SUPERCRITICAL WATER GASIFICATION IN A VERTICAL CONTINUOUS APPARATUS

[1]ELISKA PURKAROVA, [2]KAREL CIAHOTNY, [3]SIARHEI SKOBLIA, [4]LUCIE ZODEROVA

[1,2,3,4]University of Chemistry and Technology Prague, Department of gas, coke and air protection, Czech Republic
E-mail: [1]purkaroe@email.cz, [2]ciahotnk@vscht.cz, [3]skobljas@vscht.cz, [4]zoderovl@vscht.cz

Abstract- Supercritical water gasification is a thermochemical conversion process, where water under supercritical conditions ($t>374^0$C, $p>22,1$MPa) acts as a solvent, reagent and gasification medium at the same time. In this environment are organic substances converted into gaseous products (methane, hydrogen, carbon oxides etc.) In this contribution is presented the supercritical water gasification technology studied on vertical continuous apparatus using model organic compounds (isopropyl alcohol) and real organic industrial wastes.

Index Terms- Supercritical water gasification, continuous apparatus, organic wastes.

I. INTRODUCTION

The worldwide growing energy demand is leading to the search for new technologies for energy recovery. Hydrothermal gasification technology can potentially gain energy in the form of combustible gases from organic waste streams. [1] [2]

Supercritical water gasification (SCWG) is an allothermic process. This assumption possibly allow this technology to produce a high quality gaseous fuel because the converted matter does not need to be oxidized to provide the heat for process reactions. On the other hand SCWG need external heating which makes the unit more complicated and more expensive. [3]

Water under supercritical conditions dramatically changes its properties. One of the most important changes in this technology is a lower of dielectric constant of water. As a result of this decrease that water behaves as non-polar solvent. By dissolving organic compounds, the interphase barrier is eliminated. Thanks to the absence of the interphase barrier, reactions taking place are homogeneous which helps the gasification process. Good solubility of organics in supercritical water provides effective conversion into gaseous products along with other changed properties as: high diffusivity, low viscosity and low surface tension. These properties help to improve the mass and energy transfer in the reactor. [1] [4]

As previously mentioned water has many roles in this process (reagent, medium, solvent), therefore is convenient to gasify liquid organic wastes. Waste with high moisture content is difficult to dispose by conventional removal technologies (combustion etc.). The conversion of SCWG, unlike the conventional gasification processes, is not affected by the moisture content of the substance that is gasified. [5]

Another advantage of the process is the very simple separation of the gas and liquid products through separation funnel, which provide clean gas of high heating value. Tar and solid particles are separated before the gas leaves the high pressure system. [6]

Main disadvantages of the process are high capital and operating costs. These expenses are caused by extreme temperatures and pressures in the system, which leads to the need of special materials and operating equipment. Also the big quantity of water, which must be heated up and cooled down raise cost of the whole technology. In future problems can be solved due to evolving industrial and material engineering. [7]

SCWG became a popular topic in last few years. There's no commercial unit so far, due to complexity of whole process which is multidisciplinary. But even so a lot of experimental units are operated over the world and a lot of research groups focus their efforts on this technology. Presented experiments and results in this work was based on previous measurements on a horizontal continuous apparatus. [8]

II. EXPERIMENTAL

A. Apparatus and process conditions.

On Fig.1 is shown vertical continuous apparatus for hydrothermal gasification. Volume of the apparatus was 75.3 ml – 40.6 ml was volume of the reactor and 34.7 ml was volume of cold parts of the equipment. As can be seen there are two high pressure pumps ($p<50$MPa) with a flow range of 0.1-9.9 ml/min and volume 400 ml. The first pump was for pumping water and the second for feeding the organics. Reactor was made from stainless steel AISI 316, which was chosen for low cost and acceptable process conditions ($t<600^0$C,$p<30$MPa). Reactor was heated up by three separately controlled furnaces. There wer three thermometers which measure the temperature of each furnace in the space between reactor and the respective furnace. Another four thermometers were on the surface of the reactor, measuring its temperature. And the last three thermometers were in the reactor protected by a stainless steel case. Thermometers in the reactor were purposely situated directly against the first three thermometers on the surface of the reactor aiming to see how efficient was heat transfer in the apparatus. Temperatures were recorded continually by an MS Data Logger COMET MS6D.

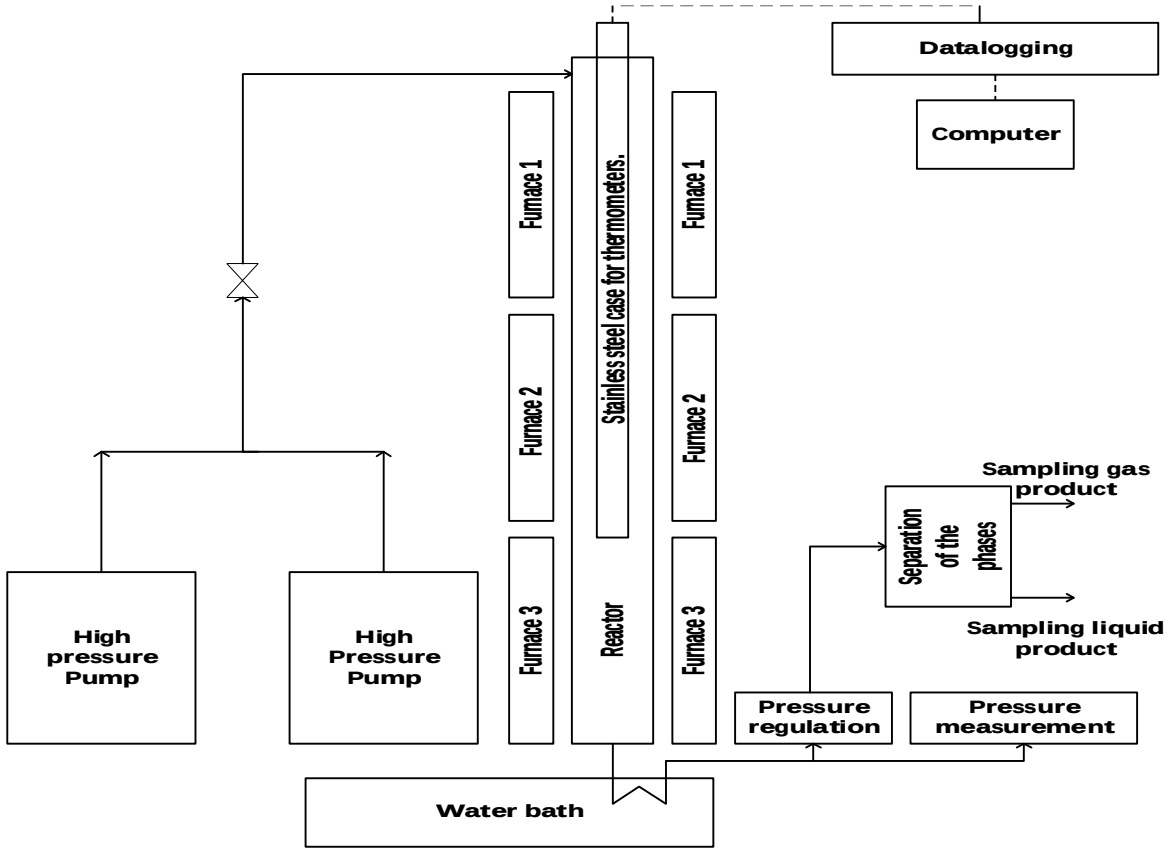


Fig 1. Vertical continuous apparatus for supercritical water gasification.

After heating up the solution cooled down in a water bath, set at 80^0C. At the end was pressure regulator, whose function was also to divide pressured and non-pressured part of the apparatus. Phases of the product were separated then in the separation funnel with bottom valve for liquid product.

B. Analysis.

An HP 6890 chromatograph equipped with two analytical channels was used for the analysis of gas samples. The first channel with flame ionization detector was used for the analysis of hydrocarbons from methane to toluene (C1-C8). The second channel with thermal conductivity detector was used for analysis of permanent gases.

Liquid products are analyzed on elementary CHNS-O analyzer FlashEA 1112 series (ThermoElectronCorporation). The elementary analysis provided the mass ratio of carbon in the liquid sample. There was almost no inorganic carbon present in liquid samples. The value of total carbon therefore agreed with the value of total organic carbon (TOC).

Conductivity of feedstock and liquid samples was measured by conductometer GMH 3430 (Greisinger electronic).

C.Experiments with model compounds.

Isopropyl alcohol (IPA) is chosen as a model compound to obtain basic parameters of the apparatus. IPA did not produce any tar and char, was easy to manipulate and great organic model compound.

At the start of each experiment was the first pump filled with water, than water was pressurized to 25 MPa and directed to the apparatus. Flow rate of the water and consequently of the IPA solution was 2 ml/min. After the whole apparatus was filled with water and pressure in entire system was set to 25 MPa, all three furnaces were set to 620^0C. While the reactor was heating up (about 75 min) was prepared the model compound with concentration of IPA 50 g/l. This concentration corresponded to value of TOC 25 g/l. Than the second pump was filled with the model solution.

After reactor was heated up and all temperatures were stable, reactor was closed by the valve to separate high pressure in the reactor from the pumps. Subsequently the first pump with water stopped and the second pump was pressurized to 25 MPa. In the last step was opend the valve and IPA solution was heading to the reactor. After sufficient amount of time for starting conversion processes and producing of gas has passed, gas and liquid products can be collected. After sampling flow rate was lowered to 1 ml/min to examine the effect of residence time which was according to our previous experience a key parameter for effective gasification. Subsequently the sampling of gaseous and liquid product was repeated.

D.Experiments with real industrial wastes.

As an example of industrial liquid organic waste was used gasification of tall soup from paper industry and gasification of rinse waters from paint shop.

Tall soup is thickened liquid waste from leaching of wood chips with high concentrated hydroxide. So it is

full of organic residues from wood (parts of lignin etc.). For experiment was prepared solution with concentration of 50 g/l which represent value of TOC 32 g/l, the rest of tall soap is water and inorganic. Solution was filtrated before feeding into the pump, because of solid particles which can cause damage to the high pressure pump.

There were obtained 4 different types of rinse waters, whose input properties are depicted in Table I. These waters were gained from different degrees of concentration of rinse water.

Table I. Characteristics of rinse waters.

Sample Number	Conductivity (mS/cm)	TOC (g/l)
1	0,6	2
2	4,3	3,5
3	48,9	17,2
4	145	25,9

As you can be seen concentration of total organic carbon is not very high so the samples were fed undiluted, only filtrated from solid parts. High conductivity points out that these samples contained high concentration of inorganic matter.

Experiments with these solutions were performed under similar conditions as experiments with model solution: i.e. pressure set to 25 MPa, flow rate 2 ml/min, furnaces were set up to lower temperatures 550^0C.

III. RESULTS AND DISCUSSION

E. Experiments with model compounds.

On a Fig 2. temperature data from gasification of isopropyl alcohol are depicted. With decreasing flow rapidly increases temperature in the whole apparatus especially in the area of furnace number 1. This increase of temperature reflected on composition of gas product shown in Table II. The amount of producing methane increases from 29 % to 45 % and also production of carbon dioxide increases. This change in composition is due to longer residence time of model compound in the supercritical area, which provided enough time for gasification reactions to convert carbon from liquid input to gas output.

Another correlation can be seen on the amount of higher hydrocarbons, whose concentration in gaseous product decrease with higher temperatures in reactor.

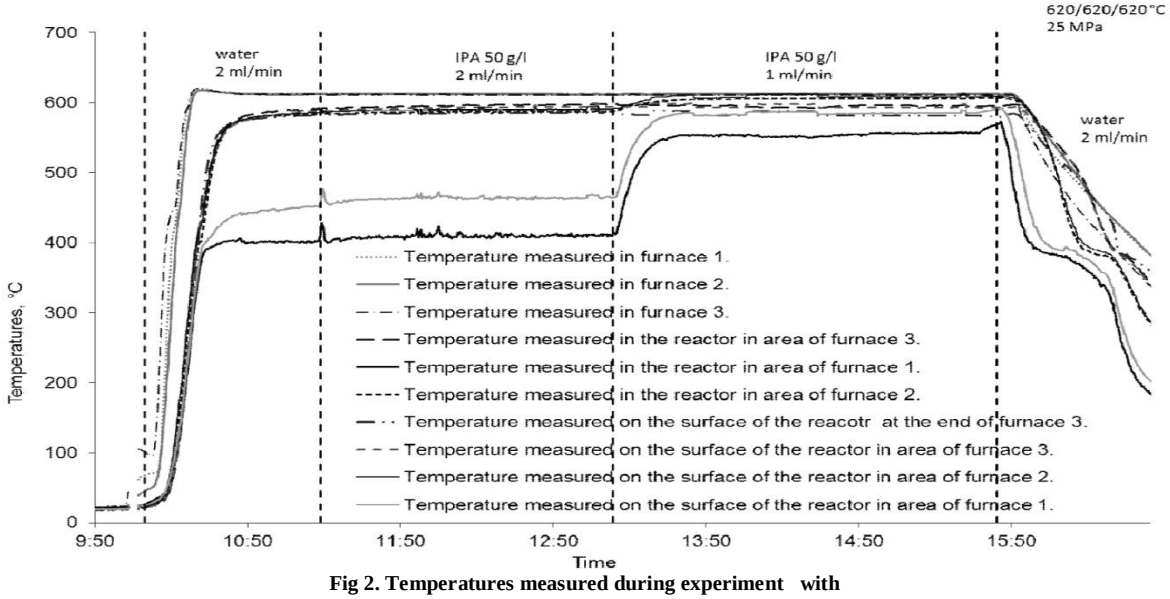


Fig 2. Temperatures measured during experiment with

Due to lower temperatures which enable pyrolysis to take place in the reactor more ethane, ethylene, propane and propene are produced

Table II. Composition of the gas produced during hydrothermal gasification of isopropyl alcohol.

Component of the gas (% vol.)	2 ml/min	1 ml/min
Methane	29	45
Hydrogen	35	20
Carbon dioxide	6	12
Carbon monoxide	4	4
Ethane	5	9
Ethylene	3	2
Propane	10	5
Propene	9	3

F. Experiments with real industrial wastes.

At first will be discussed results of gasification of tall soap. Temperatures data depicted in Fig 3. show that any unexpected anomalies or bigger fluctuations of temperatures did not occurred. Very long duration time of gas sampling (marked in Fig.3 by straight dashed line) demonstrated how low production of gas was. However decrease of the total organic carbon from 32 g/l to 7 g/l in liquid product, would suggest higher production of the gas. isopropyl alcohol.

The missing carbon in the process was in the second liquid phase which eluted after sampling. This phase was dark brown and tar-like, while first liquid product was white and water-like.

In Table III. the composition of the gas showing a higher concentration of higher hydrocarbons (ethane, ethylene, propane, propene) is depicted.

This suggested that pyrolysis was also occurring in the reactor.

Table III. Composition of the gas produced during hydrothermal gasification of tall soap.

Component of the gas	(% vol.)
Methane	23
Hydrogen	24
Carbon dioxide	17
Ethane	7
Ethylene	8
Propane	4
Propene	6

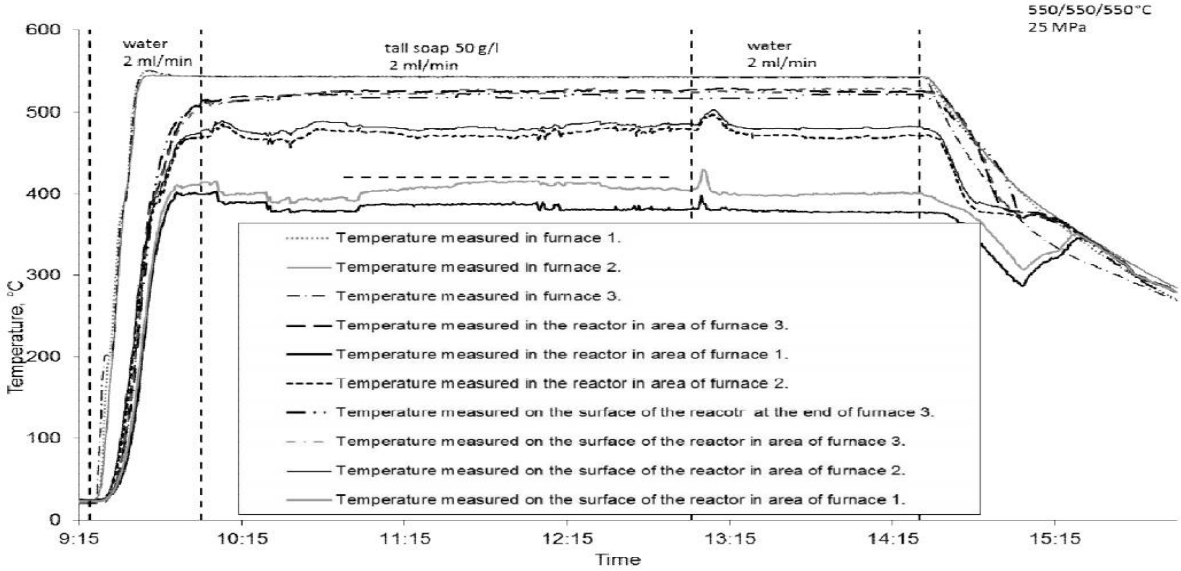


Fig 3. Temperatures measured during experiment with

First two samples of rinse water were gasified without any additional problem. But the concentration of total organic carbon in samples was so low that it was predicated, that gas production would be really low.
In sample number one decrease TOC from 2 g/l to 1.1 g/l with predominantly amount of hydrogen in gas 50 %. Sample number two had very similar results with reduction of TOC from 3.5 g/l to 2 g/l, also mostly with hydrogen in generated gas 41 %.
Sample number three with conductivity 17.2 mS/cm (water has around 0.6 mS/cm) plugged reactor after 15 minutes after starting the pump. The cause of the plugging is most probably huge amount of inorganics, which in very short time stopped dissolving in water, became solids and create deposits of salts in reactor. After this experience we even did not try gasify sample number four with even higher conductivity 145 mS/cm.
Both samples were sent to the analysis of the ions that can be seen in the table IV. In sample three dominate potassium and in sample four dominates sodium.

Table IV. Content of major inorganic in samples of rinse waters.

Ions (mg/l)/sample	3	4
Cl^-	24	118
NO_3^-	18	3826
SO_4^{2-}	290	36675
Mg^{2+}	1	16
Ca^{2+}	4	1
Na^+	278	151500
K^+	32875	348

tall soap.

CONCLUSION

There were performed several experiments on vertical continuous apparatus for purpose of supercritical water gasification. Solution of isopropyl alcohol was gasified at first as model organic compound. This test was carried out for the purpose to test former knowledge about SCWG from experiment on horizontal apparatus. Results agree with our previous experience, that residence time is key parameter of the process. Longer residence time significantly increases the degree of conversion of organic compounds.
Gasification of tall soap was examined without any obstacles, although production of gas was not satisfactory. In the reactor was partly present pyrolysis process which converted tall soap into higher hydrocarbons, but mostly into tar. Tar is an undesired product of gasification. Adding a catalyst could help the more effective conversion. As well as higher temperature and pressure, which were limited by the material of the reactor. For supercritical gasification, would be better Ni-based steel, but they face limitations due to costs.[5]
First two sample of rinse waters were gasified without any bigger success due to low concentration of TOC. Another sample number 3 plugged space of the reactor with high concentration of solid inorganic that started to occur in the environment of the supercritical water. Data from the ion analysis of the sample number 3 and 4 shows very high concentration of alkali slats. It can be concluded that high amount of inorganic ions, upon

which showed high conductivity, is not suitable for super critical water gasification or must be separated from liquid waste. Witch will unfortunately cost additional money. Results from gasification of real waste streams, even though they were not successful, are very interesting and important know-how for future development of technology.

Same as experience with maintenance of the apparatus, which must be done after experiments with real waste waters. Equipment must be cleaned properly (acetone, toluene) and deposits of salt must be removed otherwise, they will cause additional problems in the reactor in future. Finally can be said, that SCWG has potential as technology for gaining energy from liquid organic waste. But for commercial application is presently limited due to material costs. Moreover it should be noted that all materials, even expensive ones, are still subject to corrosion. With better material could technology also achieve better process conditions (higher temperatures and pressures), which helps conversion reactions and production of desired gas. To the future it would be the best to invent some low-cost new material for high pressures and temperatures. [8]

REFERENCES

[1] Kruse A. in book: Biomass Gasification and Pyrolysis, chap. 7, p. 229, Prabir Basu (2010).

[2] PETERSON, A. A., et al. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. Energy & Environmental Science. 2008, vol. 1, no. 1, p. 32-65.

[3] ZHANG, L., XU, C., CHAMPAGNE, P. Overview of recent advances in thermo-chemical conversion of biomass. Energy Conversion and Management. 2010, vol. 51, no. 5.

[4] Kruse A.: J. Supercrit. Flu. 47, 392 (2009).

[5] KRITZER, P. Corrosion in high-temperature and supercritical water and aqueous solutions: a review. J. Supercrit. Fluids, 2004, vol. 29, no. 1-2, p. 1–29.

[6] C HE, W., et al. Application of hydrothermal reaction in resource recovery of organic wastes. Resour., Conserv. Recycl., 2008, vol. 52, no. 5, p. 691–499.

[7] PETERSON, A. A., et al. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. Energy & Environmental Science. 2008, vol. 1, no. 1, p. 32-65.

[8] SUSANTI, R. F., et al. Continuous supercritical water gasification of isooctane: A promising reactor design. International Journal of Hydrogen Energy. 2010, vol. 35, no. 3.

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