

HYDROTHERMAL GASIFICATION OF REAL WASTEWATERS FROM INDUSTRIAL VARNISHING

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Currently a global problem is finding a solution for the enormous energy demand. Additionally worldwide there are many production plants that varnish their products. During this process are formed various types of wastewaters, which are usually hard to treat due to their chemical composition and high moisture content. One of the technologies that can utilize liquid wastes along with the production of energetically usable gases is supercritical water gasification (SCWG). This paper presents results from hydrothermal gasification of real waste streams from industrial activity, which produces radiators. These wastewaters were gasified in a vertical continuous laboratory apparatus using supercritical water as medium.

Key words: real wastewaters, varnishing, hydrothermal gasification, continuous apparatus.

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1. Introduction

With increasing industrial production all over the world is formed high amount of wastes and wastewaters. Thus, new technologies for waste removal are investigated. Moreover the issue of global energy demand growth needs to be faced. Taking these issues into consideration technologies, which can simultaneously deal with both problems are preferred. One of such processes is supercritical water gasification (SCWG) that is a thermochemical conversion process, where the organic substances convert into gaseous products in water under high pressures and temperatures. It means that hydrothermal gasification can remove organic matter from waste streams and turn it into energetically usable gases [1, 2].

1.1. Hydrothermal gasification

As the name suggests, hydrothermal gasification process takes place in water under supercritical conditions referred to as supercritical water (SCW). Water becomes critical fluid when it reaches its critical temperature (374 °C) and pressure (22.1 MPa) [3].

Water under supercritical conditions dramatically changes its properties. One of the most important changes in this technology is a decrease of the dielectric constant of water. As a result water behaves as a non-polar solvent. So unlike water at normal conditions SCW dissolves organic compounds instead of inorganic compounds. Nevertheless, the fact, that inorganic compounds, especially salts are not soluble in supercritical water can lead to problems, mainly when real waste streams are gasified. High amount of inorganic salt in gasified matter can form deposits in technology equipment and cause plugging [2, 3].

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 enables their effective conversion into gaseous products. SCW has other changed properties such as high diffusivity, low viscosity, low surface tension and low density. These properties also help to improve the mass and energy transfer in the reactor [4, 5].

As previously mentioned SCWG is a thermochemical conversion process, which includes also pyrolysis, liquefaction, dry gasification and combustion. Among them, gasification is one of the most favorable processes since the products can have different applications such as heat, electricity and transportation. However, dry gasification is not a suitable technology for wet or liquid substances. High moisture content is an issue since water has to be evaporated before the substance can be gasified [3, 6].

Supercritical water has many roles in the process of hydrothermal gasification, specifically it serves as reagent, medium and solvent at the same time. Therefore is suitable to gasify liquid organic wastes. SCW gasification, unlike the conventional gasification processes, is not affected by the moisture content of the substance that is gasified. Actually higher waste moisture content is much more preferred [7].

Another advantage of the process is the very simple separation of the gas and liquid products through a separation funnel, which provide clean gas of high heating value. Tar and solid particles are separated before the gas leaves the high pressure system [1, 3].

The main disadvantages of the process are high capital and operating costs. These expenses are caused by extreme temperatures and pressures in the system, which lead to the need of special materials and operating equipment. Also the big quantities of water, which must be heated up and cooled down, raise the cost of the whole technology. In future problems can be solved with the help of evolving industrial and material engineering [1,8].

Supercritical water gasification (SCWG) is an allothermic process. This assumption possibly allows 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 needs external heating which makes the unit more complicated and more expensive [7, 9].

SCWG has become a popular topic in the last few years. There is no commercial unit so far, due to the complexity of the whole process which is multidisciplinary. But even so a lot of experimental units operate all over the world and a lot of research groups focus their efforts on this technology [2, 9].

2. Experimental part

Hydrothermal gasification tests were carried out in a vertical continuous apparatus. All the gasification products were analyzed. As gasification substances were used various types of wastewaters from varnishing of radiator components.

2.1. Waste waters from production of radiators

Wastewater from radiators manufacturing are formed due to the process of varnishing individual components. Four samples of waste streams were obtained. Below the names and the steps in the process, where each wastewater is formed are listed:

K: Wastewater from the biofilter.

K-OV: Wastewater from the main varnishing plant, which goes to the evaporator for preconcentration.

K-K: Wastewater from the main varnishing plant, which were concentrated on an evaporator 5 times.

K-L: Water from varnish remover bath.

Samples were sent to the input analysis and the results in Tab. 1 showed increasing content of both organic and inorganic substances. From the results acquired after the analysis of the first two samples (K and K-OV) can be expected low gas production due to low input TOC. The other two samples showed very high conductivity due to the presence of inorganic salts, which can cause the formation of deposits during the transition into the supercritical state. Prior to filling the pump the samples were filtered through a filter paper.

Tab. 1 The results of the initial analysis of samples of wastewaters from varnishing of radiator components.

	pH	Specific conductivity (mS/cm)	TOC (g/l)	CHSK (g/l)
K	7.1	0.6	1.4	4.4
K - OV	6.2	4.3	1.5	6
K - K	6.3	48.9	17.2	45
K - L	13.1	145	25.9	79.9

Filtration was carried out to prevent solid particles flowing through the teflon ceiling of the pump, which could cause scratching. As result, pump could leak and would not be able to keep the required high pressures.

2.2. Vertical apparatus

In Fig. 2 the scheme of a vertical continuous apparatus for hydrothermal gasification is shown. The material (water / wastewaters) was dispensed into the reactor by one of the high pressure pumps HPP 5001, with the flow range from 0.1 ml/min to 9.9 ml/min and a maximum pressure of 50 MPa. Feed of material from the pump to the reactor was performed via a steel capillary. The capillary is equipped with a needle valve, which serves to separate the high pressure part from the pumps. This valve is used when switching from one pump (water) to the other (wastewaters). The body of the reactor is made of AISI 316 steel. The reactor is placed in a steel tube, which serves as protection for the heating segments, especially in case of reactor damage. The steel tube also equally transfers heat from the heating elements. Thus, improving the temperature profiles of the reactor. The tube is isolated on the top and bottom with Sibral to prevent the stack effect.

The body of the reactor is heated by three separately controlled heating segments (furnaces). 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 increased.

Temperatures in the reactor are monitored by ten temperature sensors, whose location is indicated by colored arrows in Fig. 1. Temperatures are recorded by MS Data Logger COMET MS6D and obtained curves of temperatures dependence on time are displayed online.

2.3. Experimental set up

The experiments begun by filling the first pump with water and then pressurizing the pump, with closed needle valve, to 30MPa. Thereafter, the needle valve was opened and the pump filled (flow 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 was provided at the end by a back pressure regulator. After the pressure was stabilized, the furnaces were set to 550 °C each. Simultaneously when turning on the furnaces temperature logging from the temperature sensors in the system started. Immediately after heating started the cooling bath heating was turned on. While the apparatus heated up (about 75 minutes) the second pump was filled with the filtered wastewater. After heating the reactor and the temperature was stabilized the needle valve was closed. Then the first pump with water was stopped, and was subsequently depressurized.

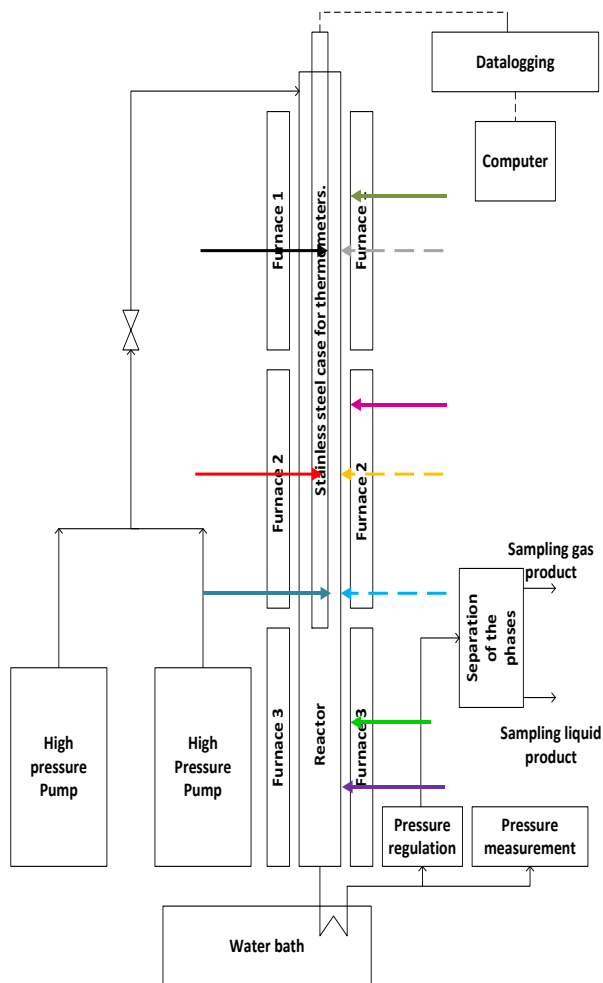


Fig.1 Scheme of the vertical continuous apparatus.

The second pump with the wastewater for the conversion was pressurized and led into the apparatus as in the case of water. After a sufficient amount of time the beginning of gasification was indicated 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 had been stabilized flow and temperature values in the system, samples were taken from separation flask for analysis.

During the sampling periods, a sampling bag was used to collect the produced gas. The accumulated liquid that flowed during this time was collected at the end, and transferred into the sampling vials. At the end of each experiment, water was pumped during the cooling period.

For the analysis of gas samples was used a gas chromatograph HP 6890, equipped with two analytical channels GC-FID/TCD. Helium was used as carrier gas. Calibration of the chromatograph was performed by gas standards, under the same conditions.

Liquid samples were analysed on CHNS-O Analyzer FlashEA 1112. For instrument calibration were used commercially available standards. 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. The value of the total

carbon 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 (CCE from TOC). From the results of gas analysis was calculated carbon efficiency (CCE).

3. Results and discussion

Three experiments with wastewaters from varnishing of radiator components were performed. In the following Figure (Fig. 2) can be seen the temperature curves from the gasification of wastewater sample from the manufacture K-OV. In Fig. 2 colors of the curves corresponds with colored arrows that indicate the individual temperatures sensor in the apparatus scheme in Fig. 1. Figure of temperatures from experiment with sample K is not showed due to its similarity with sample K-OV. Temperature fluctuation caused by produced gas was negligible. However they were higher than in sample K, which had almost flat lines. That proves increasing gas production, which corresponds with increased concentration of organic material input for the sample K-OV. However, the conversion of the material with such a low TOC content of the two samples is highly inefficient.

Conversion of the wastewater sample K-K looked more promising due to higher TOC content. However, as is evident from the temperature data showed on Fig.3 the experimental test did not take place without complications. Significant rise in temperature upon entry of the substrate into the apparatus indicates the formation of a large deposition of inorganic material. The amount of inorganic compounds was so large, that blocked the apparatus. Clogging of the reactor prevented the flow of the substrate, which caused a dramatic increase in temperatures. During experiment was possible to sample only the liquid phase. Unfortunately due to clogging the gaseous phase was not sampled. After this experiment tests with sample K-L were canceled due to an even higher value of specific conductivity of 145 mS/cm. Thus were the mentioned samples sent for analysis of chosen anions and cations, and the results are summarized in Tab. 2. The purpose of this analysis was to identify the major inorganic ions since they are undesirable substance for the process. In the process of SCWG organic compounds undergo the gasification process. Therefore their determination within the frame of this work was not necessary. Taking this into account ion balance is not reached in Tab. 2 due to missing organic ions. Sample K-K contained the largest amounts of potassium. Other minor components such as nitrites and nickel were not detected. In the case of K-L sample was observed a rapid increase in the concentration of inorganic ions, except for potassium, which was significantly less than in sample K-K. Variation of ions depends on from which part of manufacture they are come from (using both inorganic and organic chemicals). Nevertheless, without any doubt wastewater sample K-L would have caused similar or even worse damage to equipment as sample K-K.

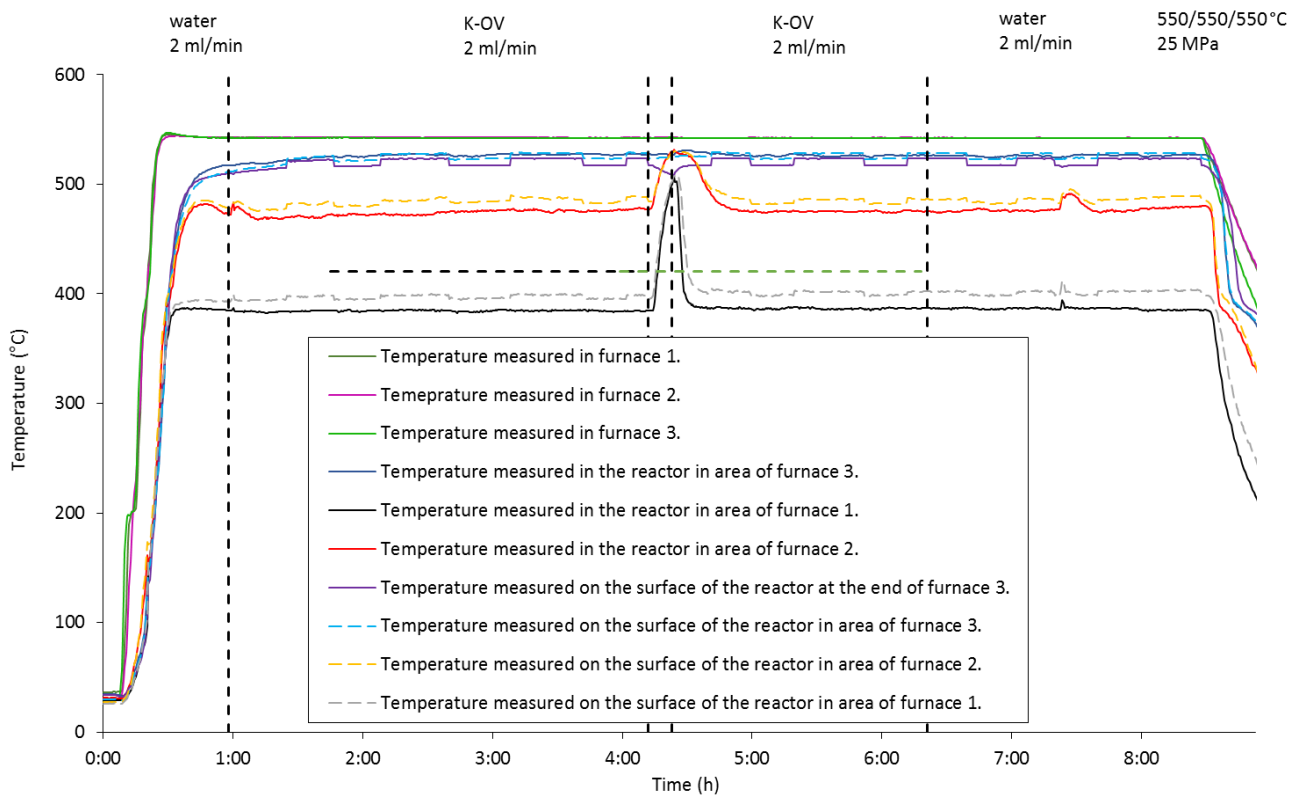


Fig.2 Temperatures measured during experiment with wastewater sample K-OV.

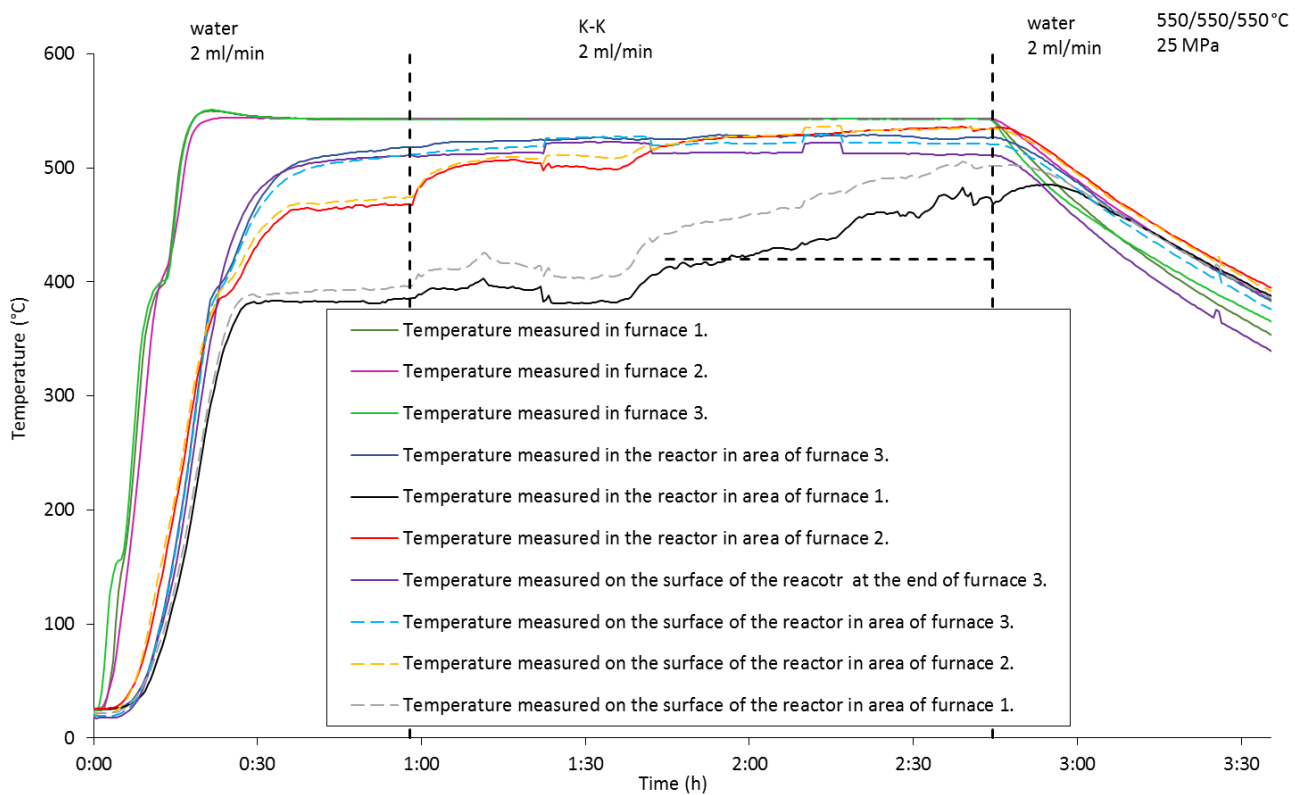


Fig.3 Temperatures measured during experiment with wastewater sample K-K.

Tab. 2 The results of chosen ions analysis of samples K-K and K-L.

Ion concentration (mg/l)	K-K	K-L
Chlorides	23.6	118
Nitrites	<0.03	3.1
Nitrates	18.4	3823
Sulphates	290	36675
Magnesium	1.1	16
Calcium	3.7	1.1
Sodium	278	15150
Potassium	32875	348
Nickel	<0.02	0.7
Chromium	0.4	0.2
Iron	1.7	0.6

Tab. 3 Results obtained during hydrothermal gasification of real wastewaters from varnishing of radiator components.

	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 (%)	CCE from TOC (%)
K	2.1	1.3	52.2	14.1	0.2	0.1	0.7	1.0	25.4	6.0	36.4	38.1
K-OV	3.8	1.9	40.8	5.3	1.3	0.3	3.5	0.8	30.4	3.8	9.7	50.0
K-K	19.0	7.0	-	-	-	-	-	-	-	-	-	63.2

From the values of both CCE is seen that there is a degradation of the carbon from the original solution (CCE from TOC), but carbon is not converted into product gas (low CCE) instead forms carbon deposits in the reactor. From the experimental test with sample K-K no sufficient gas volume needed for analysis was obtained. Taking into account high CCE from TOC probably means that sample K-K behaved similarly as sample K-OV, i.e. that organic carbon convert into solid particles instead of product gas.

4. Conclusions

Several experiments with real wastewaters from varnishing of radiator components were performed. The wastewaters were obtained from different steps of manufacture process. Therefore the obtained samples had different composition and characteristic. Waste streams were gasified on the laboratory vertical continuous apparatus via hydrothermal gasification.

Testing of hydrothermal conversion of waste water from the production of radiators shows that SCWG technology can only treat samples with lower content of inorganic salts (with specific conductivity in units mS/cm). Substrates having a specific conductivity of 50 mS/cm cannot be gasified via SCWG because there is a relatively rapid clogging of the reactor by inorganic salts secreted from the substrate. This problem can be solved by removal of inorganic ions from wastewaters, but then the technology will be more expensive and difficult to operate.

Obtained produced gas samples contain gas with the main components H₂ and CO₂. Higher hydrocarbons

The results of product analysis are summarized in Tab. 3. Results of sample K show that gasification of organic carbon is not efficient due to low content of organic matter. On the other hand, due to favorable composition of matrix, similar conductivity to tap water, only supercritical water gasification reactions takes place. That is confirmed by low concentrations of higher hydrocarbons. Also from similar values of CCE a CCE from TOC can be said that converted organic carbon was really converted into gas product.

Gas produced by the conversion of sample K-OV is predominantly made up by hydrogen and carbon dioxide. It is seen that there is a higher hydrocarbon formation, suggesting the presence of other ongoing processes except SCWG (e.g. pyrolysis), which can form undesirable secondary products.

in sample K-OV suggest other processes takes places during SCWG (e.g. pyrolysis). Samples with higher conductivity produce little gas (org. substances partially pass into the tar), and cause the formation of deposits in the reactor.

To achieve higher efficiency and high gas production the content of organic substances dissolved in water is key parameter. Substrates with low organic substances (TOC) are not economical suitable to treat via SCWG, since the formation of gas in these cases is very low.

Hydrothermal gasification is an interesting and promising future approach to obtain energy from wastewaters, but needs more examination due to the process complexity, material, equipment demands and the addressed problems in this work.

References

- Schmieder, H., et al., *Hydrothermal gasification of biomass and organic wastes*. The Journal of Supercritical Fluids, 2000. **17**(2): p. 145-153.
- Kruse, A., *Hydrothermal biomass gasification*. The Journal of Supercritical Fluids, 2009. **47**(3): p. 391-399.
- Kruse, A. and N. Dahmen, *Water – A magic solvent for biomass conversion*. The Journal of Supercritical Fluids, 2015. **96**: p. 36-45.
- Basu, P., *Biomass gasification and pyrolysis: practical design and theory*. 2010: Academic press.
- Yoshida, T., Y. Oshima, and Y. Matsumura, *Gasification of biomass model compounds and real*

- biomass in supercritical water*. Biomass and Bioenergy, 2004. **26**(1): p. 71-78.
6. Zhang, L., C. Xu, and P. Champagne, *Overview of recent advances in thermo-chemical conversion of biomass*. Energy Conversion and Management, 2010. **51**(5): p. 969-982.
 7. He, W., et al., *Application of hydrothermal reaction in resource recovery of organic wastes*. Resources, Conservation and Recycling, 2008. **52**(5): p. 691-699.
 8. Peterson, A.A., et al., *Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies*. Energy & Environmental Science, 2008. **1**(1): p. 32-65.
 9. Purkarová, E., et al., *Supercritical water gasification of isopropyl alcohol on vertical continuous apparatus: process conditions*. Paliva 2016. **9**(4): p. 126-131.