts of ethylene and ethane were detected. Possible mechanisms of this reaction are considered in Ref. [4–6]. This process has a high activation energy, and water molecules participate in the process through a multicenter transition state. In a number of works [7-10], steam reforming of ethanol was performed. Thus, in Refs. [7] it has been shown that ethanol (a reaction mixture of the composition ethanol: H₂O: N₂ with the ratio 5:15:80 (60 mL/min)) can be converted by 70-80% at 500 °C for 28 h on a CeO₂MnOxSiO₂ catalyst to H₂

and CO_2 with the selectivities 50% and 20%, respectively. In addition to gas products like methane and carbon monoxide, the catalyst-deactivating products are formed, including ethylene, acetaldehyde, and acetone. Complete steam reforming of ethanol occurs on the most active catalyst $La_{0.5}Sr_{0.5}Mn_{0.7}Ni_{0.3}O_3$ [8] (H₂O:C₂H₅OH = 12-3:1) at temperatures above 600 °C and atmospheric pressure with the selectivities to H_2 and CO_2 equal to 60% and 30%, respectively. However, even under these harsh reaction conditions, up to 10% of acetaldehyde is formed. In Ref. [9], a 100% steam conversion of ethanol with a hydrogen yield of up to 64% was achieved at 450 $^\circ\text{C},$ in this case, up to 12% of ethyl acetate and 10% of CO are formed on a CeO₂ nanocrystal catalyst modified with Co. The kinetics and mechanism of conversion of cyclohexanol in supercritical water are considered in Ref. [11]. Glycerol was also considered as a benign substrate for hydrogen production by gasification in supercritical water using Ni/ZrO₂ as a catalyst [12]. A non-catalytic process of supercritical water reforming of glycerol was also explored from the point of view of increasing valorization of biodiesel production [13].

Phenols are carcinogens and extremely toxic pollutants of the planet's water resources. There are technologies for utilization of technogenic phenols by extraction, bioconversion, chemical transformation (ozonation, photocatalytic degradation) [14–18]. The most effective disposal, in our opinion, is the gasification of phenols in a pollution environment, in an environmentally friendly solvent - supercritical water (SCW).

Gasification of saccharides, such as glucose was also studied under conditions of supercritical water [19] with nickel nanoparticles being generated in the reaction media and acting as catalytically active species.

In general, work on gasification of phenols in SCW was carried out in a periodic mode [20,21]. To exclude the catalytic activity of the walls of the metal reactor, sealed quartz tubes were used, which were filled with a solution of phenol and placed in an isothermal sand bath. Without a catalyst, the maximum conversion of phenol at 600 °C reached 68%. Except for gas products (H₂, CO, CO₂, CH₄, C₂H₆) and benzene, the yield of which did not exceed 5%, biphenyl and dibenzofuran were found in the liquid phase, the yields of which were 0.2 and 3.2%, respectively. The main gaseous products of H_2 and CO_2 were much lower. Under the same conditions, complete conversion of phenol is achieved in the presence of nickel wire

as a catalyst. The main products in the gas phase were H₂ and CO₂. The addition of a nickel catalyst increases the rate constant of phenol decomposition by 3.5 times. Experiments with supercritical water in a flow reactor were performed in the presence of catalysts and additional oxidants [21,22]. In Refs. [22], the results of the conversion of phenol in SCW are presented at 400–500 °C, 25 MPa and contact time 0.23–0.06 min in the presence of 0.2 wt % KHCO₃ as a catalyst. The conversion of phenol at 400 °C was 12%, and at 500 °C it went up to 52%. Variation of operational conditions for conversion of aqueous solutions of phenol showed [23] that the temperature profile is very sensitive to the diameter of the tubular reactor. Complete conversion of phenol at 650-750 °C and a contact time of 1-27 s is possible only in a microchannel reactor configuration, when the narrow channels of the microreactor provide a high rate of heat transfer necessary to maintain endothermic reforming in the fluid. Gasification of a 0.025 M aqueous solution of phenol in SCW was performed at 600 °C, 34.5 MPa and volume space velocity 0.1 h^{-1} in the presence of activated carbon in a flow tube reactor [24]. Phenol was converted with a conversion of 80.8% with a selectivity of 12% for gaseous products (H₂, CO, CO₂, CH₄, C₂H₆). Benzene was detected in the liquid phase. In Ref. [25], the influence of temperature and a nickel catalyst on the gasification of phenol in SCW was studied. At 600 °C and water density of 0.079 g/ cm³, the maximum conversion of phenol was 68%. In addition to the above-mentioned gaseous products, aromatic hydrocarbons are formed: benzene, biphenyl, and dibenzofuran, whose yields were 5%, 0.2%, and 3.2%, respectively. No coke was found. The conversion of phenol in SCW without catalysts and additional oxidants was studied [26] at temperatures of 500-750 °C, pressure of 30 MPa and volume space velocity of $1.2-2.0 h^{-1}$ in a flow regime. Conversion of phenol in SCW at 500-600 °C proceeds with the formation of only pyrolysis products - benzene, toluene, naphthalene, and a number of condensed aromatic compounds. Almost complete conversion of phenol is achieved at a temperature of 750 °C, with the selectivity to gas products (H2, CO2, CH4, C2H4, C2H6) not exceeding 30%. It was found that the presence of an aromatic ring, in comparison with aliphatic hydrocarbons, is the main reason behind the reduction of the rate of interaction of phenol with supercritical water.

The purpose of this study is to convert phenol, cyclohexanol (a hydrogenated analog of phenol for comparison with phenol), and ethanol into gas products in supercritical water (SCW), to compare the reactivity of their aqueous solutions with the structural features obtained from the calculated data by the method of classical molecular dynamics (MD).

Experimental

Ethanol (rectified, 95.6%), cyclohexanol (chemically pure), phenol (chemically pure), and water - bidistillate were used in the experiments. Carbon dioxide (99.95%), methane (chemically pure), carbon monoxide, helium (99.9%), and argon (99.95%) were used for calibration and analysis by GC.

The conversion of aqueous solutions of substrates (ethanol, cyclohexanol, and phenol) of various concentrations was carried out in a continuous mode in a flow setup (Fig. 1) in



Fig. 1 – The scheme of a laboratory setup: (1) aqueous solution of a substrate, (2) Knauer high-pressure liquid pump, (3) reactor, (4) tubular electric furnace with a temperature regulator, (5) needle valve, (*P*) pressure gauge.

a stainless steel AISI 316 reactor with a length of 55 cm and a diameter of 6 OD. The reagents were fed by a Knauer highpressure liquid pump, and the pressure was regulated by a needle valve (HiP, USA). The reactor was heated with a tubular electric furnace using a thermoregulator (Thermodat, Russia).

The reagent conversion 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, detector - refractometer). The conversion was calculated using the formula:

$$K = \frac{C_0 - C}{C_0} \cdot 100\%$$

where C_0 and C are the initial and final concentrations of the starting reagent in an aqueous solution (mmol/mL).

The gaseous products were analyzed on-line on a Kristall 5000.2 chromatograph equipped with Porapak Q and zeolite CaA packing columns (1.5 m \times 3 mm) and a thermal conductivity detector. The analysis of H₂, CH₄ and CO was performed using the CaA column (He as a carrier gas), and the Porapak Q column (He as the carrier gas) was used for the analysis of CH₄, CO₂, C₂H₄, and C₂H₆. Quantitative calculation of gas concentrations analyzed on the CaA column was performed using calibration curves. The concentrations of gaseous products analyzed on the Porapak Q column were calculated relative to methane as an internal standard.

The selectivity of gasification was calculated using the following equation:

$$S = \frac{V \sum (C_j n_j)}{V_1 (C_0 - C) n_0 \nu t} \times 100\%$$

where C_0 and C are the initial and final concentrations of the substrate, C_j is the molar concentration of the i-th component of the gas products, n is the number of carbon atoms, V/ V_1 is the number of moles of the collected gas mixture under normal conditions, v, t are the flow rate and duration of the supply of the substrate solution.

Classical molecular dynamic modeling of structures of aqueous solutions containing 2 wt % of ethanol, cyclohexanol, or phenol was performed in an NVT ensemble at densities of 0.997 g/cm³ and 0.133 g/cm³ that correspond to the normal (T = 298 K, P = 0.1 MPa) and supercritical conditions (T = 673 K, P = 23 MPa) of the state of the solvent, respectively. The total number of molecules in the calculation systems was 10,000, with the ratio of water and solute molecules for ethanol equal to 9920/80 (0.008 ppm), for phenol - 9960/40 (0.004 ppm), for cyclohexanol - 9963/37 (0.004 ppm). Molecular dynamic modeling of water solutions was performed using the GROMACS software package, interaction parameters were set by the OPLS-AA potential (TIP4P water model). To integrate the equations of motion, we used the leap-frog algorithm with an integration step of 0.001 PS. The constraints and coordinates of the atoms were calculated twice at each integration step. A Noze-Hoover thermostat and a Parrinello-Raman barostat were used to maintain a constant temperature and pressure. The PME (Particle-Mesh Ewald) algorithm with a cut-off radius of 10 Å was used to calculate Coulomb interactions. The cut-off radius of the van der Waals interactions was 10 Å. Details of modeling for ethanol and phenol are described in the article [27], data for cyclohexanol were obtained using a similar protocol. To characterize the clustering of phenol and alcohol molecules in an aqueous environment, the radial distance distribution (RDD) functions between oxygen atoms of hydroxyl groups were calculated as:

$$g(r) = \frac{\langle \sum_{i,j} \delta(r - r_{ij}) \rangle}{4\pi\rho r^2} \Delta r,$$

where r_{ij} is the distance between oxygen atoms, ρ is the digital density of molecules in the distance interval of Δr .

Experiments on dynamic light scattering (DLS) were performed on the "ALV/DLS/SLS-5022F Goniometer Correlator System" ("ALV-GmbH", Germany) with a He-Ne laser (wavelength $\lambda = 632.8$ nm, power 22 mW). All measurements were performed at a scattering angle of 90° in a waterethanol mixture at 25 °C. Autocorrelation functions of the scattering intensity were measured in the experiment. Processing the results using the inverse Laplace transform (CONTIN software package) allows us to obtain the distribution functions of contributions to scattering from scattering particles in solution by hydrodynamic diameters Dh (intensity-weighted distribution). Using the standard formula for the dependence of the scattering intensity on the radius for a spherical dielectric particle, we found the dependence of the mass distribution of particles in solution on the hydrodynamic diameter [28]. The viscosity of the ethanol-water mixture was determined by interpolating the data presented in Ref. [29].

Results and discussion

Transformations of organic compounds in SCW include a set of reactions of target steam reforming into base H_2/CO_2 -containing gas mixtures (1) accompanied by destructive reactions: dehydrogenation, dehydration, condensation of aromatic compounds with subsequent carbonization, hydrogenation with hydrogenolysis of organic compounds (2–5). Reactions accompanying the conversion in SCW may also include the interaction of steam reforming products: hydrogenation of carbon oxides (6–8), steam-assisted conversion of carbon to synthesis gas and methane (9,10), and the Boudoir-Bell reaction (11).

$$C_{x}H_{y+1}OH + (2x-1)H_{2}O \rightleftharpoons xCO_{2} + ((4x+y)/2)H_{2}$$
 (1)

$$C_X H_{Y+1} O H \rightleftharpoons C_X H_Y + H_2 O \tag{2}$$

 $C_X H_{Y+1} O H \rightleftharpoons C_X H_Y O + H_2$ (3)

$$C_{X}H_{Y+1}OH + yH_{2} \rightleftharpoons C_{X}H2_{Y} + H_{2}O$$
(4)

$$C_{X}H_{Y+1}OH \rightleftharpoons xC + H_{2}O + y/2H_{2}$$
(5)

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{6}$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{7}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{8}$$

$$C + H_2 O \rightleftharpoons CO + H_2 \tag{9}$$

$$C + 2H_2 O \rightleftharpoons CH_4 + CO \tag{10}$$

$$C + CO_2 \rightleftharpoons 2CO$$
 (11)

According to data presented in Table 1, ethanol with a concentration of 2 vol% in SCW is dehydrogenated to acetaldehyde by reaction (3) at temperatures of about 500 °C and pressures about 30 MPa. When the reaction temperature of the ethanol conversion increases from 500 °C to 600° SCW accelerates radical and redox reactions (4–8), which contribute to the formation of gas products. Under these conditions, the complete conversion of ethanol occurs with a gasification rate of 77%.

This transformation generates hydrogen-containing gas products with H_2 , CO, and CO₂ selectivity of 35%, 7%, and 11%, respectively. The dehydration of ethanol into ethylene (3) and its hydrogenation into ethane provides the formation of a pool of light hydrocarbons with the methane: ethane ratio of 3:1. A further increase in temperature to 700 °C at the complete conversion of ethanol to gas leads to an increase in the selectivity for H_2 up to 42% and for CO₂ up to 20% with a significant decrease in the yield of CO (less than 1%), due to the equilibrium of the water shift reaction (8). Hydrogenation of carbon oxides by reactions (8, 9), other things being equal, contributes to the accumulation of methane up to a third of the molar volume of gas products.

Table 1 – Dependence of the conversion of aqueous ethanol solutions of different concentrations on temperature under supercritical conditions (P = 30 MPa, LHSV = $3.75 h^{-1}$).										
Ethanol	ol T, °C Gas flow rate, Conversion, % Extent of nt-ration, ml/min gasification	Gas flow rate,	Conversion, %	Extent of	Content of gas products, vol%					
concent-ration, vol%		gasification, %	H ₂	СО	CO ₂	CH ₄	C_2H_4	C_2H_6		
2	500	0.6	41	0	0	0	0	0	0	0
	600	11	100	77	35	7	11	23	0	8
	650	12	100	76	42	0.8	20	21	0	5
	700	15.5	100	98	42	0.4	20	23	0	4
5	700	33	100	95	44	0.4	19	29	0	5
10	700	61.4	100	89	45	0.7	19	30	0	5
15	700	86	100	83	44	0.9	19	31	0	5

At temperatures above 600 $^{\circ}$ C, all water-ethanol mixtures are completely converted by reaction (1) into a hydrogencontaining mixture of gases with a gasification degree of 80–100%. Data on the effect of concentrations of waterethanol reagents on the degree of gasification and the yield of the hydrogen-containing gas mixture are shown in Fig. 2.

An increase in the flow rate of the formed gas mixture and the output of CO was detected with an increase in the concentration of ethanol in the initial aqueous solution from 2 to 15%, while the degree of gasification, in general, decreased. No significant changes in the gas composition of products of ethanol conversion in SCW at 700 °C and 30 MPa were observed.

Conversion of phenol or cyclohexanol aqueous solutions (2 wt%) was performed at temperatures of 500–700 °C, a pressure of 30 MPa, and a volume hourly space velocity of 2.0 h⁻¹. Table 2 shows the data on the conversion of phenol and cyclohexanol, as well as the degree of their gasification. At 500 and 600 °C, no gaseous products of phenol conversion are formed. Only at a temperature of 700 °C, gasification occurs with a gas product selectivity of 17%. The total proportion of carbon monoxide, ethane, and ethylene did not exceed a few percent. Almost complete conversion of phenol was achieved only at a temperature of 750 °C with a selectivity of 30%. The composition of gas products differed slightly. Assuming that

the low degree of phenol gasification is related to the stability of the aromatic structure in SCW, we investigated the conversion of cyclohexanol as a hydrogenated phenol derivative under supercritical conditions. The conversion of cyclohexanol in SCW is higher than that of phenol, all other things being equal, and occurs with a high yield of gaseous products. At 500 °C the main product in the liquid phase was cyclohexene produced by the dehydration reaction (2). At 600 °C and 30 MPa, a quarter of all cyclohexanol is converted to gas products: H_2 , CH_4 , C_2H_4 , C_2H_6 , CO and CO_2 . The complete conversion of cyclohexanol occurs only at 700 °C with a gasification rate of 70%. In the gas phase, naphthenic, aliphatic, and aromatic hydrocarbons were also detected in trace amounts: benzene, cyclohexene, butene-2, toluene, cyclopentene, and cyclopentadiene.

A comparative analysis of the data on the transformation of phenol and alcohols shows that in the case of alcohols, the conversion of 75–100% is achieved at 600 °C with noticeable gasification. At the same time, the conversion of phenol is only 47% and no gas products are formed at all (Fig. 3). The complete conversion of phenol is achieved at a temperature of 750 °C, while the degree of gasification does not exceed 30%.

The number of the gas products of the conversion and the group composition of this mixture in SCW at 700 $^{\circ}$ C and 30 MPa differ greatly (Table 3, Fig. 4). Due to the



Fig. 2 – The degree of ethanol gasification (700 $^{\circ}$ C and 30 MPa) and the linear flow rate of gas products depending on the ethanol concentration in the aqueous solution.

Table 2 – Conversion of phenol and cyclohexanol in SCW (30 MPa).										
Substrate	T, °C	Conversion, %	Gasification degree, %	Content of gas products, vol. %						
				H ₂	СО	CO ₂	CH_4	C_2H_4	C ₂ H ₆	
Phenol	500	2	0	0	0	0	0	0	0	
	600	47	0	0	0	0	0	0	0	
	700	54	17	49	16	28	3	1	3	
	750	96	30	45	22	27	0	1	4	
Cyclohexanol	500	63	0	0	0	0	0	0	0	
	600	77	35	30	21	5	12	18	15	
	700	100	70	20	36	18	0	4	18	



Fig. 3 – Conversion and degree of gasification of 2% aqueous solutions of phenol, cyclohexanol, and ethanol in SCW (30 MPa).

thermodynamic stability of the aromatic structures under these conditions, the total volume of gas products formed in the course of the interaction of phenol with SCW is insignificant. Gas release increases significantly when switching to non-aromatic substrates, increasing in the order: phenol: cyclohexanol: ethanol = 1:7:40. The qualitative composition of the released gas during the conversion of phenol and ethanol to SCW is the same, which indicates the occurrence of reaction (1). The molar content of hydrogen reaches half of the gas products. More than 2/3 of the gas pool consists of H₂ and CO₂ with a ratio equal to 2. Note also that only ethanol produces up to a quarter of methane by the direct methanation reaction (Sabatier reaction (7)). Hydrogen formed during the gasification of cyclohexanol in SCW, in contrast to phenol and ethanol, makes about 20% of the gas mixture formed. It is consumed by the reaction of hydrogenolysis (4) of the naphthene ring into ethane. A distinctive feature of the conversion

of phenol and cyclohexanol compared to ethanol in SCW on the background of reduced gasification degree is the formation of significant amounts of CO. During the conversion of phenol and, to a lesser extent, cyclohexanol in SCW, pyrolysis of these substrates into carbon products dominates (5). Further, carbon reacts with water (9,10) and with carbon dioxide by Boudoir-Bell reaction (11), enriching the gas phase with carbon monoxide. The apparent activation energies of the net processes of conversion of phenol, cyclohexanol, and ethanol determined from Arrhenius dependencies are equal to 35.3 kJ/mol, 18.5 kJ/mol, and 49.5 kJ/mol, respectively. It should be noted that the activation energies were determined in the region of high conversions. The highest activation energy of 49.5 kJ/mol corresponds to the process of ethanol gasification in the temperature range of 500-600 °C. Considerably lower activation energies found for phenol and cyclohexanol correspond to the processes of condensation and

Table 3 – Gas products of the phenol, cyclohexanol and ethanol conversion and the group composition of this mixture in SCW at 700 °C and 30 MPa.									
Conversion, %	Gasification degree, %	Conversion, mmol/h	Yield, mmol/h						
			H ₂	СО	CO ₂	CH_4	C_2H_4	C_2H_6	
54	17	2	1,0	0.3	0.5	0.1	0	0.1	
100 100	70 98	14 80	2.8 33.6	5.0 0.3	2.5 16.0	0.0 18.4	0.6 0.0	2.5 3.2	
	products of the p and 30 MPa. Conversion, % 54 100 100	products of the phenol, cyclohexanol and and 30 MPa. Conversion, % Gasification degree, % 54 17 100 70 100 98	products of the phenol, cyclohexanol and ethanol conversion andand 30 MPa.Gasification degree, %Conversion, mmol/hConversion, %Gasification degree, %Conversion, mmol/h5417210070141009880	products of the phenol, cyclohexanol and ethanol conversion and the gree and 30 MPa.Conversion, %Gasification degree, %Conversion, mmol/hH2541721,010070142.8100988033.6	Products of the phenol, cyclohexanol and ethanol conversion and the group of and 30 MPa. Conversion, mmol/h Image: Hammed of the group of the g	Products of the phenol, cyclohexanol and ethanol conversion and the grup vorticities and 30 MPa. Vield, Conversion, % Gasification degree, % Conversion, mmol/h Yield, H2 CO CO2 54 17 2 1,0 0.3 0.5 100 70 14 2.8 5.0 2.5 100 98 80 33.6 0.3 16.0	products of the phenol, cyclohexanol and ethanol conversion and the group sition of the and 30 MPa. Conversion, % Gasification degree, % Conversion, mmol/h Yield, mmol/h H2 CO CO2 CH4 54 17 2 1,0 0.3 0.5 0.1 100 70 14 2.8 5.0 2.5 0.0 100 98 80 33.6 0.3 16.0 18.4	products of the phenol, cyclohexanol and ethanol conversion and the group subscription of this mixt and 30 MPa. Conversion, % Gasification degree, % Conversion, mmol/h ¥ield, mmol/h H2 CO CO2 CH4 C2H4 54 17 2 1,0 0.3 0.5 0.1 0 100 70 14 2.8 5.0 2.5 0.0 0.6 100 98 80 33.6 0.3 16.0 18.4 0.0	



Fig. 4 – Composition of gas products during the conversion of phenol, cyclohexanol, and ethanol in SCW (700 °C, 30 MPa).

hydrogenolysis, respectively. Gasification of these two substrates is much less intensive compared to ethanol in the same temperature interval (Table 3).

A significant difference in the patterns of the conversion of phenol, cyclohexanol, and ethanol in SCW is also shown in the structure of their water solutions. It was revealed by the method of classical molecular dynamic modeling of structures of aqueous solutions of ethanol, cyclohexanol, and phenol that the molecules of the dissolved substance in dilute aqueous solutions (2 wt%). The substrate molecules mostly exist as monomeric units in both normal and supercritical conditions, but they can also be combined into clusters containing up to six molecules under normal conditions, and up to two molecules under supercritical conditions. For phenol, the tendency to cluster is higher than for ethanol. The results of nonempirical calculations [30] show that the stability of clusters of phenol molecules is higher than that of waterphenolic and water clusters. Fig. 5 shows the radial distribution functions (RDF) of oxygen atoms of the alcohol group of phenol, cyclohexanol, and ethanol molecules at different



Fig. 5 – Radial distribution function for oxygen atoms of phenol, cyclohexanol, and ethanol molecules at different simulation steps for normal and supercritical (SC) conditions: (a) phenol, normal conditions; (b) cyclohexanol, normal conditions; (c) ethanol, normal conditions; (d) phenol, supercritical conditions; (e) cyclohexanol, supercritical conditions; (f) ethanol, supercritical conditions. Different trajectory steps are shown in different colors. Distances are expressed in nm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

modeling steps for normal and SC-conditions. The maxima of the function reflect the presence of characteristic distances between the oxygen atoms of two molecules. In particular, the appearance of sharp peaks in the region of 0.3 nm reflects the formation of hydrogen bonds between alcohol molecules. At certain steps of the trajectory, such maxima appear for all systems under normal conditions, but their absence at other steps of the trajectory indicates instability of hydrogen bonds between dissolved molecules. In addition to the sharp maximum at 0.3 nm, one to three broad maxima are also observed for phenol in the region of 0.3-1.5 nm on the RDF, which characterize the tendency of phenol molecules to be located next to each other. In the case of cyclohexanol, a single broad maximum is observed on the curve, shifted to the region of 7-10 nm, which corresponds to the existence of clusters of solvated cyclohexanol molecules. In the case of ethanol, the broad maximum is shifted to the region of smaller distances (5–7 nm), which also reflects the formation of clusters of solvated ethanol molecules. When switching to supercritical conditions, the curves for ethanol and cyclohexanol look very similar, reflecting the uniform distribution of alcohol molecules in the system. For phenol in the range of 0.3-1.3 nm, heterogeneity of the function is observed, the available maxima are significantly higher in the amplitude than in the case of ethanol and cyclohexanol, which corresponds to the clustering of aromatic molecules.

To illustrate the features of solvation of molecules, we constructed spatial distribution functions (SDF) of the density of water molecules around ethanol, cyclohexanol, and phenol molecules for normal conditions (Fig. 6). SDF patterns were obtained for high density of water molecules, which reflects the structure of the solvate shells, and for low density, which

indicates the places of attack of solute molecules by water molecules. It is found that compact solvate shells are formed in the case of ethanol. For phenol and cyclohexanol, the solvate shells are heterogeneous, bulky and loose. Low-density SDF for ethanol indicate that water is concentrated around carbon-carbon bonds. For cyclohexanol, the concentration of water molecules over the center of the 6-member cycle is noted. During the transition to the reaction conditions of high temperatures and pressures, this arrangement of water molecules contributes to the splitting of single σ -bonds and gasification of ethanol and cyclohexanol molecules. In the case of phenol, water is primarily concentrated around hydroxyl groups, which correlates with the stability of the π -bonds of the aromatic ring under SC gasification conditions. The main direction of interaction of phenol with supercritical water is hydrodeoxygenation of the phenol group and condensation of benzene rings into polyaromatic hydrocarbons to produce carbon-like substances.

The self-aggregation of phenol molecules in comparison with ethanol has also been confirmed experimentally by the method of dynamic light scattering. Fig. 7 shows the contribution to the DLS intensity from particles of different radii in the water-ethanol mixture. At an ethanol concentration of 0.2–10 wt%, there is a wide size distribution with a maximum of about 200 nm (large clusters), while in the range of small concentrations of 0.2–2%, large clusters are dominant. With the growth of the amount of ethanol in water, clusters with radii of 26 and 23 nm, corresponding to concentrations of 5% and 10%, become the main moieties. This self-aggregation of ethanol in water-ethanol solutions correlates with a decrease in the degree of gasification with an increase in the concentration of ethanol in water (Table 1).



Fig. 6 – Spatial distribution functions: high density (at the top), low density (at the bottom). a, d - phenol, b, e – cyclohexanol, c, f - ethanol.



Fig. 7 - Distribution of DLS intensity depending on the radius of clusters in the water-ethanol mixture.



Fig. 8 – Contribution to the DLS intensity from particles of different radii in an aqueous-phenolic solution.

Compared to ethanol, phenol forms clusters in aqueous solutions, starting at a concentration of 2% and higher. At a concentration of 2%, we observed clusters of two types: with radii of 1 nm and 76.5 nm, and at a concentration of 5% only with a radius of 58.4 nm (Fig. 8). Lines with maxima at 0.20 and 0.27 nm correspond to molecular phenol, the total mass of which is significantly greater than the total mass of the clusters.

Such a stable existence of nanoscale clusters of phenol, confirmed experimentally by the DLS method and calculated by the MD method, causes a low degree of gasification of phenol in comparison with ethanol and cyclohexanol in supercritical water.

Conclusion

The transformation of phenol, cyclohexanol, and ethanol in supercritical water (SCW) at temperatures of 500–700 °C was studied at a pressure of 30 MPa in a flow mode. Complete gasification of ethanol (1 vol%) in SCW is achieved at a temperature of 650 °C, and at concentrations of 2–15 vol% it was observed at 700 °C. The maximum conversion of phenol is 96% at a temperature of 750 °C, while the degree of gasification does not exceed 30%. It was found by the method of molecular

dynamics and DLS that phenol with its aromatic structure shows a tendency to self-association in aqueous solutions with the formation of nanoclusters. In SCW conditions, the water shell of phenol clusters is unstable, which leads to incomplete gasification in SCW even at temperatures of 750 °C and to the formation of pyrolysis and condensation products. It is shown that an increase in the phenol gasification degree is possible by pre-catalytic hydrogenation of phenol into cyclohexanol. The complete conversion of cyclohexanol under conditions comparable to phenol in SCW occurs at a temperature of 700 °C with a gasification degree of 70%.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors express their gratitude to the Russian Foundation for Basic Research (RFBR) for supporting the research conducted under grant 18-29-06072 MK.

REFERENCES

- Cao W, Guo L, Yan X, Zhang D, Yao X. Int J Hydrogen Energy 2020;45:14744.
- [2] Wang W, Yang L, Qu F, Liu Z, Du G, Asiri AM, Yao Y, Chen L, Sun XJ. Mater Chem A 2017;5:16585.
- [3] Liu T, Liu D, Qu F, Wang D, Zhang L, Ge R, Hao S, Ma Y, Du G, Asiri AM, Chen L, Sun X. Adv. Energy Mater 2017;7:1700020.
- [4] Arita T, Nakahara K, Nagami K, Kajimoto O. Tetrahedron Lett 2003;44:1083.
- [5] Savage PhE, Yu J, Stylski N, Brock EE. J Supercritical Fluids 1998;12:141.
- [6] Takahashi H, Hisaoka S, Nitta T. Chem Phys Lett 2002;363:80.
- [7] Ribeiro MC, Jacobs G, Davis BH, Mattos LV, Noronha FB. Top Catal 2013;1634:56. https://doi.org/10.1007/s11244-013-0098-y.
- [8] Perin G, Guiotto M, Natile MM, Canu P, Glisenti A. Catal Lett 2018;220:148. https://doi.org/10.1007/s10562-017-2207-1.
- [9] Sohn H, Soykal II, Zhang Sh, Shan J, Tao F, Miller JT, Ozkan US. J Phys Chem C 2016;120:14631. https://doi.org/ 10.1021/acs.jpcc.6b02490.
- [10] Therdthianwong S, Srisiriwat N, Therdthianwong A. J Supercritical Fluids 2011;57:58.
- [11] Akiya N, Savage PhE. Ind Eng Chem Res 2001;40:1822.
- [12] Zhu B, Li S, Wang W, Zhang H. Int. J. Hydrogen energy 2019;44:30917.
- [13] Ziyai MR, Mehrpooya M, Aghbashlo M, Omid M, Alsagri AS, Tabatabaei M. Int. J. Hydrogen energy 2019;44:17845.
- [14] Halaouli S, Asther M, Sigoillot JC, Hamdi M, Lomascolo A. J Appl Microbiol 2006;100:219.

- [15] Kukadiya AV. Int J Eng Res Technol 2016;5:400.
- [16] Bogdan VI, Sergeeva YaE, Lunin VV, Perminova IV, Konstantinov AI, Zinchenko GE, bogdan KV. Appl Biochem Microbiol 2018;198:54. https://doi.org/10.1134/ S0003683818020023.
- [17] Al-Kandari H, Abdullah A, Mohamed A, Al-Kandari S. J Mater Sci 2016;114:1.
- [18] Chedeville O, Debacq M, Porte C. Desalination 2009;249:865–9.
- [19] DiLeo GJ, Neff ME, Savage PE. Energy Fuels 2007;21(4):2340.
- [20] Huelsman CM, Savage PhE. J Supercritical Fluids 2013;81:200.
- [21] Yong TLK, Matsumura Y. J Supercritical Fluids 2014;87:73.[22] Weiss-Hortala E, Kruse A, Ceccarelli C, Barna R. J
- Supercritical Fluids 2010;53:42. [23] Goodwin AK, Rorrer GL. Energy Fuels 2009;23:3818.
- [24] Xu X, Matsumura Y, Stenberg J, Antal M. Ind Eng Chem Res
- 1996;35:2522.
- [25] DiLeo J, Neff ME, Kim S, Savage PhE. Energy Fuels 2008;22:871.[26] Bogdan VI, Kondratyuk AV, Koklin AE, Lunin VV. Russ J Phys
- Chem B 2017;1207:11. https://doi.org/10.1134/ S1990793117070041.
- [27] Alexeev ES, Bogdan TV. Russ J Phys Chem B 2020:15. https:// doi.org/10.34984/SCFTP.2020.15.1.004.
- [28] Schärtl W. Light scattering from polymer solutions and nanoparticle dispersions. Springer; 2007. p. 191.
- [29] González B, Calvar N, Gómez E, Dominguez Á. J Chem Thermodyn 2007;39:1578.
- [30] Parthasarathi R, Subramanian V, Sathyamurthy NJ. Phys Chem A 2005;109:843.