

SUPERCRITICAL WATER GASIFICATION OF ISOPROPYL ALCOHOL ON VERTICAL CONTINUOUS APPARATUS: PROCESS CONDITIONS

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Increasing world energy consumption leads to the search for new technologies that are able to obtain power. Also due to the increasing amount of waste stream would be suitable to find mechanisms to gain energy from them. Supercritical water gasification is a conversion process that represents a potential for the technology on degradation of liquid organic wastes to produce usable energy gases (methane, hydrogen, CO, higher hydrocarbons) along with the treatment of waste water. Supercritical water gasification is a very complex process, hence is necessary a detailed examination on experimental equipment using model compounds. In this paper the results of isopropyl alcohol gasification on a vertical continuous apparatus are depicted. Experiments were carried out under various process conditions to determine the most appropriate setting for an effective gasification.

Key words: hydrothermal gasification, continuous apparatus, isopropyl alcohol, process conditions

Received 19. 08. 2016, accepted 26. 09. 2016

1. Introduction

Global energy demand and consumption has since the industrial revolution augmented drastically and keeps on increasing. Therefore, new energy gaining technologies such as supercritical water gasification (SCWG) are developed and examined. Hydrothermal gasification is a thermochemical conversion process, where the organic substances are converted into gaseous products in water under high pressures and temperatures, in a medium known as supercritical water [1-3].

1.1. Supercritical water

Water becomes critical fluid when it reaches its critical temperature (374 °C) and pressure (22.1 MPa). Properties of supercritical water (SCW) are very different from properties of water at normal conditions as well as from those of steam. At temperatures near the critical temperature water has a high specific heat capacity. When the temperature reaches a critical point specific heat capacity reaches its maximum, which is above 100 kJ.kg⁻¹.K⁻¹. The maximum value of heat capacity is related to phase change of the fluid at that point. Amount of heat required to heat 1 kg of water by 1 °C is at that point maximum, which determines its excellent heat transfer properties and excellent cooling characteristics [3, 4].

The value of the dielectric constant of water drops gradually as the temperature rises to a value comparable to dielectric constants of organic compounds. As a result of its decrease, SCW acts as a nonpolar solvent, thus organic compounds (wastes) can be converted into energetically usable gases. Nevertheless, the change in the dielectric constant also decreases the solubility of inorganic salts. This can cause depositions or even plugging in case

of gasification of real waste material, which usually contain inorganic salts. Decrease of the dielectric constant along with decrease of other properties of SCW are shown in Fig.1. [3, 5, 6]

Additionally, solubility of gases and reaction intermediates in SCW is excellent. From this perspective is water at supercritical conditions an ideal reaction medium for gasification since it allows reactions to take place without the interphase barrier. Thanks to the absence of the interphase barrier ongoing reactions are homogeneous. Thus the gasification process can be carried out more effectively [3, 7].

The density of water decreases rapidly (Fig.1) with temperature. The density of SCW is lower than the density of subcritical water, but it is higher than the density of subcritical steam. The property of water that depends on its density is the ionic product because the ion product describes the number of ions per volume unit.

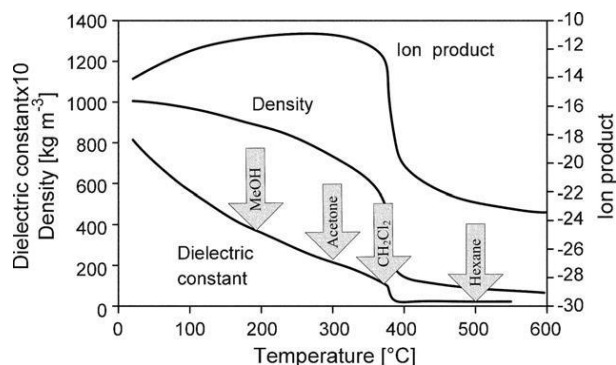


Fig.1 Dependence of density, dielectric constant and ion product on temperature, some dielectric constants of common solvents are marked for comparison [5]

The quantity of present hydrogen bonds also depends on the water density. As a result of these properties the medium has no longer the structure of a mixture of ions, but clusters of water molecules and water loses the hydrogen bond [3].

There are more properties of SCW that help the gasification process most notably high diffusivity, low viscosity and low surface tension. These characteristics help to improve the mass and energy transfer in the reactor [1,3].

2. Hydrothermal gasification

The main advantage of hydrothermal gasification is that it is suitable for gasification of very wet compounds or water (waste) solutions containing organic matter. The conversion of SCWG, unlike the conventional gasification processes, is not affected by the feedstock moisture content [8, 9].

Other great advantage of the SCWG process is without any doubt the simplicity of product separation. Hydrogen and methane are separated from water in the high pressure separator because their solubilities decrease rapidly with temperature. Inorganic compounds stay dissolved in the liquid phase as well. Solid particles and liquid organic products leave the system with the aqueous phase. The gas produced by SCWG is therefore relatively clean (low dust and tar content), and leaves the system at high pressure. As a result any further treatment or utilization of the produced gas is considerably simpler [7,10].

The main disadvantage of SCWG are high capital and operating costs. These are caused by the extreme conditions that the process requires and big amount of water that is heated and cooled. An application of heat exchangers is therefore necessary for future industrial technologic applications. In addition to that, the process conditions place great demands on the mechanical and thermal properties of the used materials [11-13].

Supercritical water gasification can take place under a wide range of conditions and it is affected by a number of operating parameters. It is necessary to understand how changes in operating parameters affect the process and its results in order to be able to successfully operate or design an SCWG unit. Some of the operating parameters can be changed independently for instance concentration. Others can be mutually linked. For example, with change of the flow-rate, the heating rate and the residence time are affected. This interrelation between experimental parameters makes it difficult to understand the influences of different operating parameters on the process operation and efficiency [14, 15].

Another problematic aspect to determine the impact of different operating parameters on the process is the fact that the gasification unit design itself can affect the SCWG process. Thus a different apparatus can show a different behavior because of the reactor design. The reactor material also has to be taken into consideration because of the catalytic effect of reactor walls [16, 17]. All these issues and the fact that research groups over the world perform experiments on different apparatus make

it difficult to draw general conclusions about the effects of operating parameters [16, 18].

3. Experimental part

Hydrothermal gasification tests were carried out in a vertical continuous apparatus. All the gasification products were analyzed. As gasification substances were chosen isopropyl alcohol (IPA) based on other experimental works. There were used prepared aqueous solutions with concentration of 50 g/l and 75 g/l. To verify the influence of the catalyst was used, based on literature review, potassium carbonate in concentration 5 g/l [19, 20].

3.1. Vertical apparatus

In Fig. 2 the scheme of a vertical continuous apparatus for hydrothermal gasification built at UTC Prague at the turn of 2014/2015 is shown. The material (water / isopropyl alcohol solution) is dispensed into the reactor by one of the high pressure pumps HPP 5001 (Laboratory devices Prague). Pump parameters are the following: volume of 400 ml, flow range from 0.1 ml/min to 9.9 ml/min and a maximum pressure of 50 MPa.

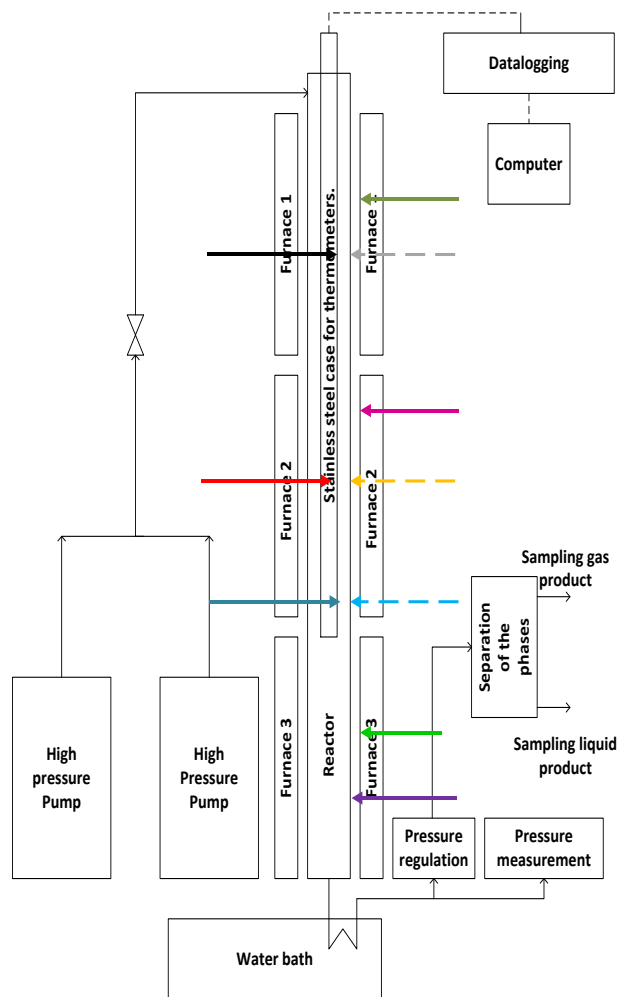


Fig. 2 Vertical continuous apparatus.

Feed of material from the pump to the reactor was performed via a steel capillary with an internal volume of 2.2 ml. The capillary is equipped with a needle valve, which serves to separate the high pressure part with the reactor from pumps. This valve is used when switching from one pump (water) to the other (isopropyl alcohol). The body of the reactor is made of AISI 316 steel and the volume is 40.6 ml. The reactor is placed in a steel tube with an inner diameter of 100 mm, which serves as protection of the heating segments, especially in case of reactor damage. The steel tube should also equally transfer heat from the heating elements. Thus improving the temperature profiles of the reactor. The tube is isolated on top and bottom with Sibral to prevent the stack effect.

The body of the reactor is heated by three separately controlled heating segments (furnaces) supplied by Kanthal, Sweden. Individual segment consist of two semicircular sections, each with a maximum output of 900 W. The heating elements were delivered already insulated by Sibral. Furnaces cover the entire length of the reactor, in order to eliminate heat loss. As a result the residence time of material in the supercritical zone is hereby increased.

Temperatures in the reactor are monitored by ten temperature sensors, whose location is indicated by colored arrows in the scheme. Temperatures are recorded by MS Data Logger COMET MS6D and obtained curves of temperatures dependence on time is displayed online on computer in MS+ software.

3.2. Experimental set up

The experiments begin by filling the first pump with water and then pressurizing the pump, with closed needle valve, to 30MPa. Thereafter, the needle valve is opened and the pump filled (flow 1 or 2 ml/min) the whole apparatus with water, and pressurized the apparatus to 25MPa (maximum pressure due to material of the reactor).

Setting up the pressure in the whole system is provided at the end by a back pressure regulator. After the pressure is stabilized, the furnaces are set to the 620 °C each. This temperature was chosen based on previous experience with the apparatus and due to reactor material. Simultaneously when turning on the furnaces started temperature logging from the temperature sensors in the system. Immediately after heating up started was turned on the heating of the cooling bath.

While the apparatus heated up (about 75 minutes) the second pump was filled with the isopropyl alcohol solution. After heating the reactor and the temperature was stabilized the needle valve was closed. Then was stopped the first pump with water, which was subsequently depressurized. The second pump with the prepared solution for the conversion was pressurized and led into the apparatus as in the case of water. After a sufficient amount of time was indicated beginning of the gasification by fluent evolution of the gas. This phenomenon could be seen in the bubbler filled with water, which was connected with the top of the separation flask. Once pressure has been stabilized flow and temperature values in

the system, samples were taken from separation flask for analysis.

During the sampling periods, a sampling bag (previously cleaned 3 times with N₂) was used to collect the produced gas. The gas-liquid separator was emptied from the previous liquid before gas sampling. The valve was closed during the sampling. The accumulated liquid that flowed during this time was collected at the end and homogenized before transfer into the sampling vials.

At the end of each experiment, water was pumped during the cooling period. Water is the most suitable medium for heating and cooling since if organic compounds will be used side reactions at lower temperatures can take place. The side reactions can lead to tar, char or polymers formation that can deposit in the reactor.

For the analysis of gas samples was used a gas chromatograph HP 6890, equipped with two analytical channels. The first channel is fitted with the flame ionization detector and was used for the analysis of hydrocarbons from methane to toluene (C1 - C8). The second channel fitted with the thermal conductivity detector was used for the analysis of permanent gases. Helium was used as carrier gas. Calibration of the chromatograph was performed by gas samples of known composition, under the same conditions. It was used external standard method. Calculations were performed using HP Chemstation software and the results were normalized to zero oxygen content. Volume of the gaseous sample collected into a sample bag was determined using a wet gas meter.

Liquid samples were analysed on CHNS-O Analyzer FlashEA 1112. The weights of analysed samples ranged between 2 and 3 mg. The device was equipped with an automatic system for dispensing samples. Commercially available standards were used for calibration. Accuracy of basic methods for determination of C, H, N, S, given by the manufacturer was <0.1 % for each element. Elemental analysis provided information on the mass fraction of the total carbon content of the liquid sample. Samples did not contain almost any inorganic carbon. Total carbon content in these samples is therefore identical with the value of total organic carbon (TOC).

From the results of gas analyses, was established the composition of gas mixtures. From the analysis of TOC was seen a decrease of organic carbon in the liquid. From the results of gas analysis was calculated CCE (carbon efficiency = (1 - carbon ratio at the reactor gas outlet / carbon (TOC) at the reactor inlet) * 100).

4. Results and discussion

Four experiments with IPA with various adjustment of the conditions were performed. Basic experiment was carried out with flow rate 2 ml/min concentration of IPA 50 g/l and without addition of catalyst K₂CO₃. In Fig. 3 temperature data from basic experiment with subsequent reduction of flow to 1 ml/min is depicted. In Fig. 3 colors of the curves corresponds with colored arrows that indicate the individual temperatures sensor in the apparatus scheme in Fig. 2. After feeding of IPA solution into supercritical reactor temperature fluctuations occurring at

lower temperatures can be observed. They are probably caused by irregular gas production along with side reactions which take place at low temperatures. With decreasing flow and thus prolonging residence time, temperature rises and fluctuations almost disappear. In Fig. 3 dashed horizontal lines show the time of sampling of the gaseous product.

Complete results obtained from analysis of liquid and gas product are presented in Table 1. From values of TOC can be seen that the biggest drop of carbon content in liquid phase is achieved in the experiment with lower flow rate. This result suggests that for this vertical apparatus longer residence time is the most important factor for a more effective gasification. Lower flow rate results in higher temperatures in the reactor, as previously mentioned, which also contribute to a higher efficiency of the process. Also carbon efficiency at low flow rate was the highest. During the mentioned experiment was produced

as well the largest amount of methane, which was our goal product considering its wide usage.

According to TOC values, the second most important factor in our equipment for SCWG is catalyst addition. Similarly as lower flow rate, catalyst addition results in higher temperatures in supercritical areas, which again help the efficiency of the process. However potassium carbonate increases hydrogen yield in the product gas. It should be mentioned that hydrogen was not as a desired product as methane. Addition of catalyst also prevents other reactions except gasification from taking place. This effect can be confirmed by low amount of higher hydrocarbons, which are pyrolysis precursors, in the produced gas. Low concentration of higher hydrocarbons is also observed in product gas of experiment with lower flow rate. This fact also supports the hypothesis, that longer residence time is one of the key parameter of this technology.

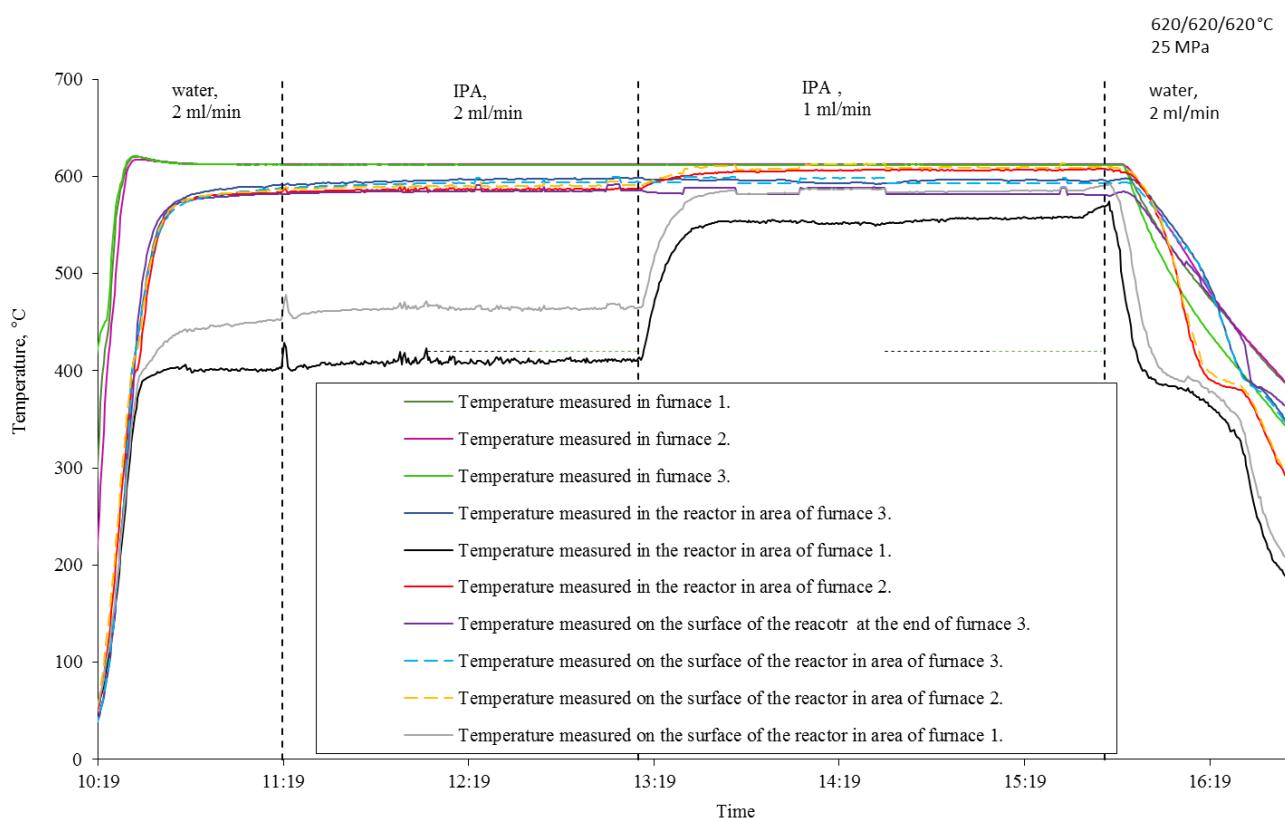


Fig. 3 Temperatures measured during experiment with isopropyl alcohol.

Table 1 Results obtained during hydrothermal gasification of isopropyl alcohol.

C _{IPA} [g/l]	Q [ml/min]	TOC _{in} [g/l]	TOC _{out} [g/l]	H ₂ [vol%]	CH ₄ [vol%]	C ₃ H ₆ [vol%]	C ₃ H ₈ [vol%]	C ₂ H ₄ [vol%]	C ₂ H ₆ [vol%]	CO ₂ [vol%]	CO [vol%]	CCE [%]
50	1	25	9.2	24.1	38.4	1.5	4.3	1.3	8.2	11.7	2.3	49.6
50	2	25	16	33.2	28.6	8.5	9.8	2.9	5.2	5.5	3.5	29.1
50K*	2	24	12	42.4	33.5	0.6	2.6	0.5	2.8	15.3	0	40
75	2	36	23	35.4	26.1	5.1	9.8	2	5.8	5.3	2.9	36.1

*The sample labeled K includes the addition of 5 g/l catalyst K₂CO₃.

Experiment with higher concentration of IPA showed not a significant decrease of TOC value compared to experiments with catalyst or lower flow rate. Production of methane was the lowest form all experiments and the amount of higher hydrocarbons is similar to the basic experiment. Thus increasing concentration of substrate without change of any other parameter is not effective.

5. Conclusions

Effects of flow-rate, concentration of substrate and presence of catalyst were tested on a vertical continuous supercritical gasification apparatus with isopropyl alcohol.

The most positive effect on carbon efficiency and decrease of carbon in feedstock has decreasing flow rate. Thus longer residence time along with higher temperatures in reactor caused both by lower flow rate results in a better conversion of organic matter and desired gasification reaction takes place. This assumption was also confirmed by the low content of higher hydrocarbons in the produced gas.

Another key parameter of this technology is addition of catalyst, potassium carbonate. Results of the experiment are very similar to those from experiment with lower flow rate. However addition of catalyst increases the amount of hydrogen in product gas which was not as desirable as methane. The highest amount of methane in gas was in the experiment with lower flow rate. Product gas in the presence of catalyst contains the lowest concentration of higher hydrocarbons. This fact suggests that the addition of catalyst prevents from forming undesired secondary products such as tar and char. It is important for further experiments with real waste waters where the formation of these products is expected.

Increasing substrate concentration does not have that large impact on the efficiency of the gasification process. However gasification efficiency can be improved by additional optimization of the other parameters such as lower flow rate or catalyst addition.

The data acquired from the experimental results will be used as a pattern for further experiments with real organic waste compounds. Super critical water gasification is a promising future approach to obtain energy from such compounds, but needs more examination due to the process complexity, material and equipment demands.

Acknowledgments

The presented work was financially supported by specific university research MSMT No. 20-SVV/2016.

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