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Supercritical
Water Oxidation

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Supercritical Water Oxidation

by

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ABSTRACT

The supercritical water oxidation process and its uses in environmental protection are discussed. A pilot scale supercritical water reactor is described. The results of supercritical water oxidation of 4 mg/l, 190 mg/l and 8 % glucose and 1 % ethanol solutions are reported. The oxidation of the 8 % glucose solution is at a much higher concentration than in previously reported work Under suitable supercritical conditions essentially 100% of these materials can be oxidized to carbon dioxide and water. Organic acids such as acetic acid are shown to be intermediates in the oxidation of ethanol and glucose. The higher the residence time in the supercritical water oxidation reactor and the higher the temperature, above the critical temperature, the greater the degree of oxidation and the faster its occurrence. Applications of the supercritical water oxidation process are discussed. Work is also being done on fouling of reactor surfaces and corrosion in supercritical water reactors. No evidence of fouling or corrosion has yet been observed in the reactor.

ACKNOWLEDGMENTS

Financial support for this research has come from the Sustainable Forest Management Network, the Science Council of British Columbia (through a grant to NORAM Engineering and Constructors Ltd.), NORAM Engineering and Constructors Ltd. and PAPRICAN (through a faculty research associates grant to Richard Branion). NORAM has granted $20,000 per year for five years to Richard Branion and Steven Rogak in support of this work. This grant has been matched by an NSERC Industrial Partners Grant. NSERC Operating Grants to Steven Rogak and Daniel Fraser have also contributed to the support of the supercritical water oxidation project. This financial support is gratefully acknowledged, without it the work could not have been done.

We are particularly indebted to NORAM who, in addition to being the largest financial contributor, also did most of the equipment engineering. NORAM staff have assisted with the construction of the equipment, with its start-up and continue to assist in operating it. The project was conceived by Edward Hauptmann and the NORAM staff engineer assigned to the project was and still is Stuart Gairns. Stuart has been assisted by Joseph Kish, John Lota and Simon Overton.

Steven Rogak and Dan Fraser, Assistant Professors of Mechanical Engineering at UBC and their students Paul Teshima, Danijela Filopovic, Xu Li and Majid Bazargan have provided much needed assistance on many occasions as have Alex Podut and Davor Baros.

PRAXAIR has generously donated the oxygen required for use in this project.

INTRODUCTION

Pulp and paper mills and their waste water treatment processes generate a variety of waste products (e.g. waste fibre, waste activated sludge, etc.) some of which may be difficult to get rid of (e.g. toxic sludges that cannot be landfilled). There are also waste emissions from this, and other industries, which contain contaminants that are resistant to conventional biological treatment and which, for various reasons, cannot be discharged to the environment. For these some alternative form of treatment for the destruction of the offending compounds is necessary. Supercritical water oxidation is one such process.

In some industries (e.g. the pulp and paper industry) there is a trend towards eliminating all water discharges so as to avoid environmental contamination and any accompanying regulatory problems. This means that internal recycle has to be practiced. If an operable zero liquid effluent process can be developed this may mean that those contaminants formerly sent to the wastewater treatment system will have to be purged from the recycle streams. Supercritical water oxidation is a process that has the potential for the purging of these materials and returning purified water to the process.

At temperatures and pressures above its critical point (374°C and 22.1 MPa) water exists as a single phase fluid known as supercritical water. Supercritical water has properties that are different from those of the better known forms of water, i.e. liquid water, ice and steam. For example supercritical water tends to behave like a non-polar solvent for various materials (hydrocarbons, benzene, etc.) which are more or less immiscible with liquid water, which is a polar solvent. Conversely things such as inorganic salts which are quite soluble in polar, liquid water are not very soluble in non-polar, supercritical water.

Oxygen under supercritical water temperatures and pressures is readily soluble in supercritical water. If then oxygen is supplied to a solution or suspension of some organic material in supercritical water that material should be oxidized to simple inorganic materials like carbon dioxide and water. For example for ethanol (C_2H_5OH)

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad [1]$$

This suggests that a variety of difficult to degrade organic materials could be disposed of by using supercritical water oxidation. These materials include a variety of environmentally harmful compounds such as dioxins and furans (Modell 1989, Modell et al. 1992, McBrayer, R.N., Griffith, 1996). Supercritical water oxidation then can be viewed as a sort of incineration process. It differs from the usual atmospheric pressure, combustion type incineration in that oxygen is used instead of air so production of undesirable air pollution in the form of oxides of nitrogen (NO_x) is avoided. Moreover the reaction, as we use it, takes place in a long, narrow, tubular reactor. Thus bypassing of un-oxidized reactants through the well controlled reaction zone is close to impossible. The reaction products are not, as they are in conventional incineration, diluted with a lot of nitrogen. Moreover they are contained within the reactor piping. Thus it is possible that they can be recovered, if they have commercial value, or be directed to some downstream destruction process. Modell et al. 1996 suggest that the carbon dioxide product could be recovered for sale. Since supercritical water has a high density relative to the combustion gases formed in conventional incineration, the size of equipment for supercritical water oxidation is smaller. Energy recovery in supercritical water oxidation is also easier than it is in incineration.

Because of the complete miscibility of oxygen with supercritical water it is unlikely that mass transfer of oxygen to the material to be oxidized will be the rate limiting step in the overall oxidation process. This can be the case in some competitive processes such as wet air oxidation.

Critics of the supercritical water oxidation process complain that it is unworkable as an environmental cleanup device due to fouling of the reactor surfaces with inorganic salts that precipitate as the water, in which they were dissolved, goes supercritical. This is a real, but not insurmountable problem (see McBrayer and Griffith 1996) and is being addressed by other members of our supercritical water research group (Teshima, Rogak and Teshima and Rogak, Rogak, Filopovic). Another criticism is that supercritical water in the presence of oxygen is very corrosive. In our research we are monitoring corrosion in the reactor, but so far have not observed any.

A frequent initial response of the uninitiated to the use of supercritical water oxidation is that since it is a high temperature process, heat will have to be added and that such heat addition would make it prohibitively expensive. Provided that here is a sufficient amount of oxidizable material in the waste stream being processed (e.g. around 7 % solids in waste activated sludge) there is enough heat recoverable from the oxidation process to heat the incoming fluid to above supercritical temperatures. At even higher concentrations of oxidizable solids, by-product steam could be generated. At lower concentrations it may be possible to add some low cost fuel to the waste stream so that sufficient heat would be generated to achieve supercritical temperatures. In any event several cost estimation studies have indicated that supercritical water oxidation costs compare favourably with those of the more widely used incineration process (Modell et al. 1992, McBrayer and Griffith, 1996).

RESEARCH OBJECTIVES

The objectives of this research project are to build a pilot scale, continuous, supercritical water oxidation process. Then to use it to destroy a variety of waste materials that cannot be discharged untreated to the environment and to use the laboratory scale process information as the basis for the design of full industrial scale supercritical water oxidation reactors. We are in the process of doing studies on this oxidation process to determine the level of fouling of heat transfer and reactor surfaces caused by precipitation of inorganic salts that are insoluble in supercritical water, the heat transfer characteristics of supercritical water, the corrosivity of supercritical water and the reaction kinetics of supercritical water oxidation of various materials. The kinetic study is the one of most interest to the Sustainable Forest Management Network.

In this kinetic study we began by investigating the supercritical oxidation of simple compounds to test the ability of the equipment to perform its intended functions and for us to evolve an operating procedure. Ethanol was chosen as one model compound to be tested because -

- it is oxidizable
- it is soluble in water and it vapourizes
- other researchers have investigated its destruction in a supercritical water oxidation process (Helling) so we can compare our results to theirs.

Glucose was chosen as another model compound to be tested because -

- it is oxidizable and is readily soluble in liquid water,
- it is presumably not soluble in supercritical water (it isn't soluble in steam)
- other researchers have investigated its destruction in a supercritical water oxidation process (Holdgate) so we can compare our results to theirs.
- it is the monomer of polysaccharides such as cellulose, hemicellulose and starch all of which can be found in a variety of waste water streams and in recycle streams in pulp and paper manufacturing processes.

We will test supercritical water oxidation of starch and some soluble form of cellulose (e.g. carboxmethyl cellulose) to see if these materials exhibit any tendency to char, thereby fouling and possibly plugging the reactor, and if they do char is the resultant char oxidizable under supercritical water conditions?

One of our goals is to demonstrate the use of this process for the oxidation of waste activated sludge. This material is difficult to dispose of because before final disposition by incineration or land filling it has to be dewatered from about 2 - 3 % solids to between 25 and 40 % solids.. The dewatering process requires the addition of expensive polymeric coagulants and flocculants. The required dosages of these polymers could be much reduced if the material could be supercritically oxidized economically. Dewatering of the sludge to around 7 - 10 % solids should permit sufficient heat to be generated during the oxidation to supply the heat necessary to bring the sludge to supercritical temperatures.

Another projected study is to use supercritical water oxidation to purge undesirable organic matter from papermachine whitewater. This organic matter is dilute, so heat will have to be supplied to achieve supercritical temperatures. We are planning experiments in which we will add a cheap, supplementary, liquid fuel to the white water to generate supercritical temperature conditions. A similar sort of study is contemplated for the destruction of undesirable organics and hydrogen sulfide in kraft pulp mill foul condensates.

EQUIPMENT DESIGN AND CONSTRUCTION

The supercritical water oxidation process itself is only a part of this research project. The other components are studies of solids deposition on heat transfer surfaces (Professor Rogak) and of heat transfer characteristics under supercritical conditions (Professor Fraser). For these studies a supercritical oxidation reactor was not required. Thus the first stage of the equipment construction consisted of building a supercritical water generator and a test section.

The necessary pressure was generated by a high pressure, positive displacement pump. The heat necessary to achieve supercritical temperature conditions was obtained by passing an electrical current through the tubing of the reactor preheaters. Figure 1 is a flow sheet of this part of the supercritical water oxidation process, which was built before the reactor was installed and which is designated the Phase I System.

Since supercritical water oxidation occurs at elevated temperatures and relatively high pressures a number of problems had to be addressed in designing the research equipment in terms of safety of operation.

Materials and Safety Precautions

Since temperatures and pressures in the supercritical oxidation process are relatively high the materials used in this process's reactors must be able to resist the stresses generated. Moreover the process can be corrosive thus corrosion resistant materials must be chosen. We chose to use Inconel tubing for the reactor tubing. The reactor fittings were of stainless steel, the other fittings are of Inconel. The fittings have to be carefully connected to the tubing (torque wrench) because the coefficients of thermal expansion of the two types of metal are not the same. The system was pressure tested to 70 MPa.

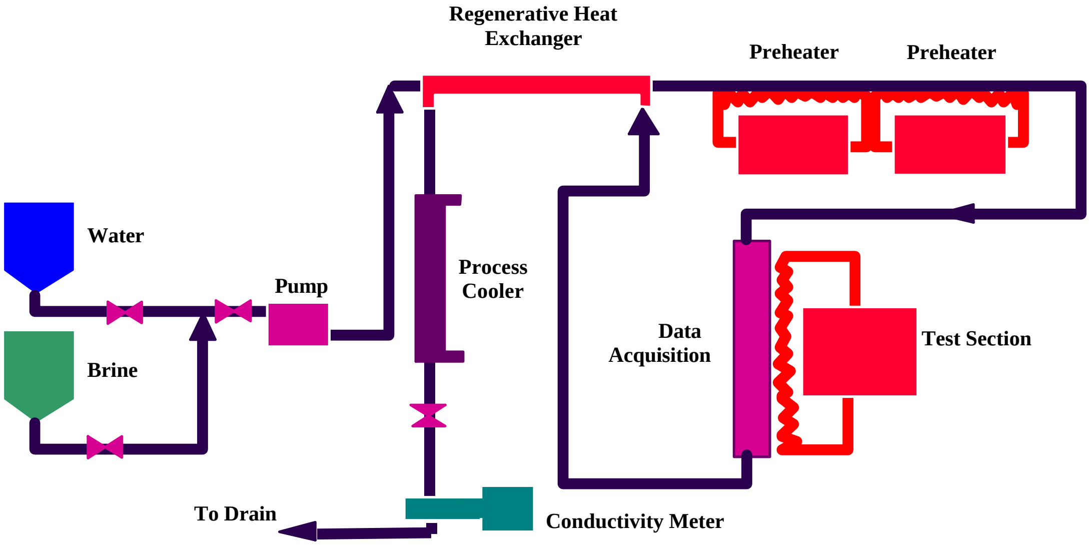


Figure 1. Phase I SCWO Flowsheet

Operators of the supercritical water oxidation process unit are protected from any leakages that may occur by sheet metal spray shields. The system is equipped with temperature and pressure sensors which activate if the temperature and/or pressure exceed preset limits, shutting down the system and sounding alarms. Operators must receive a training program and a users manual for operating the supercritical water oxidation system has been prepared.

Corrosion will be monitored by inserting wires made of the materials being tested into the reactor and examining them periodically for evidence of corrosion (e.g. weight loss of wires and loss in reactor tube wall thickness). Whenever the tubing has to be dismantled it is examined for any signs of corrosion by a corrosion metallurgist. Effluent samples are analyzed for metal ion concentrations to see if there is metal dissolution resulting from corrosion. To date no such evidence has been found of either corrosion or fouling of the reactor.

Reactor

The reactor is a tubular reactor 116 m in length with an inside diameter of 6.2 mm (outside diameter = 9.5 mm). Liquid flow rates of up to 0.033 l/s can be employed, leading to liquid residence times of 105 s and up. Temperatures up to 600°C can be accommodated.

Oxygen (kindly supplied free by Praxair) for the reactions is obtained in a tank having a capacity of 200-220 kg. The pressure in the supply tank is 1378-1723 kPa, this is raised to supercritical water pressure and above by a three stage air driven compression system. The oxygen flow rate can be monitored and controlled so as to give the desired ratio of oxygen to reactants. Oxygen can be mixed with the feed stream to be oxidized before the preheaters, or can be injected just before the entrance to the reactor, after the preheaters.

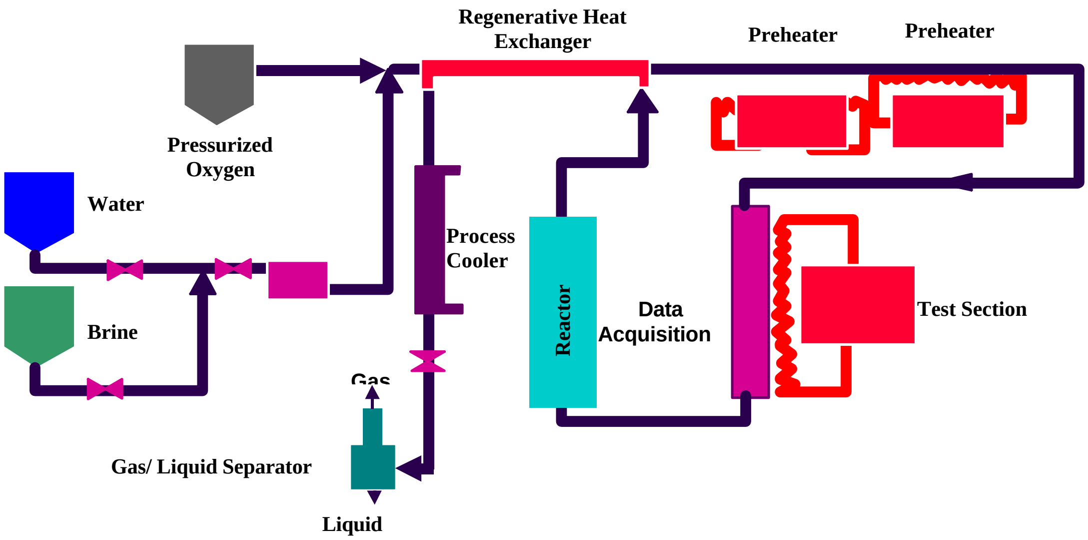


Figure 2. Phase II Flowsheet of SCWO Process Including Reactor

Instrumentation

Samples for analysis of the reactants and products in supercritical water oxidations can be withdrawn from the entrance to the system, the entrance to the reactor, the exit from the reactor and at five intermediate points in the reactor. Product gas samples can also be obtained at the reactor outlet. There are sensors for measuring absolute pressure, pressure drop, temperatures inside the reactor and the temperatures of the reactor's outside wall surfaces. All temperature and pressure data are logged automatically and processed by a computer.

Figure 2 is a flow sheet of the system including the reactor. This system is referred to as the Phase II System.

RESULTS and DISCUSSION

Preliminary Experiments with Glucose

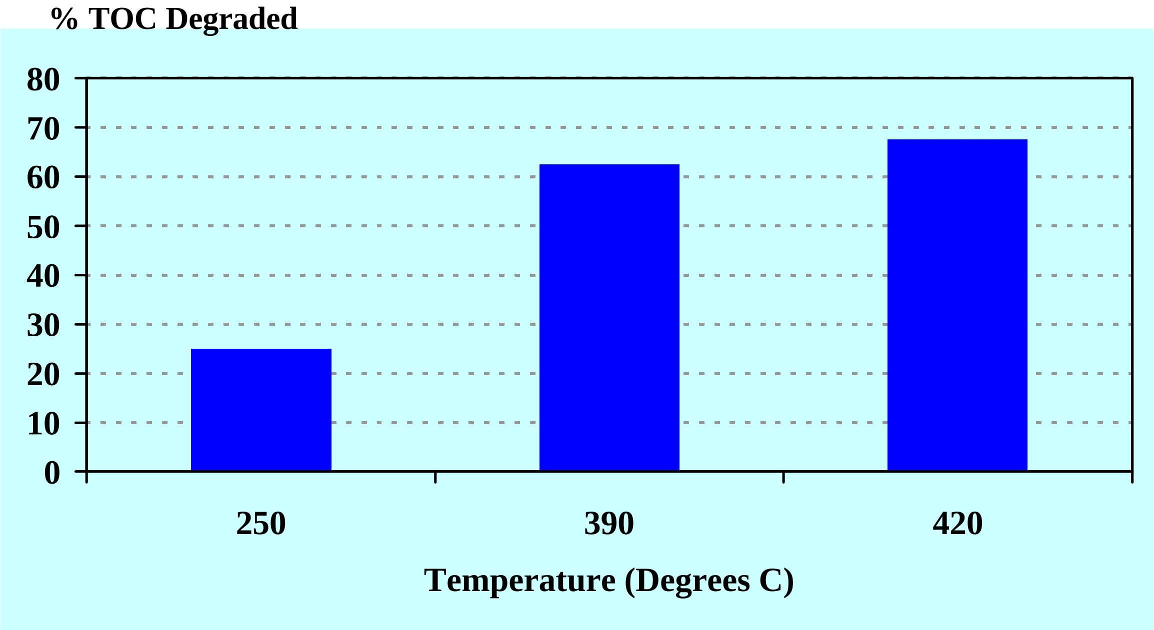
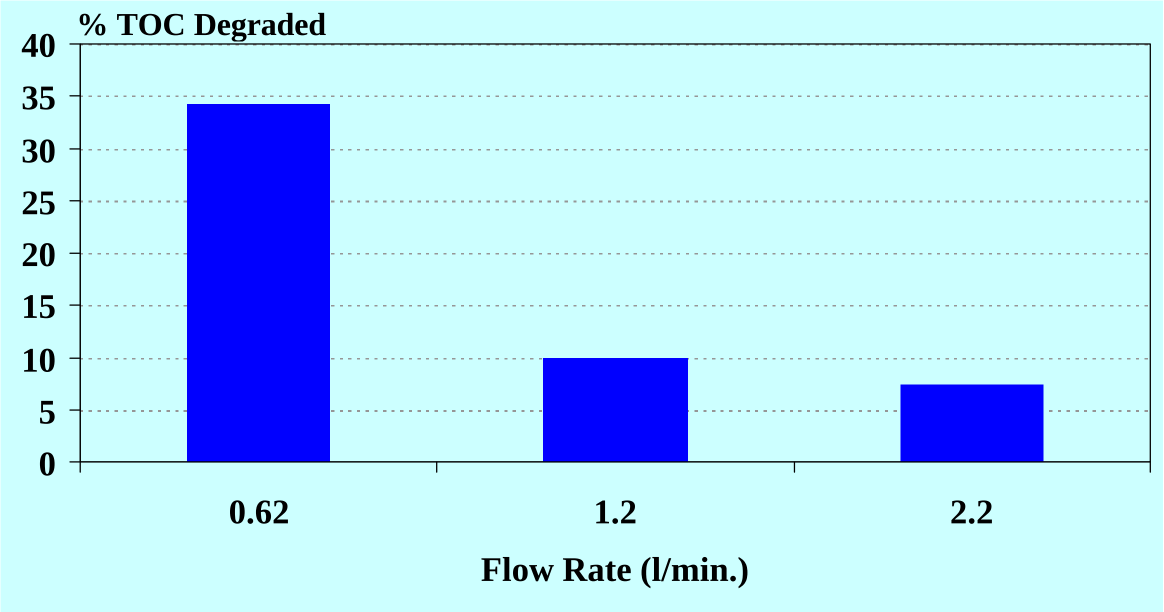


Figure 3. TOC Removal at Various Temperatures for Oxidation of Glucose
Glucose Concentration in Feed :4 mg/l

Using the Phase I system, before the oxygen delivery system was installed, the destruction of glucose as a model test compound was studied. To deal with the lack of an oxygen delivery system we saturated the test water with oxygen and chose a glucose concentration (4 mg/l) that was stoichiometrically compatible with that dissolved oxygen concentration. In all of the tests reported in this document the pressure was 3600 psi (24.9 MPa).

Figure 3 shows the results of this experiment in which it was observed that 25 % of the added glucose (as measured by total organic carbon concentration(TOC)) was destroyed at 250° C (subcritical), 62 % at 390°C (≈ critical) and 69 % at 420°C (supercritical). Initially the glucose solution had a pH of 5.8. At 250°C the pH of the outlet solution was 4 indicating that some acidic intermediate products had been produced. At the higher temperatures the pH of the outlet solutions was the same as that of the influent feed solution.



Glucose Concentration in Feed :190 mg/l, Temperature 393-420 °C

Another trial was done using the Phase I equipment at a higher glucose concentration (190 mg/l). At that concentration there was insufficient oxygen for complete oxidation of the glucose. Tests were done at several feed flow rates. The results are presented in Figure 4 wherein it can be seen that as the flow rate increased (residence time decreased) the amount of TOC degraded decreased. Nevertheless TOC was degraded in the absence of sufficient oxygen, thus some form of pyrolysis reaction must have been occurring. In these tests the pH dropped from an inlet value of 6.5 to an outlet value of 3.5, see Figure 5. This again suggests the formation of some acidic intermediates.

Experiments with Ethanol

After the oxygen delivery system and the reactor had been installed, the Phase II system was complete so the supercritical water oxidation process was tested using ethanol as the material to be oxidized. Destruction of ethanol was determined by measuring the total organic carbon and ethanol (gas chromatography) concentrations in the inlet to the reactor, the outlet from the reactor and at an intermediate sampling point that was 6.1 m downstream from the reactor entrance. The inlet ethanol concentration was 1 % by volume; the amount of oxygen supplied was 100 % in excess of the stoichiometric requirement. Oxygen was introduced before the preheaters, thus some oxidation could occur during passage of the reactants through the preheaters and test section.

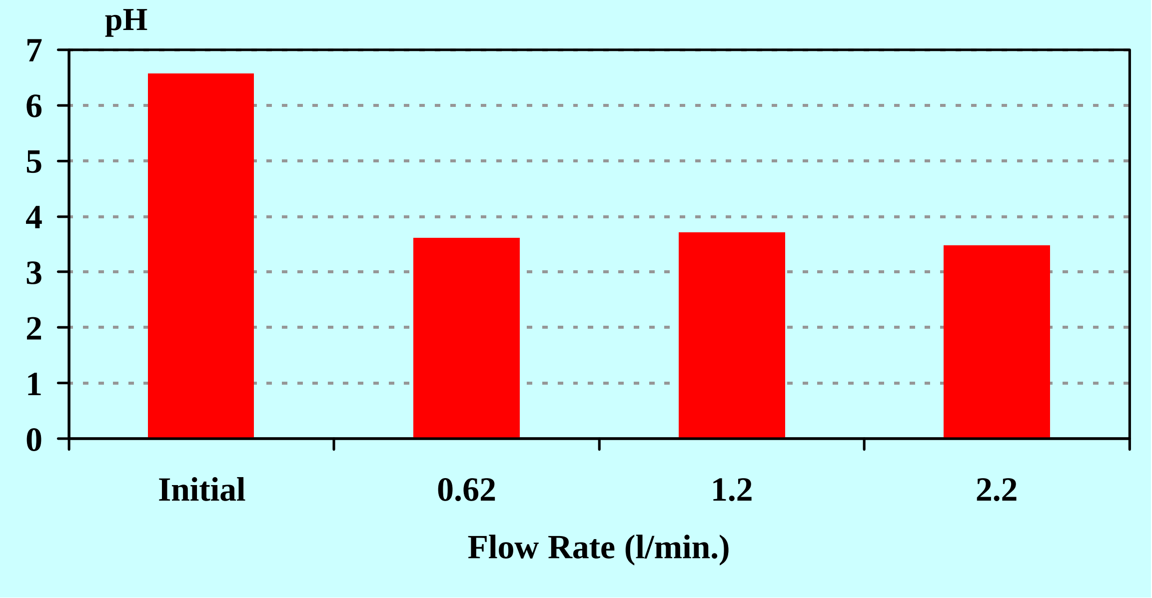


Figure 5. Effluent pH at Various Flowrates for Oxidation of Glucose
Glucose Concentration in Feed :190 mg/l, Temperature 393-420 °C

Figure 6 provides the results of one set of experiments using ethanol. In it it can be seen that in the temperature range 408 - 420°C approximately 80 % of the ethanol, expressed as total organic carbon, was destroyed. At the two higher temperature ranges almost 100 % destruction was noted. Temperature ranges are specified here because the reactor is more or less adiabatic. Thus as ethanol is oxidized heat is released and, since the reactor is insulated, the temperature at the reactor outlet can be higher than at the inlet if too much heat is generated, or lower if too much heat is lost through the reactor walls and insulation.

Figure 7 plots % ethanol converted vs. temperature range. In all of the temperature ranges investigated almost all of the ethanol was converted to something else. For the two higher temperature ranges almost all of the total organic carbon was destroyed also, thus implying that the ethanol had been completely oxidized to carbon dioxide and water. In the lowest temperature range most of the ethanol was completely oxidized but some of it remained in the form of an organic intermediate, perhaps acetic acid.

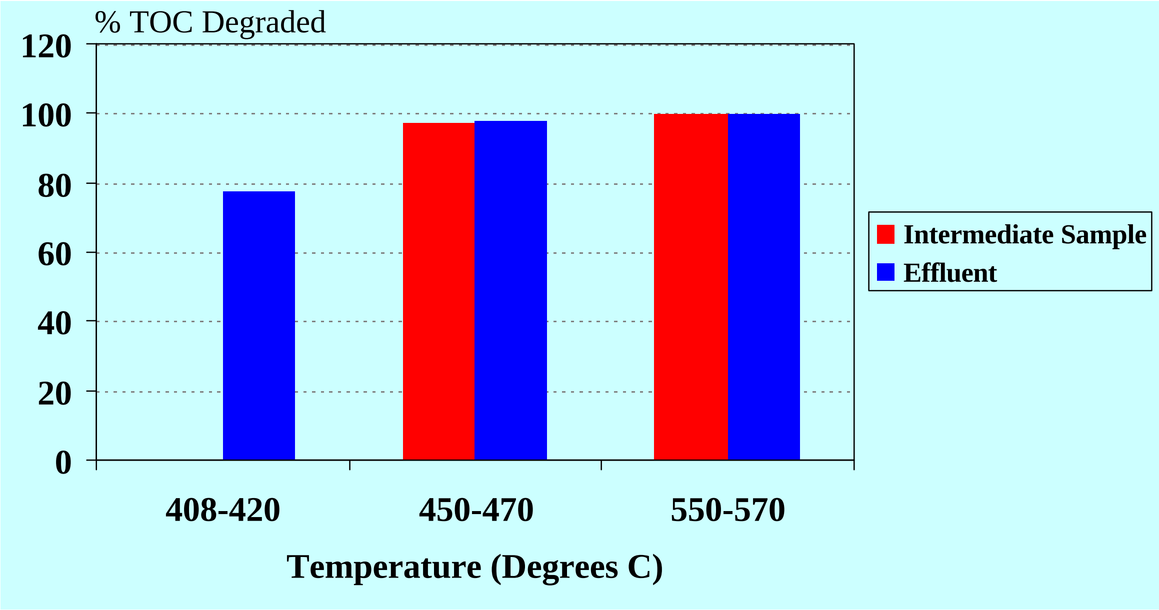


Figure 6. % TOC Degraded for Various Temperatures Ranges for the Oxidation of Ethanol

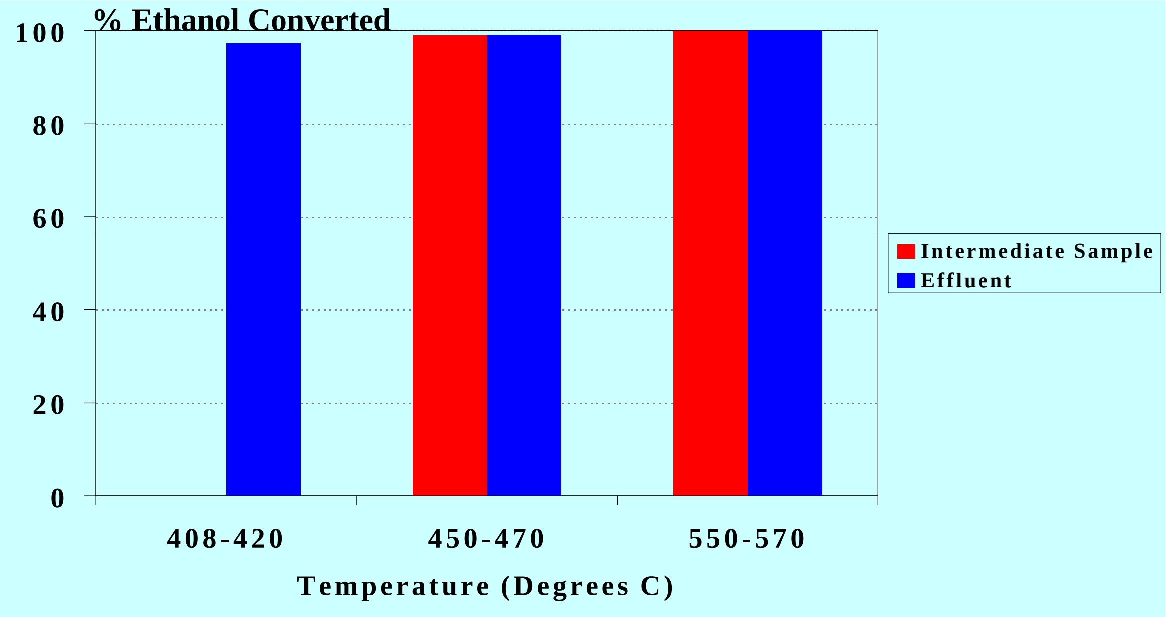


Figure 7. % Ethanol Converted vs. Temperature Range

The pH measurements made are shown in Figure 8. There was a significant drop in pH as a result of the supercritical water oxidation which supports the concept of organic acid formation in the lowest temperature range. However it's not clear why the pH should drop in the two higher temperature ranges where almost all the organic matter had disappeared. pH values this low cannot be entirely attributed to the pH of water in equilibrium with CO_2.

Another set of ethanol tests was done. This time the temperature of the second preheater (the one just before the reactor) was controlled and was used as the independent variable in the following figures. Figure 9 plots the destruction of ethanol (as total organic carbon) vs. preheater temperature. As that temperature increased the amount of ethanol destroyed increased. There was a large difference between the % ethanol degraded at 340°C measured at the intermediate sampling point, where the temperature was probably subcritical, compared to what was measured at the reactor outlet. The higher the temperature the smaller the difference between the % TOC degradation at the sample point and at the outlet to the reactor. Thus at the higher temperatures most of the reaction occurred at the beginning of the reactor, or in other words, the higher the temperature the shorter the reactor residence time necessary for TOC degradation.

Figure 10 is a plot of ethanol (measured as ethanol) conversion vs. temperature. In all cases almost all of the ethanol was completely or partially oxidized by the time it reached the reactor outlet. As the temperature increased more and more ethanol was oxidized by the time it reached the intermediate sampling point. This indicates that the higher the temperature the closer the oxidation zone is to the reactor inlet.

Figure 11 indicates that methanol was an intermediate reaction product in the oxidation of ethanol. Figure 12 indicates that acetic acid was also an intermediate reaction product. Figure 13 reports the composition of the dry gas leaving the reactor via the outlet's gas liquid separation device. The nitrogen comes from air infiltration into the sample bag.

Experiments with High Concentrations of Glucose

After the inclusion of the reactor and oxygen system, the SCWO facility was tested with a high concentration glucose solution. Since some pulp and paper wastes have high organic concentration, testing a high concentration of one of our model compounds would be beneficial to see how the SCWO test facility pilot plant would respond to such solutions.

The first set of experiments was performed using an 8% glucose solution. Two reactor temperatures were studied, 456 and 610 °C. Oxygen was supplied at 50% excess. Effluent analysis showed TOC removals of 95.6% for the experiment conducted at 456 °C and 99.99% for a temperature of 610 °C. Therefore, as illustrated with our earlier work, higher temperatures showed better organic degradation.

Organic degradation was very rapid. Samples were collected at various locations along the system and analyzed for TOC removal; this is illustrated in Figure 14. Figure 14 shows the locations of the various sampling points from the start of the system. For both temperatures studied, greater than 60% of the TOC is degraded during heating of the organic mixture. In Figure 14 PH2_ OUT means the sample point at the outlet from preheater 2, RL2_IN means the inlet to reactor length 2. RL10_IN is further into the reactor than RL2_IN.

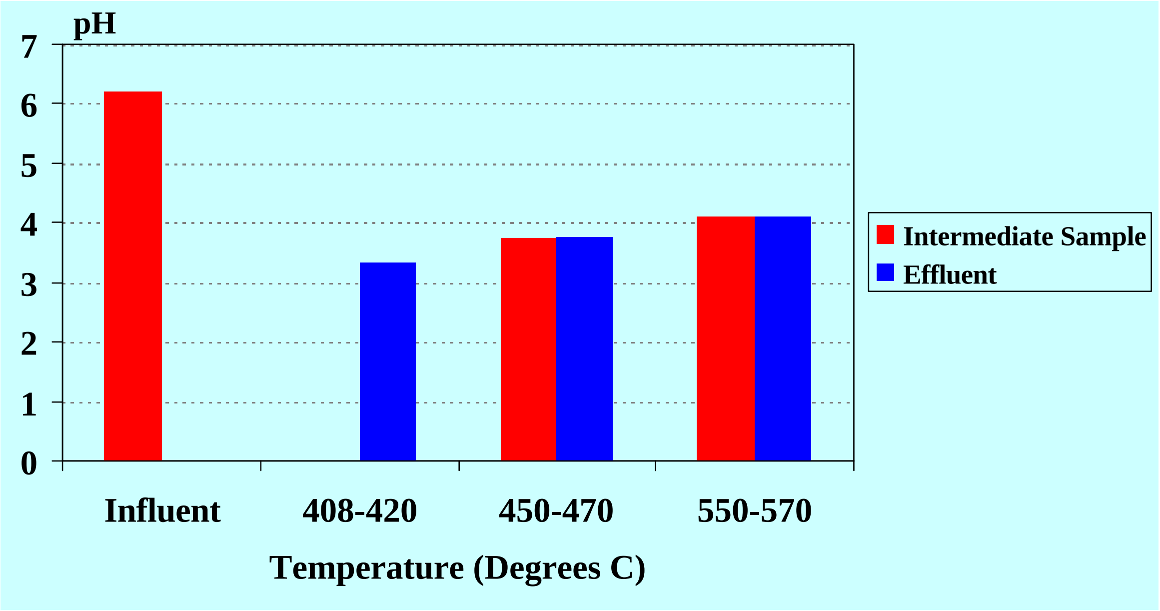


Figure 8. Effluent pH vs. Temperature Range for the Oxidation of Ethanol

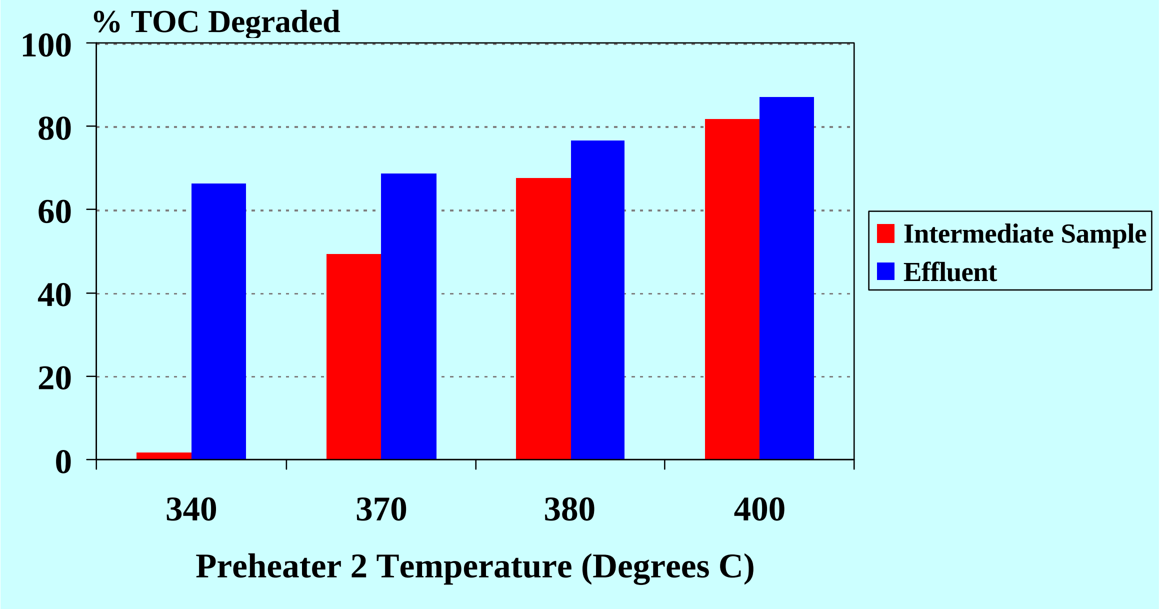


Figure 9. % TOC Degraded for Ethanol Oxidation
Temperature Controlled by Preheater 2

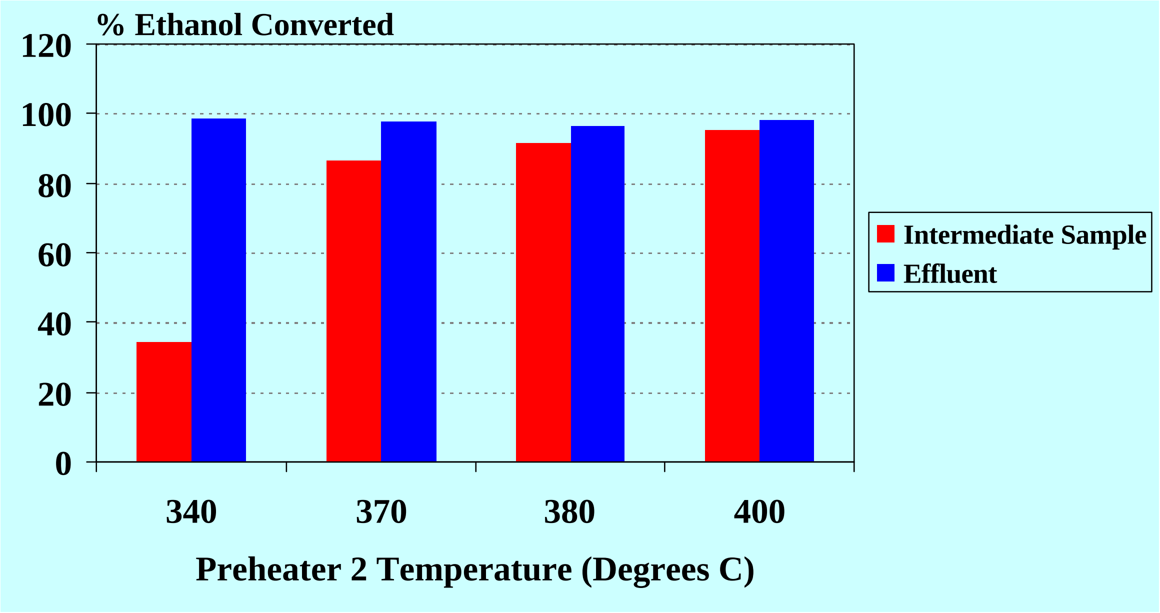


Figure 10. Ethanol Conversion vs. Temperature

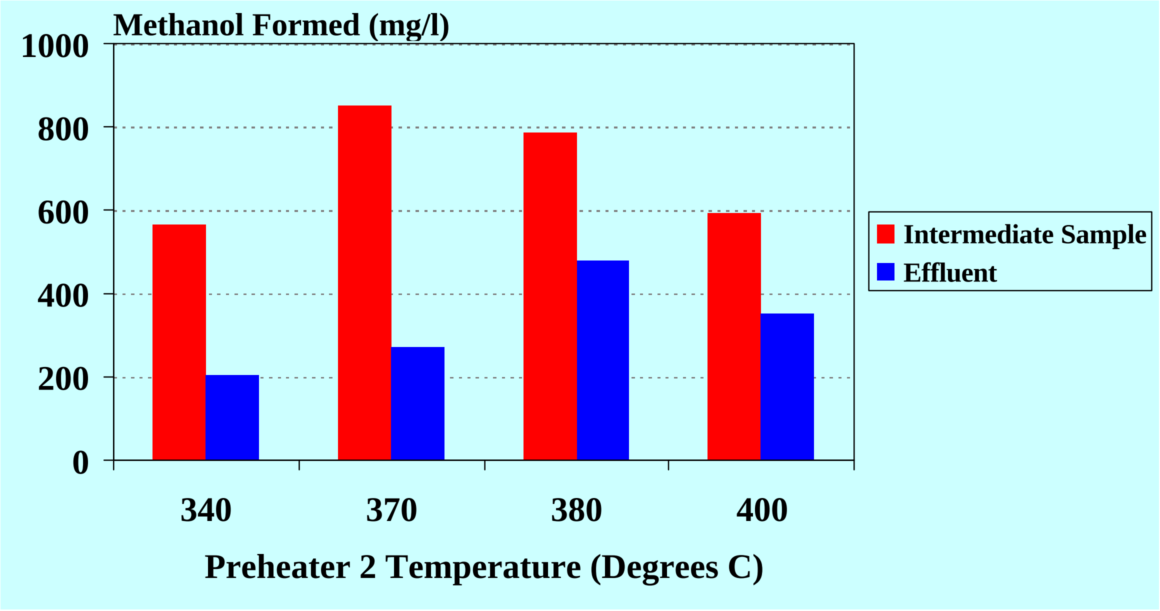


Figure 11. Methanol Concentration in Intermediate Sampling Point and Effluent

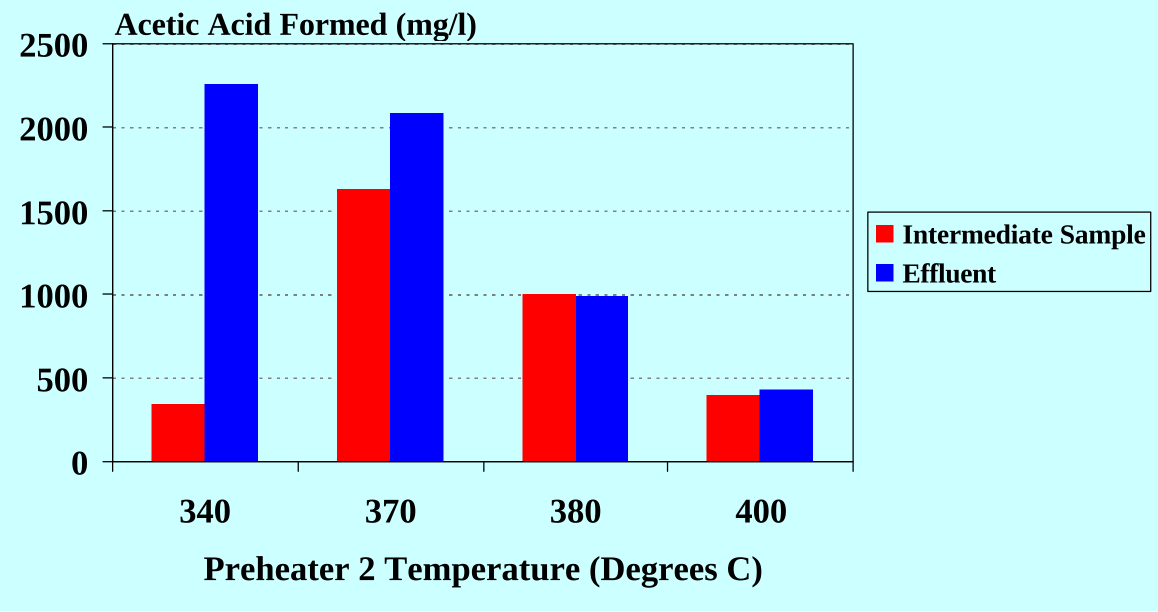


Figure 12. Concentration of Acetic Acid Present as Intermediate Product in Intermediate Sample and Effluent

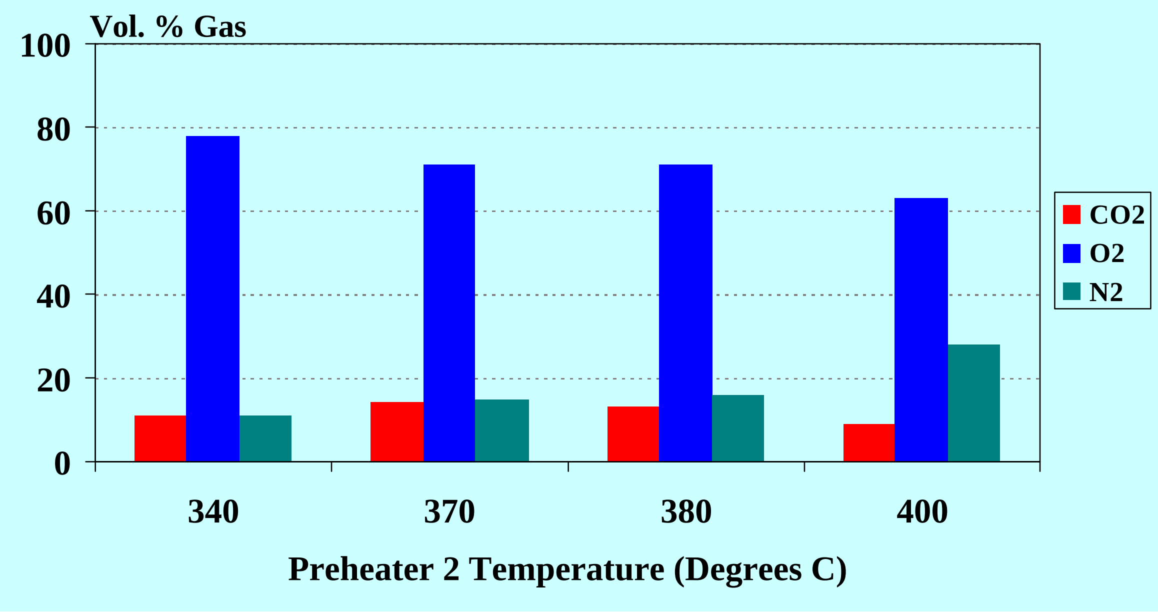


Figure 13. Composition of Product Gases

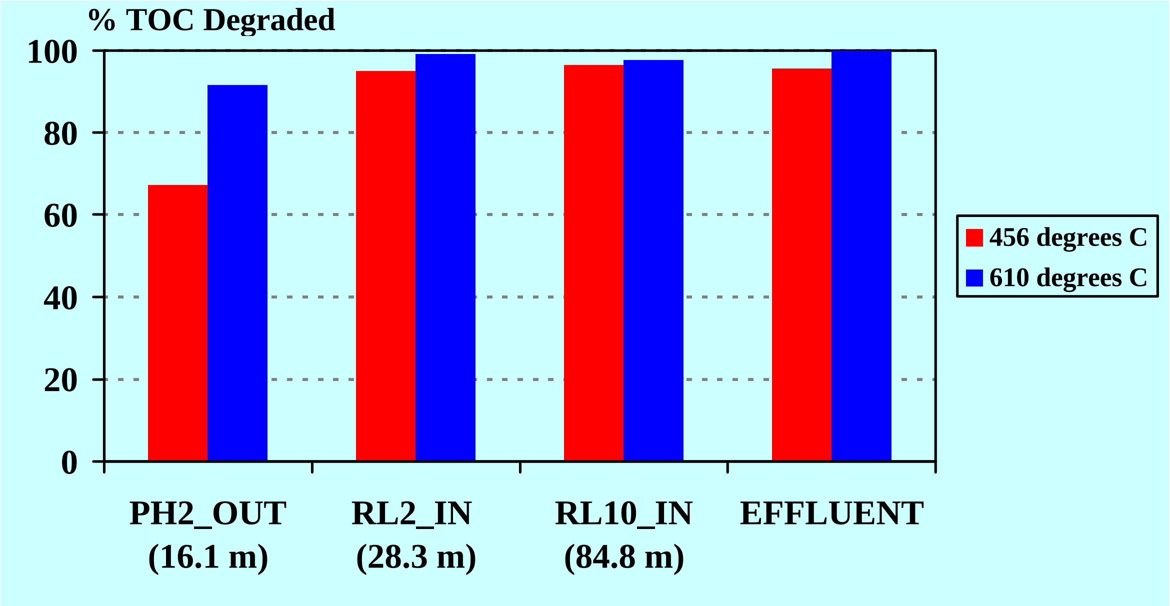


Figure 14. TOC Degradation Along SCWO System for
Oxidation of 8% Glucose Solution

Another test was performed with the 8% glucose solution. This test was at 610 °C as before, but this time 20% excess oxygen, rather than 50%, was used. The effluent TOC removal in this case was 99.98%. This shows that organic degradation is possible with close to stoichiometric requirements for oxygen.

A further set of tests using glucose concentrations of around 8 % by weight was done. In these tests the effects of excess oxygen level, temperature and feed flow rate (residence time) were investigated. Detailed results for these tests can be found in the spreadsheets of Appendix I. Figure 15 presents the results for TOC removal vs. excess oxygen level. Control of the amount of oxygen supplied was not very precise in these tests. The target values were 5 % (designated low), 20 % (medium) and 50 % (high). The target values are somewhat higher than the average of the actual values which fluctuated during the experiments. In Figure 15 it is clear that essentially all of the TOC supplied was destroyed under all of the test conditions used.

Figure 16 provides the actual TOC concentration at various points in the SCWO system for a glucose solution feed rate of 1.2 l/minute. Note that this and following concentration plots have a logarithmic scale on the concentration axis. In it we see that most of the reduction in TOC concentration has occurred before the inlet to the first preheater. Not much change occurred in passage through the second preheater. On occasion an apparent increase in TOC concentration was noted in preheater 2. A significant drop in TOC concentration happened as the solution went from preheater 2 to the initial stages of the reactor. For the tests done at 550 °C as the solution proceeded through the reactor the TOC concentration rose and then went back down again. At the moment we can’t explain this; probably it has to do with the sampling devices. Such behaviour was not observed in the 600 °C tests in which the TOC concentration was always declining through the reactor. No significant differences, attributable to differences in the level of excess oxygen, were noted in the preheaters, however in the reactor itself the higher the level of excess oxygen the lower the TOC concentration at all positions and temperatures. Near the inlet of the reactor the effect of temperature on TOC concentration was small, but towards the reactor outlet the higher the temperature the lower the TOC concentration.

Figure 17 shows how acetic acid concentration varied as the feed solution passed through the SCWO system. There was no acetic acid in the feed but some was formed during passage through the preheaters. The level of excess oxygen appeared to have no influence on the acetic acid concentration in the preheaters. At position RL2_IN in the reactor the higher the level of excess oxygen the lower the acetic acid concentration for both temperatures. At position RL6_IN (further into the reactor) the high level of excess oxygen resulted in lower TOC concentrations but there was no significant difference between the low and medium excess oxygen levels. At position RL10_IN no measurements were made at the high level but for both the low and medium levels of excess oxygen there was lower TOC concentration at the higher temperature. In the effluent sample the high the excess oxygen level the lower the TOC concentration. The effects of temperature on acetic acid concentration are not pronounced in Figure 17 except at the reactor outlet where the higher temperature produced lower TOC concentrations. The TOC concentration for the high excess oxygen, 600 °C sample was so low (0.93 mg/l) that it doesn’t show up on the plot.

Figure 18 is a similar plot for propionic acid concentration at various positions in the SCWO system. These concentrations are very low relative to those of acetic acid. Nevertheless since there was no propionic acid in the feed it must have been generated during the oxidation process. Similar remarks apply to Figure 19 for isobutyric acid.

Figure 20 presents the results of an experiment similar to the one shown in Figure 16 in terms of TOC concentration. The difference is that the feed flow rate in Figure 20 was 0.8 l/min. whereas in Figure 16 it was 1.2 l/min. Thus the residence time in the reactor was lower in the Figure 20 data. Again it can be seen that the TOC concentration dropped prior to preheater 2 but didn’t change much in passing through preheater 2. There was no effect of the level of excess oxygen or temperature on the TOC concentration into or out of preheater 2. At RL2_IN the higher the temperature the lower the TOC concentration. Excess oxygen level did not exhibit any significant effects at this point in the reactor. At RL2_IN at the higher temperature there was a lower TOC concentration. At this sample point the differences between 550 and 600 °C are more marked than in preheater 2. No obvious effect of excess oxygen level could be discerned here.

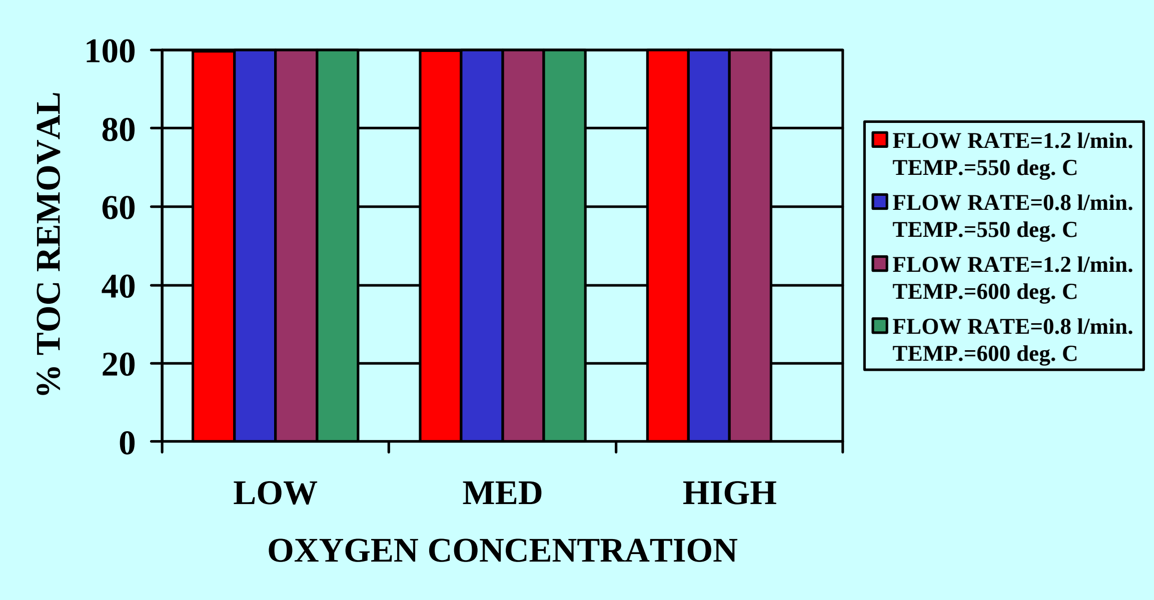


Figure 15. % TOC Removal vs. Oxygen Concentration

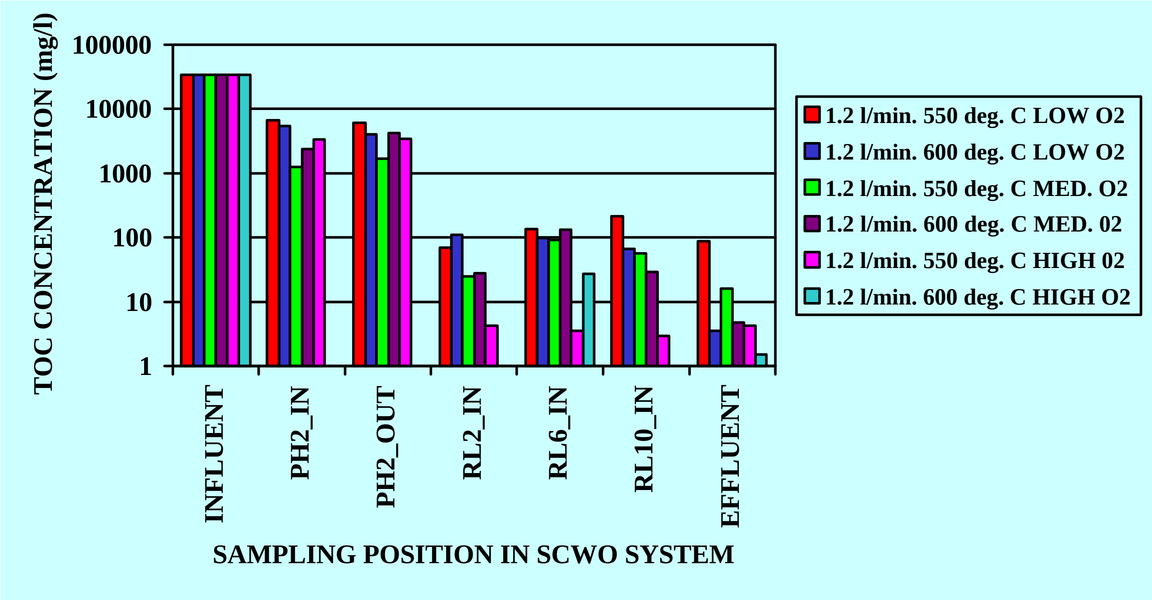


Figure 16. TOC Concentration at Various Sampling Positions
Flow rate = 1.2 l/min.

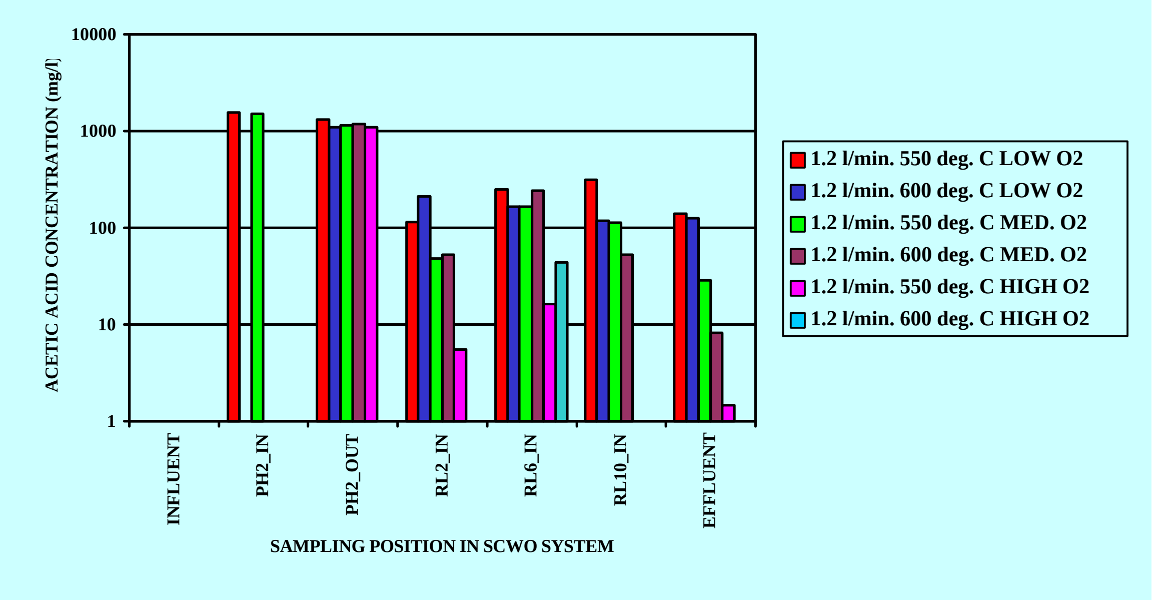


Figure 17. Acetic Acid Concentration at Various Sampling Positions
Flow Rate = 1.2 l/min.

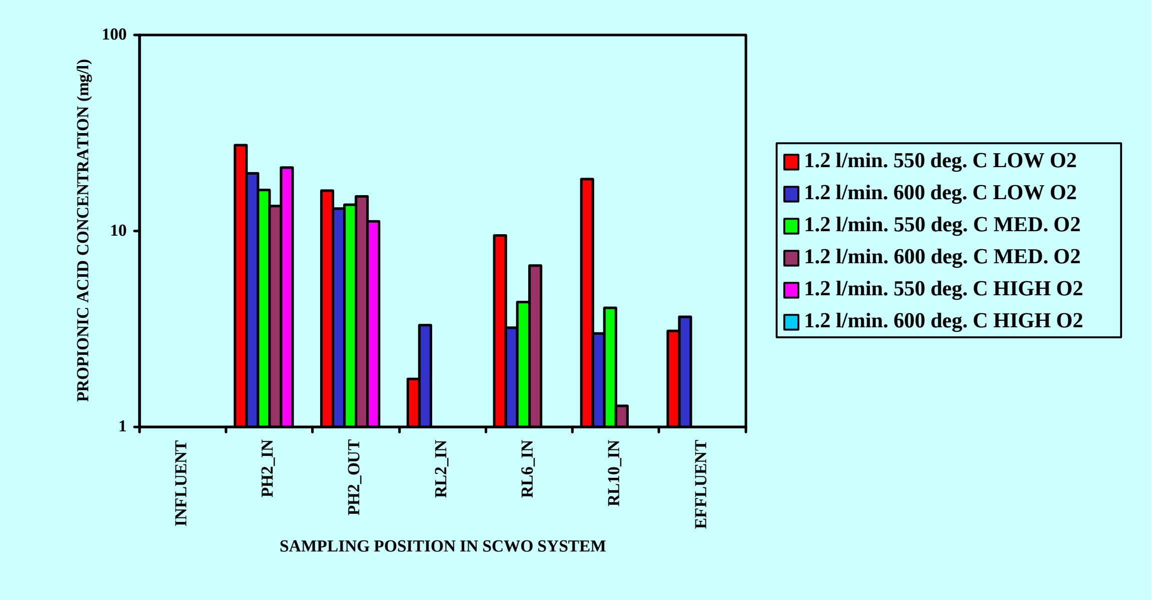


Figure 18. Propionic Acid Concentration at Various Sampling Positions
Flow Rate = 1.2 l/min.

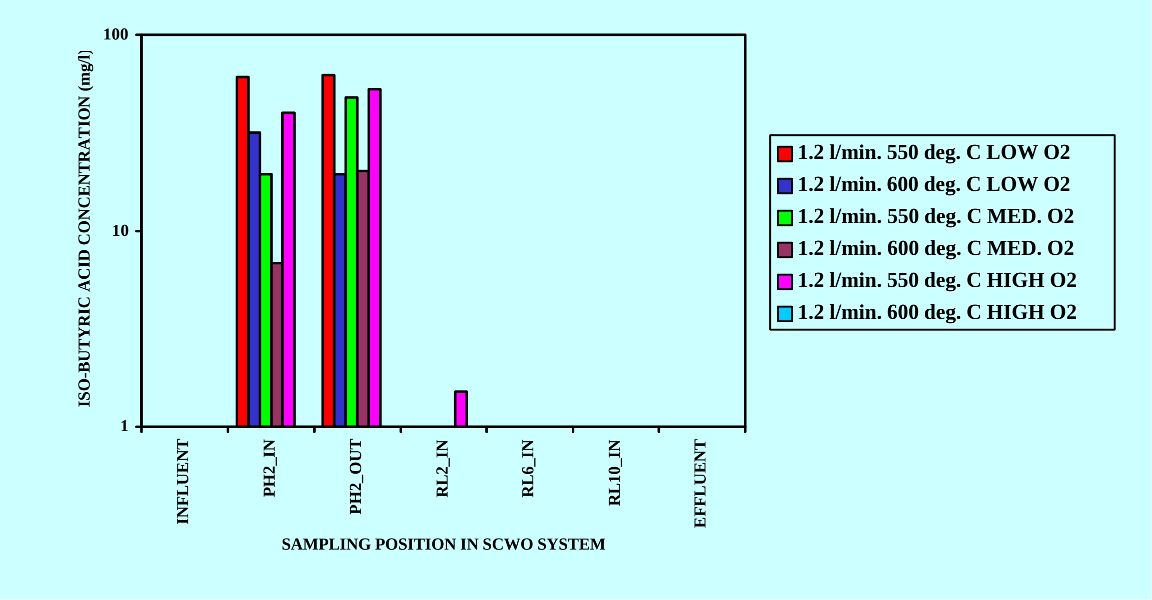


Figure 19. Iso-butyric Acid Concentration at Various Sampling Positions
Flow Rate = 1.2 l/min.

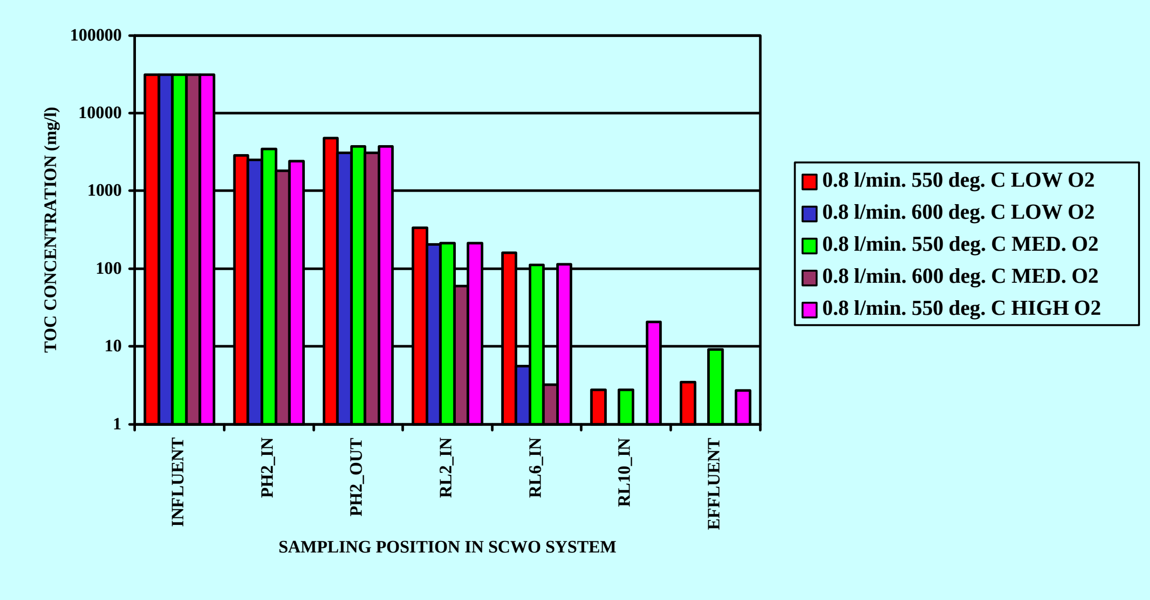


Figure 20. TOC Concentration at Various Sampling Positions
Flow Rate = 0.8 l/min.

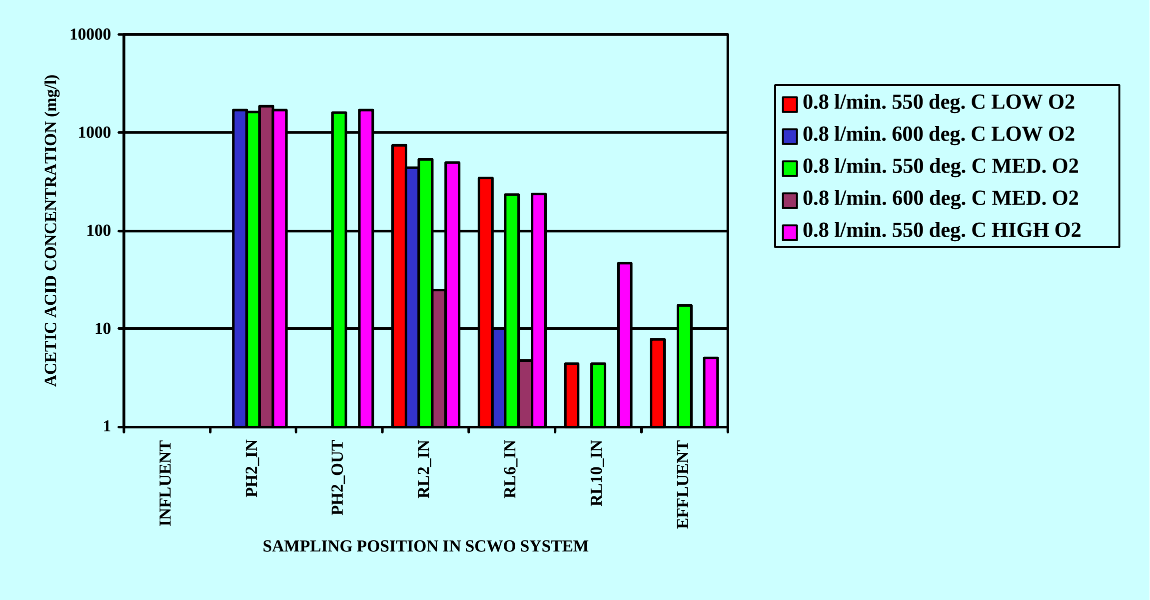


Figure 21. Acetic Acid Concentration at Various Sampling Positions
Flow Rate = 0.8 l/min.

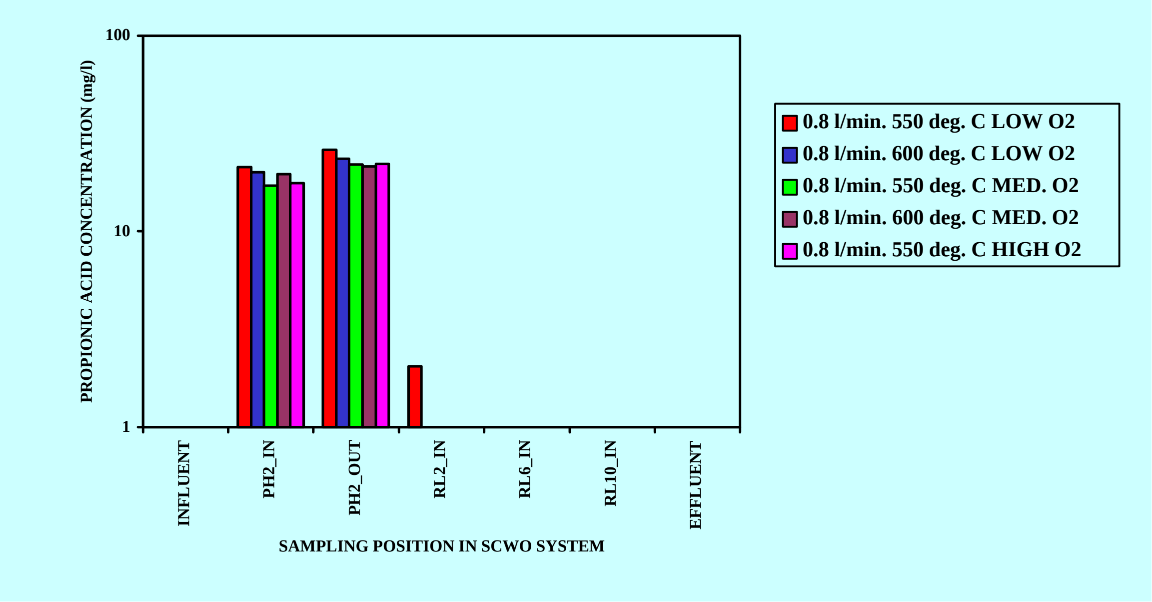


Figure 22. Propionic Acid Concentration at Various Sampling Positions
Flow Rate = 0.8 l/min.

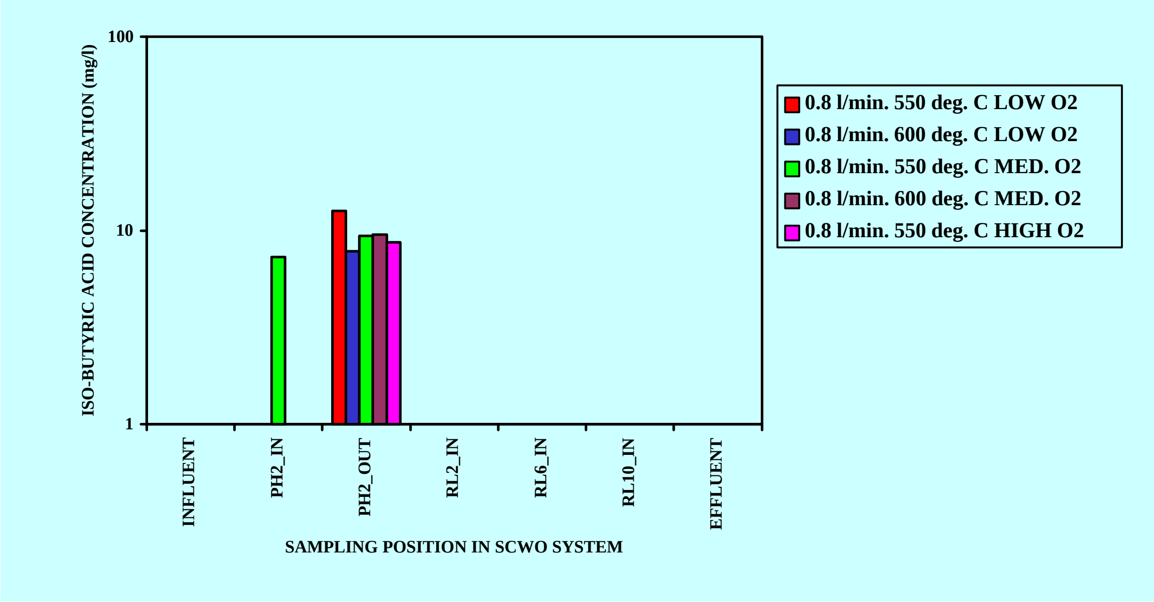


Figure 23. Iso-Butyric Acid Concentration at Various Sampling Positions
Flow Rate = 0.8 l/min.

In comparing the results of Figure 16 with those of Figure 20 there was no decisive effect of differences in feed flow rate on TOC concentration into and out of preheater 2 at 550 °C. The TOC concentration was lower into and out of preheater 2 at 600 °C. At RL2_IN the TOC concentration was lower at the higher flow rate at both temperatures. At sample point RL6_IN at 550 °C the TOC concentration was lower at the higher flow rate while at 600 °C the opposite was noted. Most of the measurements of TOC at RL10_IN indicated that TOC was lower at the lower flow rate and the higher temperature. In the effluent all or almost all of the TOC was gone; the lower values were observed at the lower flow rate and the higher temperature.

Figure 21 is a plot of acetic acid concentrations at various sampling positions along the supercritical water reactor. Again this Figure is at a feed flow rate of 0.8 l/min., and can be compared with Figure 17 for which the flow rate was 1.2 l/min. Acetic acid was generated somewhere in the system before preheater2 and its concentration was unaffected by passage through preheater 2 at both 550 and 600° C. The level of excess oxygen had no effect in this preheater either. Going through the reactor the concentration of acetic acid declined from the inlet to the outlet. The apparent exceptions to this for 550° C and a high level of excess oxygen at RL10_IN and 550° C and medium excess oxygen in the effluent should be disregarded as they can be attributed to the very low concentrations. Recall that the concentration scale in these plots is logarithmic, because of the range of concentrations to be plotted. A test at high levels of excess oxygen at 600° C was not done in this set of experiments.

At RL2_IN The higher the excess oxygen level the lower the acetic acid concentration at both flow rates and both temperatures. Lower concentrations were observed at the higher flow rate in all but one case. No evidence for a temperature effect was seen. At sample point RL6_IN it was noted that at 550° C with 0.8 l/min. there was no effect of excess oxygen level: at 1.2 l/min. the acetic acid concentration decreased as the level of excess oxygen increased. No trends could be seen for the data at 600° C. At 550° C acetic acid concentrations at all levels of excess oxygen were lower at a flow rate of 1.2 l/min. The opposite was the case at 600° C. At RL10_IN there was no evidence of any discernable trends in acetic acid concentration. In the low flow rate effluent sample at 600° C there was no detectable acetic acid. In the higher flow rate sample the effluent acetic acid concentration decreased as the level of excess oxygen increased. At 550° C there was no effect of excess oxygen on acetic acid concentration at the lower flow rate: at the higher flow rater the concentration decreased as the level of excess oxygen increased. At 600° C the acetic acid concentrations were lower than they were at 550° C.

Figures 22 and 23 present results for propionic and isobutyric acids respectively at a flow rate to the reactor of 0.8 l/min. These concentrations are low but finite indicating that such compounds were formed in the supercritical water oxidation process. The absence of a bar in all but one case in these plots indicates that the concentration was nondetectable. In the case of the above mentioned exception the concentration was not measured.

Experiments with Nitrobenzene Compounds

Several experiments were conducted in cooperation with NORAM on synthetic wastewaters that simulate the composition of typical wastewaters (red water) from the production of nitrobenzene. These experiments again demonstrated that supercritical water oxidation could destroy over 99% of such materials. During several of these trials data were obtained to determine a material balance on the process. More than 95 % of the carbon introduced into the system could be accounted for in the liquid and gaseous effluents.

APPLICATIONS

As noted in the Introduction to this report this supercritical water oxidation process is potentially applicable to any waste destruction problem in which the waste, to be destroyed, is pumpable, is organic in nature and does not contain an excessive amount of inorganic salts. It is currently in use on an industrial scale for the destruction of petrochemical wastes.

The supercritical water oxidation process is potentially applicable to any waste destruction process which utilizes incineration or wet air oxidation. Its virtues are –

- • an enclosed system so process products can be recovered if valuable, or easily collected for conveyance to a downstream process involving another treatment step.
- good mixing of oxygen with the waste to be oxidized.
- unlike biological wastewater treatment systems supercritical water oxidation is insensitive to the presence of toxic compounds in the wastewater.
- no oxides of nitrogen (an air pollutant) generated during oxidation.

- the process is compact and thus could be built to be portable on a truck or barge to visit sites where small quantities of hazardous waste have been stored for subsequent destruction.

The economics of this process have not been widely studied. Estimates indicate that it is competitive but at the high end of the $ per ton treatment cost scale. One of the purposes of this, and other's, research is to better understand the process so that the supercritical waster oxidation process costs can be reduced via better understanding of the process.

For the Pulp and Paper industry potential applications of this process include

- sludge destruction from activated sludge plants and sludge dredged from aerated stabilization basins (Cooper et al.).
- purging of undesirable contaminants such as anionic trash, excess polymers, pitch etc. from papermachine white water when the degree of white water closure is high.
- destruction of foul condensate compounds such as methanol, mercaptans and hydrogen sulfide in the kraft pulping process, particularly as kraft mills move towards zero liquid effluent discharges.
- destruction of bleach plant effluents containing chlorine which cannot be incinerated in a recovery furnace, although the effect of chlorine on corrosion of the supercritical water reactor is an unknown here.
- destruction of any segregated, high concentration wastewater streams which contain high BOD, COD or toxicity which are resistant to biological degradation, e.g. plug screw feeder effluent, turpentine, methanol, etc.

CONCLUSIONS

A small, pilot scale supercritical water oxidation system has been built and tested. This unit is now capable of characterizing the destruction of a wide variety of waste materials. Such characterization has begun for waste waters from benzene nitration plants.

Tests of supercritical water oxidation of solutions of 1 % ethanol have shown that close to 100 % destruction of ethanol can be achieved. Acetic acid and methanol have been shown to be intermediates in the oxidation of ethanol, ultimately to carbon dioxide and water.

Tests of supercritical water oxidation of 8 % glucose solutions have shown that close to 100 % destruction of glucose can be achieved. Acetic acid, propionic acid and isobutyric acid have been shown to be intermediates in the supercritical waster oxidation of glucose.

Generally speaking the higher the temperature is above the critical point the more effective the oxidation despite very low required residence times.

The lower the residence time (the slower the feed flow rate) is the more effective the oxidation process.

The amount of excess oxygen supplied does not seem to play a major role in the supercritical water oxidation process for the materials studied, provided it is greater than the stoichiometric quantity by an amount that has yet to be precisely defined, but appears to be of the order of 10 % excess.

REFERENCES

Cooper, S.P., Folster, H.G., Gairns, S.A., Hauptmann, E.G., “Treatment of Lagoon Sludge, Primary Clarifier Sludge and Bleach Plant Effluent by Supercritical Water Oxidation”, Pulp & Paper Canada, 98(10), T365, 1997.

Filopovic, D.,”Fouling Rates from a Sodium Chloride Solution in Supercritical Water Reactors”, M.A.Sc. Thesis in progress, Department of Mechanical Engineering, UBC.

Helling, R. K., "Oxidation Kinetics of Simple Compounds in Supercritical Water", D.Sc. Thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, 1986.

Holdgate, H.R., Meyer, J.C., Tester, J.W., “Glucose Hydrolysis and Oxidation in Supercritical Water”, AIChE Journal, 41(3), 637, 1995.

McBrayer, R.N., Griffith, J.W., "Turn Off the Heat", Industrial Wastes, 4(4), 43, 1996.

Modell, M., "Super Critical Water Oxidation", Chapter 8.12 in Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman ed., McGraw Hill, New York 1989

Modell, M., Larson, J., Sobczynski, S.F., "Supercritical Water Oxidation of Pulp Mill Sludges", Tappi, 75(6), 195, 1992.

Rogak, SN., Teshima, P., “Deposition of Sodium Sulphate in a Heated Flow of Supercritical Water”, AIChE Journal, 45,240,1999.

Rogak, S.N., Teshima, P. “Particle Formation ina Heated Flow of Supercritical Water”, Proc. CSME Forum 1998, Volume 1: Thermal and Fluids Engineering. Eds. M.A.Rosen, J.G.Kawall, Pyerson Polytechnic University,Toronto, 1998.

Teshima, P., "Fouling Rates from a Sodium Sulfate-Water Solution in Supercritical Water Reactors", M.A.Sc. Thesis, Department of Mechanical Engineering, University of British Columbia, Vancouver, 1997.

APPENDIX I

Test Description	TOC (mg/l)	Removal %	Acetic Acid (mg/l)	Propionic Acid (mg/l)	Iso-Butyric Acid (mg/l)
July 13/99					
Influent	31550				
Test 16	**5% excess O2 Target Reactor Temp. 550 deg. C Flowrate: 0.789 l/min**				
PH2_In	2880	90.87	Non-detectable	21.39	Non-detectable
PH2_Out	4750	84.94	Non-detectable	26.10	12.65
RL2_In	340	98.92	740.10	2.05	Non-detectable
RL6_In	162	99.49	343.07	Non-detectable	Non-detectable
RL10_In	2.8	99.99	4.38	Non-detectable	Non-detectable
Effluent	3.5	99.99	7.74	Non-detectable	Non-detectable
Test 14	**20% excess O2 Target Reactor Temp. 550 deg. C Flowrate: 0.789 l/min**				
PH2_In	3480	88.97	1622.09	17.11	7.296
PH2_Out	3760	88.08	1605.79	21.95	9.387
RL2_In	215	99.32	535.15	0.944	Non-detectable
RL6_In	112	99.65	232.54	Non-detectable	Non-detectable
RL10_In	2.8	99.99	4.381	Non-detectable	Non-detectable
Effluent	9.2	99.97	17.322	Non-detectable	Non-detectable
Test 15	**50% excess O2 Target Reactor Temp. 550 deg. C Flowrate: 0.789 l/min**				
PH2_In	2400	92.39	1693.09	17.613	Non-detectable
PH2_Out	3760	88.08	1696.94	22.13	8.668
RL2_In	215	99.32	493.63	0.734	Non-detectable
RL6_In	115	99.64	237.29	Non-detectable	Non-detectable
RL10_In	20.8	99.93	46.71	Non-detectable	Non-detectable
Effluent	2.7	99.99	5.06	Non-detectable	Non-detectable
Test 17	**5% excess O2 Target Reactor Temp. 600 deg. C Flowrate: 0.789 l/min**				
PH2_In	2510	92.04	1686.44	20.13	Non-detectable
PH2_Out	3060	90.30	Non-detectable	23.454	7.835
RL2_In	205	99.35	438.02	0.949	Non-detectable
RL6_In	5.6	99.98	10.029	Non-detectable	Non-detectable
RL10_In	0.2	100.00	Non-detectable	Non-detectable	Non-detectable
Effluent	0	100.00	Non-detectable	Non-detectable	Non-detectable
Test 18	**20% excess O2 Target Reactor Temp. 600 deg. C Flowrate: 0.789 l/min**				
PH2_In	1800	94.29	1864.5	19.587	Non-detectable
PH2_Out	3080	90.24	Non-detectable	21.543	9.534
RL2_In	60	99.81	24.957	Non-detectable	Non-detectable
RL6_In	3.2	99.99	4.707	Non-detectable	Non-detectable
RL10_In	Not measured	Not measured	Not measured	Not measured	Not measured
Effluent	0	100.0	Non-detectable	Non-detectable	Non-detectable

Test Description	TOC (mg/l)	Removal %	Acetic Acid (mg/l)	Propionic Acid (mg/l)	Iso-Butyric Acid (mg/l)
July 6/99					
Influent	34100				
Test 3	**5% excess O2 Target Reactor Temp. 550 deg. C Flowrate: 1.201 l/min**				
PH2_In	6560	80.76	1545.83	27.23	61.07
PH2_Out	6040	82.29	1310.81	16.00	62.31
RL2_In	70	99.79	113.04	1.75	Non-detectable
RL6_In	135	99.60	250.49	9.49	Non-detectable
RL10_In	215	99.37	314.22	18.37	Non-detectable
Effluent	87	99.74	138.96	3.07	Non-detectable
Test 4	**20% excess O2 Target Reactor Temp. 550 deg. C Flowrate: 1.201 l/min**				
PH2_In	1265	96.29	1508.99	16.14	19.34
PH2_Out	1661	95.13	1141.03	13.63	47.72
RL2_In	25	99.93	47.84	Non-detectable	Non-detectable
RL6_In	92	99.73	164.47	4.32	Non-detectable
RL10_In	56.4	99.83	111.66	4.04	Non-detectable
Effluent	16	99.95	28.40	Non-detectable	Non-detectable
Test 5	**50% excess O2 Target Reactor Temp. 550 deg. C Flowrate: 1.201 l/min**				
PH2_In	3322	90.26	Non-detectable	21.04	39.92
PH2_Out	3410	90.00	1093.82	11.14	52.74
RL2_In	4.3	99.99	5.47	Non-detectable	1.51
RL6_In	3.5	99.99	16.23	Non-detectable	Non-detectable
RL10_In	2.9	99.99	Non-detectable	Non-detectable	Non-detectable
Effluent	4.3	99.99	1.44	Non-detectable	Non-detectable

Test Description	TOC (mg/l)	Removal %	Acetic Acid (mg/l)	Propionic Acid (mg/l)	Iso-Butyric Acid (mg/l)
July 12/99					
Influent	34100				
Test 9	**5% excess O2 Target Reactor Temp. 600 deg. C Flowrate: 1.213 l/min**				
PH2_In	5456	84.00	Non-detectable	19.598	31.476
PH2_Out	4004	88.26	1089.5	12.969	19.352
RL2_In	110	99.68	209.97	3.294	Non-detectable
RL6_In	98	99.71	163.428	3.204	Non-detectable
RL10_In	66	99.81	117.398	2.985	Non-detectable
Effluent	3.5	99.99	125.768	3.648	Non-detectable
Test 10	**20% excess O2 Target Reactor Temp. 600 deg. C Flowrate: 1.213 l/min**				
PH2_In	2420	92.90	Non-detectable	13.35	6.86
PH2_Out	4180	87.74	1180.55	15.05	20.27
RL2_In	28	99.92	52.32	Non-detectable	Non-detectable
RL6_In	131	99.62	239.83	6.65	Non-detectable
RL10_In	29.2	99.91	52.60	1.28	Non-detectable
Effluent	4.8	99.99	8.16	Non-detectable	Non-detectable
Test 12	**50% excess O2 Target Reactor Temp. 600 deg. C Flowrate: 1.213 l/min**				
PH2_In	Not measured		Not measured	Not measured	Not measured
PH2_Out	Not measured		Not measured	Not measured	Not measured
RL2_In	Not measured		Not measured	Not measured	Not measured
RL6_In	27	99.92	43.554	0.592	
RL10_In	Not measured		Not measured	Not measured	Not measured
Effluent	1.5	100.00	0.931	Non-detectable	Non-detectable