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Valorization of Waste Solvents through Supercritical Water Gasification

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The supercritical water gasification of various organic species belonging to the groups of organic acids, aldehydes, ketones, alcohols and phenols, has been studied as a possible waste disposal method for polluted water stream produced in industries and laboratories. Gasification has been investigated using a 200 cm^3 down flow reactor working continuously at 24 MPa and 660 °C. Supercritical water gasification (SCWG) is effective for the syngas production at very high conversion rate for all the species investigates, but phenol. Phenol, when mixed with other species, has an inhibitory effect of the radical chain gasification mechanism that dramatically reduced the gasification performance. Moreover, the effect of acetic acid concentration and the effect of molecular structure of three organic acids on the gasification performance were studied.

1. Introduction

Industrial processes, laboratories, hospitals and other activities produce a huge amount of organic liquid waste. Such waste liquids include wastewater contaminated with toxic chemicals, solvents, oils, heavy hydrocarbons and tars for which purification costs are excessive. Some of these wastes fall into the category of hazardous waste. In many cases, waste liquids at low water content are burned as fuels in incinerators designed for solids disposal or properly designed for liquid firing alone. In many cases, disposal by purification or incineration is not effective, economical and environmentally sound. Moreover, liquid waste incineration has several drawbacks for safety and environmental reasons. Air pollution, disease extension and social problems encourage research towards new technologies that are able to overcome drawbacks of incineration. Supercritical water based processes could be one of such technologies, if some technical problems were solved.

Supercritical water based processes were developed since the '70s of the last century to exploit the extraordinary properties that water exhibits above its critical point (22.1 MPa and 374°C): a drastic decrease in pH, dielectric constant, ionic product, viscosity and thermal conductivity (Brunner 2014). At these conditions, SCW essentially acts as a non-polar fluid with solvation properties resembling those of low-polarity organic fluids and is able to dissolve organic matter breaking down molecules. Properties of supercritical water have been exploited for the treatment of organic matter through two main processes: supercritical water gasification (SCWG) and supercritical water oxidation (SCWO). The main idea of SCWG is to benefit from the special properties of SCW as solvent and reaction partner for fast hydrolysis of organic matter and consequent production of pressurized gases (mainly H_2, CH_4 and CO_2). High solubility of the intermediates in the reaction medium significantly inhibits tar and char formation that are one of the main drawback of conventional gasification. Indeed, the reactive species originating from organic matter are solvated in water and consequently the reaction rate of polymerization to unwanted products like tar and char is reduced. Altogether, this leads to high gas yields at relatively low temperatures.

SCWG has been mainly studied for the valorization of biomasses such as ligneous-cellulosic materials, sewage sludge and wastes from agro-food industry. However, until now this technology has not found an industrial scale operating application (Kruse, 2009).

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This work proposes a study of SCWG of various organic solvents commonly produced in industries and laboratories. Particularly, SCWG of alcohols, organic acids, phenol aldehydes, ketones and mixtures of them has been performed in order to exploit the capability of SCWG as a waste disposal process.

2. Experimental apparatus and procedure

Gasification experiments were carried out in a 200 cm^3 continuous down flow reactor. Details of the apparatus and procedure can be found in a previous paper (Caputo et al. 2016a). Wall temperature was set at 660°C, which is the maximum value at which the reactor can work. The reactor was fed from the top side with two streams: organic solvent with 2.5 mL/min flow rate and a water stream with flow rate of 5 mL/min. These flow rate values allowed working at residence times of 128 s. The system was pressurized by adjusting the back-pressure regulator. The products were cooled down to room temperature by means of a coil immersed in a cooling bath. After cooling and expansion of the products to atmospheric pressure, the output stream of the reactor was passed through a liquid/gas separator.

A typical gasification run lasted 12 hours comprising heating up of the reactor and washing at the end of the experiment. This long run time allowed verifying the reliability of the plant to work in continuous manner. Flow rate of the produced gas was monitored continuously by means of a gas mass flow meter; gas composition was measured at regular intervals by means of online gas chromatography. Each run was repeated two times. During each run, gas flow rate was monitored continuously and data were integrated over time. Gas composition was measured at constant intervals of one hour.

3. Materials and methods

Ethanol, acetic acid, phenol, ethyl acetate and acetone purity 99% were used.

The composition of the product gas was determined using an Agilent 7890B gas chromatograph to quantify all the gaseous species including H_2, CO_2, CO, CH_4, C_2H_4 and C_2H_6. The GC was equipped with a thermal conductivity detector, sampling valve and a silica capillary column (SUPELCO, Carboxen-1010 PLOT). Argon (99.999%) was used as carrier gas.

The carbon content in the liquid product was analyzed using a Shimadzu total organic compounds analyzer (TOC-L CSN). The performance metrics used for the definitions of the product yields in this study are Gasification Efficiency (GE), that measures the conversion of the feedstock to product gases and can be described as the ratio between the sum of the masses of product gases and that of the feedstock and the carbon efficiency (CE) that measures the mass percentage of carbon converted from the initial organic matter towards gases products, according to the formula in Eq(1) and Eq(2):

$$GE\ (\%) = \frac{Gas\ Mass\ Flow\ Rate\ Out}{mass\ of\ organic\ matter\ in\ the\ feed} \cdot 100 \tag{1}$$

$$CE\ (\%) = \frac{moles\ of\ carbon\ in\ the\ gas\ product}{moles\ of\ carbon\ in\ the\ feed} \cdot 100 \tag{2}$$

H_2 yield (%) is defined as the mass percentage of hydrogen converted from the initial biomass towards gas molecular hydrogen.

4. Results

In order to verify the potentiality of SCWG as a disposal method for organic solvents, gasification of five common organic solvents has been performed. At first, each solvent has been gasified at 1 wt. % concentration in the feed to know the gasification efficiency and gas composition of each of them in the absence of interaction with other components. Afterwards, a mixture of the five solvents with a total concentration of 5 wt. % was gasified. In all cases, gasification was performed at a reactor wall temperature of 660 °C, pressure of 24 MPa and residence time of 128 s because in previous work (Caputo et al. 2016b) it was show the efficacy of gasification at these conditions.

The desired amount organic substance was suspended in water (at concentration of 1 or 5 wt. %) and pumped at flow rate of 2.5 mL/min. A second water stream was pumped into the reactor at a flow rate of 5 mL/min causing the effective concentration entering the reactor to be 0.33 or 1.67 wt. %.

Results are summarized in Table 1. Gasification is effective for acetic acid, ethanol, ethyl acetate, and acetone with very high values of GE and CE. Particularly, in the case of acetone and ethanol GE values are higher than 100%. This is not surprising, because H and O atoms that are present in the product gas come not only from the conversion of the organic matter that is present in the feed, but also from the reaction of water molecules. In these cases, CE is a better parameter to express the conversion of the organic matter, because the reacting water does not influence it. It is worth to note that in the case of acetone, conversion of carbon is total (CE=100%). In the case of ethanol, CE is not very high (68%), whereas hydrogen is completely converted.

For what concerns the gas product composition, depending on the substance a different behaviour is observed. Acetic acid and acetone give rise to a gas composed mainly by methane and carbon dioxide and with a low hydrogen grade. On the contrary, hydrogen concentration is very high in the case of ethanol (75 %). Ethyl acetate has an intermediate behaviour with hydrogen at 14% and methane at 39.6%.

Phenol has a behaviour completely different from the other solvents. Indeed, conversion is poor in term of both GE and CE. Particularly, carbon efficiency is very low (9.17%).

The SCWG of a mixture of the five organic solvents reflects the resistance to gasification of the various components. A GE value of 61.8 % and a CE value of 47.15 % was obtained which is intermediate between the vales obtained for phenol and the other components.

Table 1: Gasification performance of five solvents and of a mixture of them at 660 °C, 24 MPa, residence time 128 s.

	Acetic Acid	Ethanol	Phenol	Ethyl Acetate	Acetone	Mixture of five components
Concentration in the feed	1 wt.%	1 wt.%	1 wt.%	1 wt.%	1 wt.%	5 wt.%
GE (%)	91.55	122.75	19.33	96.18	127.65	61.81
CE (%)	94.72	68.92	9.17	86.38	100.0	47.15
H_2 YIELD (%)	5.67	139.10	23.66	12.33	5.46	11.87
TOC (mg/L)	4.32	93.79	1916.50	21.96	107.50	3055.00
Gas product composition (mol %)						
H_2	5.65	75.17	56.24	14.34	5.16	20.47
CO	0.00	0.00	0.00	0.00	0.00	0.66
CH_4	50.88	8.06	21.23	39.62	66.09	33.17
CO_2	43.47	16.77	22.54	31.22	28.75	40.26
C_2H_4	0.00	0.00	0.00	8.18	0.00	2.52
C_2H_6	0.00	0.00	0.00	6.65	0.00	2.92

Hypothesizing a linear gasification behaviour of the five components in the mixture, an ideal GE and CE can be calculated by using the following expressions:

$$GE\ \%_{MIX\ IDEAL} = \sum_i GE_i X_i$$

$$CE\ \%_{MIX\ IDEAL} = \sum_i CE_i X_i$$

where GE_i and CE_i are the gasification and carbon efficiencies of each component when it is gasified alone, and Xi is its mass fraction in the mixture.

In Figure 1 the experimental values of GE and CE of the mixture are compared with the ideal values.

As clearly shown in Figure 1 (left), both parameters are lower of about 30% with respect to the calculated ideal values. Thus, the presence of phenol, which is among the various components the more resistant to gasification, strongly reduces the capability of SCWG to efficiently convert the organic matter to valuable gases. Weiss-hortala et al. (2010) observed a similar behaviour during the gasification of glucose in the presence of phenol. They found that a mixture 1 % glucose+1 % phenol produces the half quantity of gas than that produced by the two species separately.

Another useful comparison can be made between the total organic carbon (TOC) values of the liquid residue obtained after gasification. Figure 1 (right) shows the TOC of the 5 wt.% mixture, that has a value of 3055 mg/L, and the TOC of the ideal mixture, obtained as the sum of the TOC values for the single component that has a value of 2144 mg/L. This latter value is 30% lower than the former one. Thus, there is a strict correspondence between the analysis on the gas phase and that on the liquid phase, which confirms the role played by phenol as gasification inhibitor.

The resistance of phenol to gasification is known from the literature: it is caused by the stability of the aromatic ring and the absence of oxygen in the molecule (Yong 2013). Moreover, phenol is a strong radical scavenger that reduces the reactivity of the radical chain reaction that characterize SCWG at high temperature. (Di Leo et al. 2007; Weiss-hortala et al. 2010). Castello et al. (2014) studied a glucose/phenol mixture at different weight ratio of phenol from 0 to 30 %. Their results cannot be directly compared with that of this study because they were obtained at a much lower temperature of 400 °C. Answering to the question: can phenol be «considered as a sort of inert, or does it play a real inhibitory effect on glucose gasification? », they found that phenol seems to behave as a sort of inert in terms of syngas production.

According to these authors, the presence of phenol in a mixture reduces the amount of gas produced proportionally to the amount of phenol that is present in the mixture, because phenol does not gasify, but is converted to liquid products.

We argue that this behaviour is likely true at low temperature at which conversion of phenol to gas product is very low and the reaction mechanism is still influenced by ionic reactions in the solution. On the contrary, working at 660°C only free radical reaction occurs and thus, we observed a significant amount of gas produced from phenol (Table 1), but the effect played by phenol as radical scavenger reduces the overall amount of gas produced by other organic components in a manner that is more than proportional to the phenol concentration in the feed mixture.

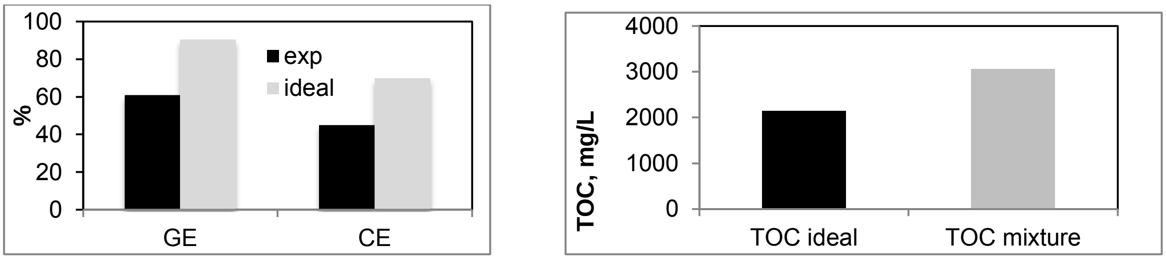

Figure 1: Comparison of the GE and CE (left) and TOC (right) obtained during SCWG of a 5 wt.% mixture of acetic acid, ethanol, ethyl acetate, acetone and phenol and the ideal values calculated as linear combination of the values obtained in the gasification of the single components.

Overall, these data show that the molecular structure of the organic matter has a strong effect both on conversion and gas composition, even when SCWG is carried out at severe conditions (660°C and 25 MPa).

In order to examine in more depth, the relationship between molecular structure and gas composition, the gasification behaviour of acetic acid has been performed and compared with that of formic acid and tartaric acid that differ for the number of carboxylic groups and methyl groups.

Results are summarized in Table 2. As it can be observed, for all three compounds the only products of gasification are methane, carbon dioxide and hydrogen, while carbon monoxide is never formed. In the case of acetic acid, the product gas is composed mainly by methane and carbon dioxide and a small quantity of H_2. The presence of CH_4 and CO_2 as main gas products confirm the reaction mechanism Eq(3) proposed by (Chakinala et al. 2013):

$$\mathrm{CH_3COOH} \rightarrow \mathrm{CH_4} + \mathrm{CO_2} \qquad (3)$$

in which hydrogen extraction from carboxylic group is favoured, that produces equimolar quantity CH_4 and CO_2, with respect to C-H scission that would result in polymerization and formation of coke. The effect of NaOH as catalyst of the gasification of acetic acid has been studied. From the literature (Guo et al. 2011) it is known that inorganic salts exerts catalytic effect on SCWG, enhancing gas yield and H_2 formation. NaOH as solid crystals at 0.1 wt. % concentration has been added to the reactor feed containing acetic acid at 1 wt. %. As shown in Table 2, in this case NaOH has no beneficial effect of the gasification performance of acetic acid.

Table 2: Gasification of three carboxylic acids at 660 °C, 24 MPa, residence time 128 s.

	Acetic Acid	Acid acetic + 0.1 wt.% NaOH	Formic Acid	Tartaric Acid
GE (%)	91.55	86.24	100.06	110.73
CE (%)	94.72	91.31	99.9	96.54
H_2 YIELD (%)	5.67	1.11	74.33	72.53
TOC (mg/L)	4.32	8.05	1.0	9.10
		Product gas composition (mol %)		
H_2	5.65	1.20	42.27	36.00
CO	0.00	0.00	0.00	0.00
CH_4	50.88	55.29	0.0	4.77
CO_2	43.47	43.52	57.73	59.19

NaOH increase the rate of water gas-shift reaction that produces hydrogen from carbon monoxide and water according to the Eq(4):

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \tag{4}$$

As a matter of fact, acetic acid decomposition does not produce carbon monoxide. Thus, the catalytic effect of NaOH cannot be exerted in the particular case of acetic acid. Thus, this behaviour confirms the prevalent reaction mechanism based on hydrogen extraction from carboxylic group that favours CH_4 and CO_2 formation and does not form carbon monoxide.

In the case of formic acid, a complete gasification was obtained in term of both GE and CE. At the bottom of the separator, a clear liquid was recovered with a TOC value below the detectable limit of 1 mg/L. The product gas is composed by hydrogen and carbon dioxide.

The gas composition indicates that the reaction mechanism follows a decarboxylation route Eq(5):

$$HCOOH \rightarrow CO_2 + H_2 \tag{5}$$

which is favoured with respect to the dehydration route Eq(6):

$$HCOOH \rightarrow CO + H_2O \tag{6}$$

that would produce carbon monoxide instead of carbon dioxide (Yu and Savage, 1998).

Finally, in the case of tartaric acid, the product gas is very similar to that obtained with formic acid, but with the formation of a small amount of methane (4.7 %). Because the molecule of tartaric acid can be view as the combination of two glycolic acid molecules, and because from the literature (Klingler and Vogel 2007) it is known that this compound through gasification forms methanol, the small amount of methane derives from the rupture of the -OH bond of methanol and formation of the radical $–CH_3$.

4.1 Effect of the concentration of organic matter in the feed.

Previous experiments have been performed at a relatively low concentration of organic matter in the feed (1 wt. %). Although, working at low concentration is useful to obtained preliminary results at laboratory scale, this low concentration is impractical for an industrial disposal process.

Indeed, to reach high plant productivity and authothermal conditions for SCWG, concentration of about 20 wt.% should be used (Fiori et al. 2012). Unfortunately, at this concentration value the quantity of gas product was to much high to be handled by our plant. Indeed, when the gas product flow rates increases, instability in the down flow section of the plant is observed that produces strong oscillation of the pressure and noise.

Thus, in order to verify the effect of the concentration on the performance of the gasification, a set of experiments at a maximum of 10 wt. % concentration of acetic acid in the feed was performed.

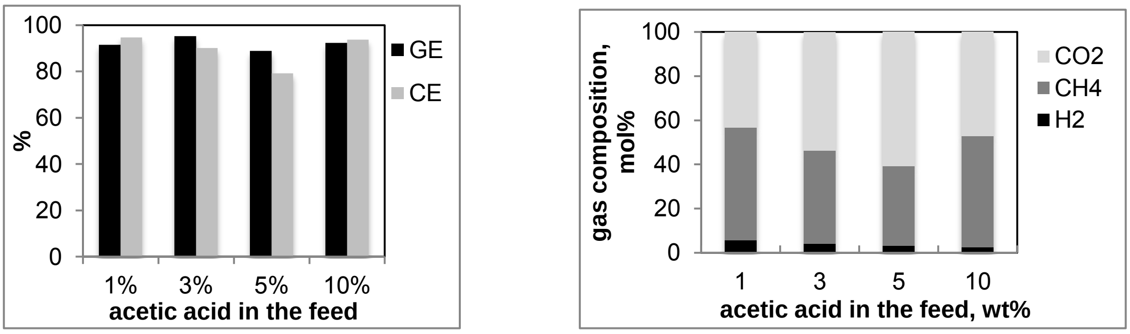

Figure 2: Effect of concentration of acetic acid on the SCWG performance at 660 °C, 24 MPa, residence time 128 s. GE and CE (left), gas product composition (right).

As shown in Figure 2, GE and CE were high at all the concentration investigated and the gas product composition was not significantly influenced by the concentration. A poorer performance at 5 wt. % is likely due to experimental uncertainty.

On average, the gas product is composed of 50 % CH_4, 45 % CO_2 and 5 % H_2. After separation of carbon dioxide from the product gas, a syngas composed of about 90 % methane and 10 % hydrogen would be obtained. It is worth to note that the absence of carbon monoxide and other noxious gas such as NOx, that are usually obtained from conventional gasification. Thus, SCWG can be proposed as method for disposal of organic solvents contained in water streams at high concentration with very high conversion value and valuable syngas recovery.

5. Conclusions

Supercritical water gasification of various organic species diluted in a water, belonging to the groups of organic acids, aldehydes, ketones, alcohols and phenols, was successfully performed in a continuous reactor working over day with input slurry having up to 10 wt. % concentration. It was shown that SCWG is effective for the syngas production at very high conversion rate for all the species investigates, less for the phenol. It is worth to note the absence of carbon monoxide and other noxious species such as NO_x in the product gas, which are usually obtained from conventional gasification. Thus, SCWG can be proposed as a method for disposal of organic solvents contained in water streams.

Phenol when mixed with other species has an inhibitory effect of the radical chain gasification mechanism that dramatically reduced the gasification performance. Longer residence time and selective catalysts should be considered to improve conversion of polluted water streams that eventually contain high quantity of phenols.

Reference

Brunner G., 2014, Hydrothermal and Supercritical Water Processes, Elsevier, Amsterdam, the Nederlands.

Caputo G. et al., 2016a, Experimental and fluid dynamic study of continuous supercritical water gasification of glucose. Journal of Supercritical Fluids, 107, 450–461, Available at: http://dx.doi.org/10.1016/j.supflu.2015.09.022. DOI: 10.1016/j.supflu.2015.09.022.

Caputo G. et al., 2016b, Supercritical water gasification of microalgae and their costituents in a continuous reactor. Journal of Supercritical Fluids, 118, 163-170, Available at: http://dx.doi.org/10.1016/j.supflu.2016.08.007. DOI: 10.1016/j.supflu.2016.08.007.

Castello D., Kruse A. & Fiori L., 2014, Low temperature supercritical water gasification of biomass constituents : Glucose / phenol mixtures. Biomass and Bioenergy, 73, 84–94, Available at: http://dx.doi.org/10.1016/j.biombioe.2014.12.010. DOI: org/10.1016/j.biombioe.2014.12.010.

Chakinala A.G. et al., 2013, Supercritical water gasification of organic acids and alcohols : The effect of chain length. The Journal of Supercritical Fluids, 74, 8–21, Available at: http://dx.doi.org/10.1016/j.supflu.2012.11.013. 1 DOI: 0.1016/j.supflu.2012.11.013.

Fiori L., Valbusa M. & Castello D., 2012, Supercritical water gasification of biomass for H2 production : Process design. Bioresource Technology, 121, 139–147, Available at: http://dx.doi.org/10.1016/j.biortech.2012.06.116. DOI: 10.1016/j.biortech.2012.06.116.

Guo Y. et al., 2011, Gasification of two and three-components mixture in supercritical water : Influence of NaOH and initial reactants of acetic acid and phenol. International Journal of Hydrogen Energy, 37(3), 2278–2286. Available at: http://dx.doi.org/10.1016/j.ijhydene.2011.10.074. DOI: 10.1016/j.ijhydene.2011.10.074.

Klingler D. & Vogel J. B. H., 2007, Hydrthermal reactions of alanine and glycine in sub-supercritical water. Journal of Supercritical fluids, 43, 112-119, Available at: http://dx.doi.org/10.1016/j.supflu.2007.04.008. DOI: 10.1016/j.supflu.2007.04.008.

Kruse A., 2009, Hydrothermal biomass gasification. Journal of Supercritical Fluids, 47(3), pp.391–399.

Di Leo G.J., Neff M.E. & Savage P.E., 2007, Gasification of Guaiacol and Phenol in Supercritical Water. Energy &Fuels, 2136(12), 2340–2345.

Weiss-hortala E. et al., 2010, Influence of phenol on glucose degradation during supercritical water gasification. The Journal of Supercritical Fluids, 53(1–3), 42–47, Available at: http://dx.doi.org/10.1016/j.supflu.2010.01.004. DOI: 10.1016/j.supflu.2010.01.004.

Yong T.L.Y., 2013, Reaction Pathways of Phenol and Benzene Decomposition in Supercritical Water Gasification. Journal of the Japan Petroleum Institute, 56(5), 331–343.

Yu J. & Savage P.E., 1998, Decomposition of Formic Acid under Hydrothermal Conditions. Ind. Eng. Chem. Res., 5885(97), 2–10.