# Energy Recovery from Effluents of Supercritical Water Oxidation Reactors

Yoana García-Rodríguez, Fidel A. Mato*, Alexandra Martín, M. Dolores Bermejo and M. José Cocero

High Pressure Processes Group, Department of Chemical Engineering and Environmental Technology. EII Sede Mergelina. University of Valladolid. 47011 Valladolid, SPAIN

* Corresponding author, TEL: +34-983423169, e-mail: fidel@iq.uva.es

## Abstract

Supercritical Water Oxidation (SCWO) reactors can process waste effluents achieving high conversions, but the required extreme pressure and temperature operational conditions entail high-energy operational expenditure. SCWO has the potential to be considered a clean energy generation process, as the process effluent is a high temperature, high pressure stream with a high enthalpy content that can be converted to heat and shaft work. This ensures the self-sustained reaction and can generate excess shaft power to drive both the high-pressure pump and the air compressor. On the contrary, an efficient heat and power recovery from SCWO reactors outlet streams using conventional procedures presents several problems. First, Rankine cycles impose indirect heat transfer to the working fluid and are unable to recover the pressure energy and second, direct expansion of the effluents entails costly development of specific, efficient expansion equipment.

In this work, we investigate the options for energy recovery of SCWO reactors coupled with commercial gas turbines (GT). SCWO outlet streams are mainly composed of water, nitrogen and carbon dioxide. These operating values nearly resemble the well-known and already-implemented GT steam injection procedures. The temperature of the flue gases (approx. 500 ºC) and the direct shaft work usage offers adequate energy integration possibilities for both feed preheating and compression. The wide range of commercially available GT sizes enables process scaling.

**Keywords:** SCWO, shaftwork, energy recovery, gas turbine (GT), steam injection, simulation.

## 1. Introduction

Supercritical Water Oxidation (SCWO) is an intensive energy process to eliminate organic wastes. For many years the process has been developing technical solutions to achieve results for corrosion and plugins problems [1, 2]. Although its industrial development progresses slowly, in 2013 two industrial plants for chemical weapons and sludge treatment were under construction [3].

One of the SCWO challenges is the energy recovery to get shaft work and heat in order to get net energy [4]. Existing literature on SCWO process focusing on clean energy production has been reviewed. Most of the practical development is based on recovering the heat released by waste oxidation and generating steam. Many theoretical works point that the process would be much more efficient if the compression energy could be recovered as work. The efficient thermal and pressure energy recovery will open the opportunity to use SCWO as an efficient and clean energy production processes from wastes or biomass [5].

Depending on the SCWO process different alternatives can be applied for heat recovery. Conventional tubular reactors are thin tubes, with evident plugging problems from solid precipitation. In practice, industrial plants work with two reactors, one under operation and the other undertaking the cleaning of deposited solids. Even isolated tubular reactor loss energy by the long surface area, and furthermore cleaning is a highly energy and time consuming step. These reactors can operate with air or oxygen, both alternatives work properly. Oxygen is the most usual oxidant to reduce the energy consumption of the air compressor. The oxidation by oxygen requires lower reactor volume and less work to compress the liquid oxygen than the gas air, but the oxygen cost is the limit issue. The election depends on the economic balance. For operation below ignition temperature, reaction time is about several minutes and the reactor volume is minimized by the use of oxygen. Air is more conventional oxidant but requires higher reactor volume associated to nitrogen. To implement the use of air as oxidant the reactor volume could be minimized by the use of faster kinetic and by recovering the energy associated to the compression if the work from effluent depressurization could be retrieved by a turbine.

The reactor effluent energy can be recovered by a Closed Rankine Cycle through indirect heat transfer to a working fluid but the process is still highly energy demanding [6].

For operation at temperatures above the ignition, supercritical water oxidation with hydrothermal flame as internal heat source allows to use air or oxygen and the faster kinetics minimizes the reactor volume. The operation under hydrothermal flames allows total oxidation of the waste within milliseconds residence times, which opens the possibility of developing small combustors to produce high-pressure gas/vapor streams. The application of hydrothermal flames opens a wide field for the production of energy from wastes [7]. The cooled wall reactor developed at University of Valladolid is the only reactor prototype currently in operation with hydrothermal flame as internal heat source that produces a reduced liquid effluent with dissolved solids and a high-pressure and high-temperature effluent at 600-650 ºC and 23 MPa, that is able to produce work and thermal energy in a more efficient way that the below ignition tubular reactors effluent [8].

Even when the option of direct expansion of the effluent is, by far, the most energetically efficient, it will be not applicable in the short term. This is mainly due to the fact that the composition of the effluent (50-80% mole of water, carbon dioxide and nitrogen if air is used as oxidant) makes it not suitable for expansion in a conventional turbine. This composition makes the effluent one of intermediate characteristics between the pure water used in steam turbine and the flue gases, products of combustion used in gas turbines. The starting conditions of this mixture, around 600 ºC and 23 MPa, determine the near-isentropic path needed for an efficient expansion and route it down this path to an early condensation in terms of a full harnessing of the mixture enthalpy content; depending on course on the specific composition of the mixture. Thus, technical issues concerning the expansion of two-phase streams prevent the effective implementation of direct expansion in the short term. Furthermore, the detailed design of a dedicated, effective turbine would be costly and would take a long time to be carried out. Moreover, the design of such a turbine would be highly dependent on the mass flow rate of the effluent stream, not allowing for wide variation without loss of efficiency.

Therefore, a commercial gas turbine is proposed, where the reactor outlet stream is injected in or after the combustor. Before the injection, this stream is mixed with the combustion gases, this method allows the energy recovery using a conventional equipment (expander turbine section) because this doesn't change in excess the expanding flue gases stream properties.

## 2. Material and methods

### 2.1. Pilot Plant description

The simplified PFD (Process Flow Diagram) of the cooled wall reactor facility placed at Universidad de Valladolid is shown in Figure 1. The plant can be used to oxidize various compounds with air as oxidant in an aqueous environment. The maximum operating pressure is 30 MPa at temperatures between 400°C and 700°C with a maximum treatment capacity of 25 kg/h of feed.

The main equipment of this pilot plant is the reactor. This device has three inlet lines and two outlet lines [8]: the feed line, entering at the bottom of the reactor vessel and proceeding down-up inside of a tubular injector to the top of the reactor, consist of a pumpable mixture of water and fuel which is pressurized and preheated electrically; air line is introduced at the bottom of the reactor after compression, heating and mixing with the feed; and the third inlet line consists of an auxiliary downward flow of water at the top of the reactor intended to protect the reactor wall from high temperature. The liquid products line leaves the reactor from the bottom and is mainly composed of water and salts; and the vapor line flows from the top of the reactor and is mainly composed of water vapor, nitrogen and carbon dioxide with composition depending on the nature of the fuel waste. The outlet lines are cooled and depressurized.

The reaction chamber consists of a vertical tube. It is surrounded and contained in a pressure vessel. Between the pressure vessel and the reaction chamber the down flow of cooling water keeping the temperature of the pressure standing wall under 400°C. The feed is premixed with air and enters the reaction chamber through a tubular injection lance [9]. Usually the hydrothermal flame is produced above the lance, at the top of the reaction chamber, where the maximum temperature is detected [9]. To preheat the reactor at the start up of the process there are two electrical heaters. The room temperature cooling water enters at the top end of the reactor flowing down between the walls of the reaction chamber and pressure vessel. At the bottom end it forms a pool of liquid water where it mixes with the reaction products and can solve salts to avoid large salt deposits inside the reaction chamber.

Data from this facility are used as the base of this work [8].

## 2.2. Energy Integration

As stated above, the use of supercritical water as reaction media requires extreme pressure and temperature operational conditions entailing high-energy operational expenditure. Liquid water can be compressed using a pump with affordable energy costs. The use of supercritical fluids makes necessary to supply heat of high quality (≈ 400ºC). Because of this, it is necessary to study reasonable solutions which are able to solve this part of the process with a viable efficiency. One solution could be the integration of supercritical processes with energy production in cogeneration or Combined Heat and Power (CHP) cycles. Cogeneration is defined as the simultaneous production of various forms of energy –being the most frequent heat and shaft work, i.e., power– from one power source. The implementation of CHP processes is often joined to the use of gas turbines (GT). Nowadays, the most extended fuel used in gas turbines is natural gas. This kind of internal combustion turbines own several advantages over steam turbines and diesel engines, such as, higher yields, better flexibility and higher efficiency [10]. Besides, it is a compact engine, with lower manpower operating needs and ready availability [11]. Also, the gas turbine engine is further recognized for its better environmental performance manifested in curbing of air pollution and reducing the greenhouse effect [12]. For all these advantages it is proved that over the last two decades, GT has seen tremendous development and market expansion. Gas turbines representing only twenty percent of the power generation market twenty years ago, they now claim approximately forty percent of new capacity additions [13].

The SCWO process produces a high pressure reactor outlet stream, being these mainly composed of water, nitrogen and carbon dioxide and can be thermally integrated if there is a necessity of heat in other parts of the process. If there are no other heat requirements, it is possible to use the excess heat to implement a steam injection in the gas turbine, which will improve the efficiency of the global process. This mechanism links the process of SCWO with the cogeneration process. Steam injection is a technique which can increase the ability of a plant to generate extra power without burning extra fuel and requiring moderate capital investment. Furthermore a decrease in $NO_x$ emissions from the gas turbine is produced and also the electric generation efficiency of the simple and regenerative cycles is improved [14]. Steam Injected Gas Turbines (STIG) systems operate as an enhancement to the Brayton cycle. High quality steam is used to increase the power output and improve operating efficiency of the basic Brayton cycle. The definite place at which this steam is injected differs according to the design of the particular gas turbine; however mainly, high pressure steam is injected into the high-pressure sections of the gas turbine via the combustor fuel nozzles [11]. In its most basic form, steam injection works by increasing the global mass flow rate through the gas turbine without increasing the mass of air to be compressed. This increase in the expanded mass flow generates an increase in the rotational torque and power output. Steam injection technology offers a clear improvement over the Brayton cycle while providing a fully flexible operating cycle [15].

One of the key parameters that must be considered for the design of a SCWO system for energy production is the choice of the oxidant. From the reaction point of view, using air or oxygen shows no influence on the conversion of the feed oxidized [16]. Air is the cheapest material, but it contains a large amount of nitrogen that has to be pressurized, and that acts as a diluent that reduces the temperature of effluents and, therefore, its thermal quality. On the other hand, cryogenic liquid oxygen carries no diluents, and air compressors could be replaced by low consumption cryogenic pumps. Furthermore, pure oxygen does not need to be preheated up to feed injection temperature. However, the cost and energy consumption of producing pure oxygen could affect the viability of the process. An intermediate option is the use of oxygen-enriched air [4].

### 2.3. Analyzed schemes and methods

In this research, different possibilities for energy recovery from the upper stream of the SCWO cooled wall reactor are explored. This stream is gaseous and mainly composed of water, nitrogen and carbon dioxide. Energetic efficiencies are studied and compared using a simulation software. Also, the mass and energy balances are calculated for the proposed schemes.

For carrying out these studies, Aspen Plus V8.0 software is used. This software can be used for a wide variety of simulation chemical engineering tasks, from parallel process monitoring to operation modes exploration to grass root design. The approach adopted in this work is to develop an Aspen simulation flow-sheet that validates against experimental runs of the pilot plant and then apply this flowsheet to explore different process setups for the recovery of energy from the top reactor effluent. In order to model the thermodynamic behavior of the mixtures the Peng-Robinson thermo package with Boston-Mathias (PRBM) modifications was used.

The initial values used in this simulation are experimental data which were obtained from the pilot plan referred above.

The feed consists of solutions of lactose in water (mass fraction: 87% $H_2O$ and 13% $C_{12}H_{22}O_{11}$) at room conditions (20ºC and 1 bar) with a mass flow rate of 13.5 kg/h. The mass flow rate of cooling water necessary is 5.6 kg/h at 20ºC and 1 bar.

Into the reactor the next reaction happens:

$$C_{12}H_{22}O_{11} + 12O_2 \;\rightarrow\; 12CO_2 + 11H_2O$$

Fractional conversion of lactose is 1, i.e. it is oxidized totally. Then, using air with 5% of oxygen in excess, the necessary mass flow is roughly 10 kg/h at 20ºC and 1 bar.

The lower reactor outlet is composed only of water, the 30% of feed volume flow goes out through the lower reactor outlet.

The simulated GT size was chosen such as the net work in the simplest case (case 0) is zero, in other words, energy production by GT is equal to the energy consumed by the whole process. Taking this into consideration, the necessary amount of $CH_4$ (NG) is 1.349 kg/h. Usually, the necessary amount of air in a turbine is three or four times the stoichiometric value. The NG is completely oxidized, therefore, the flue gases mass flow rate obtained is 80.90 kg/h.

It must be noticed that, being the flow reduced as a pilot plat scale is the origin of experimental data, the energy flows calculated from now on are also small and must be seen as a proportional comparison.

In this work, six cases, with different configurations, are simulated and calculated.

The first case (case 0) is shown in Figure 2. It is the most basic configuration and it is taken as the base case for comparison. In this case, there isn't effluent injection, heat integration is achieved from gas turbine flue gases. This gas turbine system (not a built-in Aspen device) is simulated like a compressor, a combustor and a turbine ensemble, using the Aspen built-in simulation units. Calculated temperatures, compositions and energy flows are consistent with average industrial devices.

In case 1, as shown in Figure 3, energy integration is fostered by means of injecting the effluent into the GT combustor after decompressing it in a valve to 15.6 bar – an average combustor pressure – causing an increment in the mass flow rate of flue gases through the expansion section of the GT and the work production.

In case 2, 3 and 4 (Figure 4) there is a further improvement to the case 1 through shaftwork recovery. Now, the high pressure is used to increase energy production. An ejector is elected for this aim, in an attempt to recover as much shaft work as possible from the high pressure effluent stream. The core idea underlying this election is using the pressure component of enthalpy in the effluent – as it expands to a lower pressure – to rise the pressure of a part of the atmospheric air that goes to the GT compressor and then to the combustor, thus reducing the mass flow rate through the compressor and, consequently the power spent. As this power comes directly from the expansion section (turbine) through the GT common compressor-turbine shaft, more power should be freed to the generator or other power-using device.

When trying to assess the feasibility and profitability of this setup several difficulties arise. First, no device is known to have been built, as far as the authors know, to work at these conditions, i.e., mixing two streams at 250 and 1 bar to produce an intermediate pressure stream, thus no design procedures, experimental efficiencies or operating experience is at hand. Furthermore, it's worth to consider that the design of ejectors and assessment of its efficiency is highly dependent on the fluid dynamics, spatial form and flow fields inside the device, being in addition the thermodynamic aspects of these super-sonic to stagnant flow at high pressures and temperatures very complex to describe. As an immediate, affecting consequence, the simulation software employed doesn't include an ejector or jet-steam unit. As a way to circumvent these problem, and exclusively intending to perform an exploratory assessment of the possibilities of such a setup, this equipment is simulated like an expander, a compressor, a mixer and a heat exchanger ensemble, using Aspen built-in simulation units. Compressor and turbine isentropic efficiencies used are 80%.

The principles behind the simulation follow. The effluent is supposed to expand following an isentropic path to the final mixing pressure, so an ideal isentropic expander unit is used to calculate the process and stream parameters. A part of the shaft work produced in this expansion (30% is assumed, but further research will be needed in order to quantify this assumption) is supposed to pass to an ideal isentropic compressor unit that rises the pressure of the atmospheric air feed to the mixing pressure. Then, these two streams are mixed in an adiabatic/isenthalpic mixer unit without pressure change, resulting thus the mixer outlet conditions from the pure mass and energy mixing balances of both streams as they leave the isentropic expansion and compression respectively. As the energy conservation First Law must be fulfilled, the part of the shaft work from the expansion that is not employed in compressing the air stream (70%) is supposed to degrade to heat through viscous dissipative effects and re-appear at the end; thus, this energy/shaft work flow is transformed in a heat flow and added to the final mixing stream in a later heater unit.

All energy flows, fractions of energy flows and fraction of GT combustion air that is derived to the ejector are implemented using Aspen block calculators, that allow to set some Aspen units variables as a function of other unit variables away, after any arbitrary numerical treatment along this process.

The difference between case 2, 3 and 4 is the intermediate pressure (valve outlet stream pressure, before the ejector turbine).

In the last case (case 5) (Figure 5) the valve is removed, then, the reactor outlet stream enters the ejector with a high pressure.

## 3. Results and Discussion

The proposed schemes (cases 0 to 5) cited in the previous section were implemented as Aspen simulation files using the PRBM thermodynamic package. Some difficulties relating convergence were experienced due to the multiple block calculators employed, and initial values for some parameters had been to be narrowed to finally run the cases to converged solutions without relevant errors. Results obtained from the Aspen simulations are shown in Table 1, Table 2, Table 3, Table 4, Table 5 and Table 6 of cases 0 to 5 respectively, where only the most important streams are shown. Streams Feed, Air Reactor, Reactor Inlet, Cooling Water, Lower Reactor Outlet, Upper Reactor Outlet, Air Turbine and Natural Gas remain the same for every cases for this reason these streams just appear in Table 1.

In Tables 1, 2, 3, 4, 5 and 6, the different values for principal variables can be seen.

The focus of this project is the heat integration and energy generation, for this reason, below, the energetic results are shown and the different cases are compared.

In Table 7 the energy consumed and the energy generated in the different configurations are shown. As can be seen, all of these configurations are applicable for heat integration and in addition, the net work generated, calculated as shown in equation (1), is positive (around 2-3 kW).

$$\begin{gathered}\textit{Net work} = \textit{Energy production by turbine} - (\textit{Energy consumption by compressor turbine} \\ + \textit{Energy consumption by feed pump} + \textit{Energy consumption by cooling water pump} + \\ \textit{Energy consumption by air compressor})\end{gathered} \tag{1}$$

The net work depends of the intermediate pressure between valve and ejector. The theoretical compressor of the ejector consumes a fix part of the energy generated by the theoretical turbine (30%), therefore, when intermediate pressure is higher, the compressor of the ejector can compress more air, and thus the compressor of turbine needs less energy because the amount of air is smaller and net work is increased, as expected.

Furthermore, in case 5, the net work is maximum because of the inlet pressure to ejector is the highest (230 bar, outlet pressure from reactor) among the cases.

In summary, the best case of heat integration is the case 5 because the net work produced is highest. Differences between cases 2, 3, 4 and 5 concerning the produced net work are small; this is due to the relative amount of the mass flow rate that can be derived to the ejector in order to the final injection pressure in the GT combustor to be reached. In other words, as the mass flow rate of the effluent stream is small in comparison to the mass flow rate of GT air, the fraction of it that can be compressed to the required pressure is small, and thus differences between cases are reduced, being the maximum percentage differences between those setups including ejectors (cases 2 and 5) a 4.5 %. These results are heavily dependent on the size of the GT, i.e., if the GT chosen is smaller, then the percentage recovery would be higher, as far as the mass flow rate of the effluent remains the same, causing an enhancement in the fraction of GT air that can be compressed. The choice of the GT is largely dependent on the overall, global process needs and characteristics, and thus the profitability of the proposed setup can be very variable. The improvement in work production when using the ejector setup (case 5) relative to case 0 (no injection at all) is 113.5 %, and only 9.6 % relative to case 1 (no ejector, injection at 15.6 bar), what raises serious doubts about the worth of the ejector as a power recovery device, due to the increased cost of the equipment and operation/control issues involved.

From the production and consumption is obtained the percentage of the efficiency in energy production of the system of each case as shown in equation (2).

$$Efficiency = \frac{Net\ work}{kW\ injected\ at\ the\ feed\ (lactose) + kW\ injected\ at\ the\ NG} \cdot 100$$

(2)

A parallel analysis can be raised on the GT out-coming heat flows and temperatures; the reduced mass flow rates of the effluent stream relative to the mass flow rate of GT air, and thus the small fraction of air compressed in the ejector, causes reduced temperature differences between the various cases, being the maximum differences in outlet temperature between those setups including ejectors (cases 2 and 5) 8 $^{O}$C, with the mass flow rate of flue gases remaining the same. The difference in temperature between case 0, GT without injection and case 5 is 27.5 $^{O}$C.

## 4. Conclusions

The integration of SCWO reactors with the power generation from gas turbines with steam injection showed to be a promising alternative for improving the energy balance of this operation, using compact, commercially available equipment and resulting in energetically efficient processes.

In this work several configurations were explored by simulation: GT/heat recovery as utilities (case 0, i.e., one-way integration i.e., GT used as utility with no effluent injection); reactor outlet injected into the GT (both ways integration) after pressure reduction in a valve with (cases 2, 3 and 4) and without (case 1) mixing in an ejector with a fraction of the GT combustion air. And the last case (case 5) without valve but with ejector. In every case the energy recovery from the flue gases is improved due to the increased mass flow rate. The production of shaftwork by the gas turbine is enhanced by injecting the reactor outlet produced in the process. The detailed design of an efficient ejector can be a difficult task, albeit much easier than designing a custom turbine.

Different final valve expansion pressures can have a significant influence in shaft work recovery, but this is difficult to assess due to strong dependencies of the maximum allowable value of this pressure on the specific equipment (GT) and injection details.

Case 0 is the most basic configuration, there isn't gas injection, and being for this reason the net work produced the lowest. With this configuration, heat integration is achieved to just preheat inlet stream. Energy integration is improved with gas injection in case 1.

In case 2, 3 and 4 the high pressure is used to increase energy production using an ejector. The simulation software employed doesn't include an ejector or jet-steam unit, and for this reason a simplified configuration was used.

If intermediate pressure is high, the net work is higher, therefore, case 4 is better than case 2 and case 3. These cases are improved whit the case 5. All the outlet pressure reactor is used for the ejector.

And finally, the efficiencies obtained (Table 7) in every cases are over 25 % and going to up 34.6 % in case 5.

## Acknowledgements

Y.G.R. & A.M. thanks to MS3 for PhD financial support. M.D.B. thanks MINECO for RyC fellowship (RYC-2013-13976) & MINECO project CTQ2013-44143-R for financial support.

## References

[1] G. Brunner, Hydrothermal and supercritical water processes, in, Elsevier, Hamburg, 2014, pp. 2-666.

[2] M.D. Bermejo, M.J. Cocero, Supercritical water oxidation: A technical review, AIChE J., 52 (2006) 3933-3951.

[3] P.A. Marrone, Supercritical water oxidation - Current status of full-scale commercial activity for waste destruction, J. Supercritical Fluids, 79 (2013) 283-288.

[4] J.P.S. Queiroz, M.D. Bermejo, F. Mato, M.J. Cocero, Supercritical water oxidation with hydrothermal flame as internal heat source: Efficient and clean energy production from waste, The Journal of Supercritical Fluids, 96 (2015) 103-113.

[5] M.D. Bermejo, Á. Martín, J. Queiroz, P. Cabeza, F. Mato, M.J. Cocero, Supercritical Water Oxidation (SCWO) of Solid, Liquid and Gaseous Fuels for Energy Generation, in: Z. Fang, C. Xu (Eds.) Near-critical and Supercritical Water and Their Applications for Biorefineries, Springer Netherlands, 2014, pp. 401-426.

[6] E.D. Lavric, H. Weyten, J. De Ruyck, V. Pleşu, V. Lavric, Delocalized organic pollutant destruction through a self-sustaining supercritical water oxidation process, Energy Convers. Manage., 46 (2005) 1345-1364.

[7] J.P.S. Queiroz, On the development of computational tools for the modeling and simulation of SCWO process intensified by hydrothermal flames., in, University of Valladolid, 2014.

[8] P. Cabeza, Studies in the development of supercritical water oxidation vessel reactors with hydrothermal flame as an internal heat source., in, University of Valladolid, 2012.

[9] P. Cabeza, J.P.S. Queiroz, S. Arca, C. Jiménez, A. Gutiérrez, M.D. Bermejo, M.J. Cocero, Sludge destruction by means of a hydrothermal flame. Optimization of ammonia destruction conditions, Chemical Engineering Journal, 232 (2013) 1-9.

[10] M.E. McKay, A. Rabl, A case study on cogeneration, Energy, 10 (1985) 707-720.

[11] L. Langston, Market drivers for electric power gas turbines: reasons for the revolution., in: Global gas turbine news, 1996.

[12] Y.S.H. Najjar, M. Akyurt, O.M. Al-Rabghi, T. Alp, Cogeneration with gas turbine engines, Heat Recovery Systems and CHP, 13 (1993) 471-480.

[13] T.G. Koivu, New technique for steam injection (STIG) using once through steam generation (GTI/OTSG) Heat recovery to improve operational flexibility and cost performance., Industrial application of gas turbines committe. , Paper No: 07-IAGT-02.02 (2007).

[14] K. Nishida, T. Takagi, S. Kinoshita, Regenerative steam-injection gas-turbine systems, Applied Energy, 81 (2005) 231-246.

[15] D.A. Cantero, L. Vaquerizo, F. Mato, M.D. Bermejo, M.J. Cocero, Energetic approach of biomass hydrolysis in supercritical water, Bioresource Technology, 179 (2015) 136-143.

[16] B.D. Phenix, J.L. DiNaro, J.W. Tester, J.B. Howard, K.A. Smith, The effects of mixing and oxidant choice on laboratory-scale measurements of supercritical water oxidation kinetics, Industrial and Engineering Chemistry Research, 41 (2002) 624-631.

## Tables

Table 1

| | Temperature (°C) | Pressure (bar) | Mass flow (kg/h) | Partial molar flow (kmol/h) |
|---|---|---|---|---|
| Feed | 20 | 1 | 13.5 | 0.005 $C_{12}H_{22}O_{11}$<br>0.652 $H_2O$ |
| Air Reactor | 20 | 1 | 10 | 0.073 $O_2$<br>0.274 $N_2$ |
| Reactor Inlet (Feed and Air Reactor) | 400 | 230 | 23.5 | 0.073 $O_2$<br>0.274 $N_2$<br>0.005 $C_{12}H_{22}O_{11}$<br>0.652 $H_2O$ |
| Cooling Water | 35.4 | 230 | 5.6 | 0.311 $H_2O$ |
| Lower Reactor Outlet | 700 | 230 | 9.469 | 0.526 $H_2O$ |
| Upper Reactor Outlet | 700 | 230 | 19.631 | 0.011 $O_2$<br>0.274 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Air Turbine | 20 | 1 | 80.9 | 0.589 $O_2$<br>2.215 $N_2$ |
| Natural Gas | 20 | 15.6 | 1.349 | 0.003 $CO_2$<br>0.076 $CH_4$ |
| Gas Turbine Flue Gases | 583.8 | 1 | 82.249 | 0.438 $O_2$<br>2.215 $N_2$<br>0.079 $CO_2$<br>0.151 $H_2O$ |
| Cooled Gas Turbine Gases | 192 | 1 | 82.249 | 0.438 $O_2$<br>2.215 $N_2$<br>0.079 $CO_2$<br>0.151 $H_2O$ |

Table 2

| | Temperature (ºC) | Pressure (bar) | Mass flow (kg/h) | Partial molar flow (kmol/h) |
|---|---|---|---|---|
| Injected Stream | 676.1 | 15.6 | 19.631 | 0.011 $O_2$<br>0.274 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Gas Turbine Flue Gases | 539.9 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |
| Cooled Gas Turbine Flue Gases | 235.7 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |

Table 3

| | Temperature (ºC) | Pressure (bar) | Mass flow (kg/h) | Partial molar flow (kmol/h) |
|---|---|---|---|---|
| Ejector Inlet (Valve Outlet) | 680.7 | 50 | 19.631 | 0.011 $O_2$<br>0.274 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Air Compressor Turbine | 20 | 1 | 77.552 | 0.565 $O_2$<br>2.123 $N_2$ |
| Air Ejector | 20 | 1 | 3.358 | 0.024 $O_2$<br>0.092 $N_2$ |
| Ejector Outlet | 611.1 | 15.6 | 22.989 | 0.036 O2<br>0.366 N2<br>0.062 CO2<br>0.494 $H_2O$ |
| Gas Turbine Flue Gases | 523.3 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |
| Cooled Gas Turbine Flue Gases | 227.5 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |

Table 4

| | Temperature (ºC) | Pressure (bar) | Mass flow (kg/h) | Partial molar flow (kmol/h) |
|---|---|---|---|---|
| Ejector Inlet (Valve Outlet) | 686.8 | 100 | 19.631 | 0.011 $O_2$<br>0.274 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Air Compressor Turbine | 20 | 1 | 75.929 | 0.553 $O_2$<br>2.079 $N_2$ |
| Air Ejector | 20 | 1 | 4.981 | 0.036 $O_2$<br>0.136 $N_2$ |
| Ejector Outlet | 584.1 | 15.6 | 24.612 | 0.048 $O_2$<br>0.410 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Gas Turbine Flue Gases | 519.6 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |
| Cooled Gas Turbine Flue Gases | 223.5 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |

Table 5

| | Temperature (ºC) | Pressure (bar) | Mass flow (kg/h) | Partial molar flow (kmol/h) |
|---|---|---|---|---|
| Ejector Inlet (Valve Outlet) | 692.3 | 150 | 19.631 | 0.011 $O_2$<br>0.274 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Air Compressor Turbine | 20 | 1 | 75.089 | 0.547 $O_2$<br>2.056 $N_2$ |
| Air Ejector | 20 | 1 | 5.821 | 0.042 $O_2$<br>0.159 $N_2$ |
| Ejector Outlet | 571 | 15.6 | 25.451 | 0.054 O2<br>0.433 N2<br>0.062 CO2<br>0.494 $H_2O$ |
| Gas Turbine Flue Gases | 517.6 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |
| Cooled Gas Turbine Flue Gases | 221.5 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |

Table 6

| | Temperature (ºC) | Pressure (bar) | Mass flow (kg/h) | Partial molar flow (kmol/h) |
|---|---|---|---|---|
| Air Compressor Turbine | 20 | 1 | 74.290 | 0.541 $O_2$<br>2.034 $N_2$ |
| Air Ejector | 20 | 1 | 6.620 | 0.048 $O_2$<br>0.181 $N_2$ |
| Ejector Outlet | 559.1 | 15.6 | 26.251 | 0.059 $O_2$<br>0.455 $N_2$<br>0.062 $CO_2$<br>0.494 $H_2O$ |
| Gas Turbine Flue Gases | 515.8 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |
| Cooled Gas Turbine Flue Gases | 219.5 | 1 | 101.889 | 0.449 $O_2$<br>2.489 $N_2$<br>0.140 $CO_2$<br>0.645 $H_2O$ |

Table 7

| | Case 0 | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 |
|---|---|---|---|---|---|---|
| Ejector Inlet Pressure (bar) | - | - | 50 | 100 | 150 | 230 |
| Air Ejector (mass fraction) (%) | - | - | 4.150 | 6.156 | 7.194 | 8.183 |
| Outlet combustor temperature (ºC) | 1041.4 | 950.1 | 939.3 | 934.1 | 931.4 | 928.8 |
| Gas Turbine Flue Gases Temperature (ºC) | 583.8 | 530.9 | 523.3 | 519.6 | 517.6 | 515.8 |
| Cooled Gas Turbine Flue Gases Temperature (ºC) | 192 | 235.7 | 227.5 | 223.5 | 221.1 | 219.5 |
| Energy consumption by compressor-turbine (kW) | 9.874 | 9.873 | 9.463 | 9.265 | 9.163 | 9.065 |
| Energy production by turbine (kW) | 12.674 | 15.333 | 15.189 | 15.120 | 15.084 | 15.050 |
| Energy consumption by feed pump (kW) | 0.330 | 0.330 | 0.330 | 0.330 | 0.330 | 0.330 |
| Energy consumption by cooling water pump (kW) | 0.142 | 0.142 | 0.142 | 0.142 | 0.142 | 0.142 |
| Energy consumption by air compressor | 2.328 | 2.328 | 2.328 | 2.328 | 2.328 | 2.328 |
| **Net work (kW)** | **0** | **2.660** | **2.926** | **3.055** | **3.121** | **3.185** |
| Net work from turbine (kW) | 2.800 | 5.460 | 5.726 | 5.855 | 5.921 | 5.985 |
| Improvement percentage with respect to case 0 (%) | | 95 | 104.5 | 109.107 | 111.464 | 113.75 |
| Improvement percentage with respect to previous case (%) | | 95 | 4.872 | 2.253 | 1.127 | 1.081 |
| **Efficiency (%)** | **0** | **28.934** | **31.828** | **33.231** | **33.949** | **34.645** |

## Figures

Figure 1

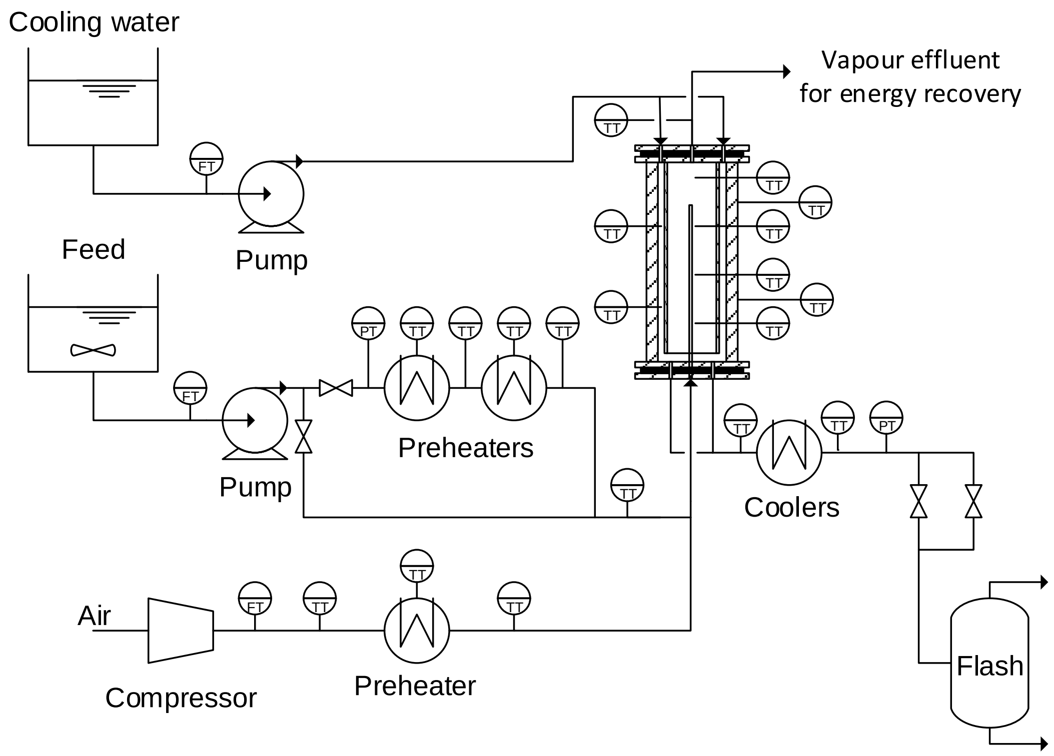
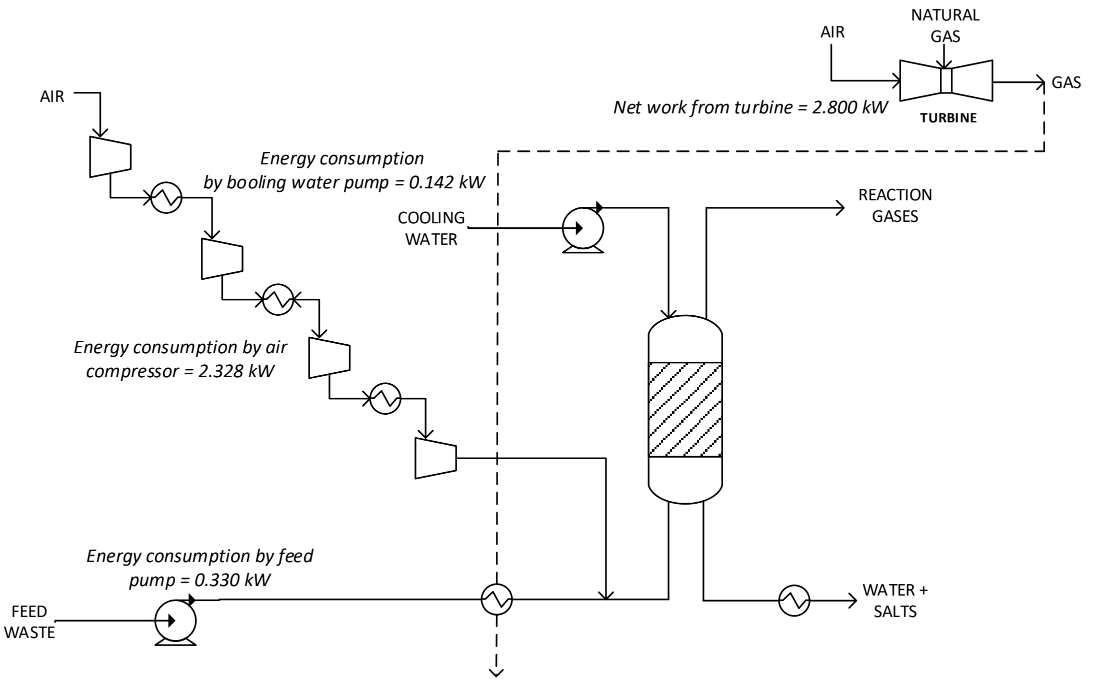


Figure 2



AIR
NATURAL GAS
AIR
GAS
Net work from turbine = 2.800 kW
TURBINE
Energy consumption by booling water pump = 0.142 kW
COOLING WATER
REACTION GASES
Energy consumption by air compressor = 2.328 kW
Energy consumption by feed pump = 0.330 kW
FEED WASTE
WATER + SALTS

Figure 3

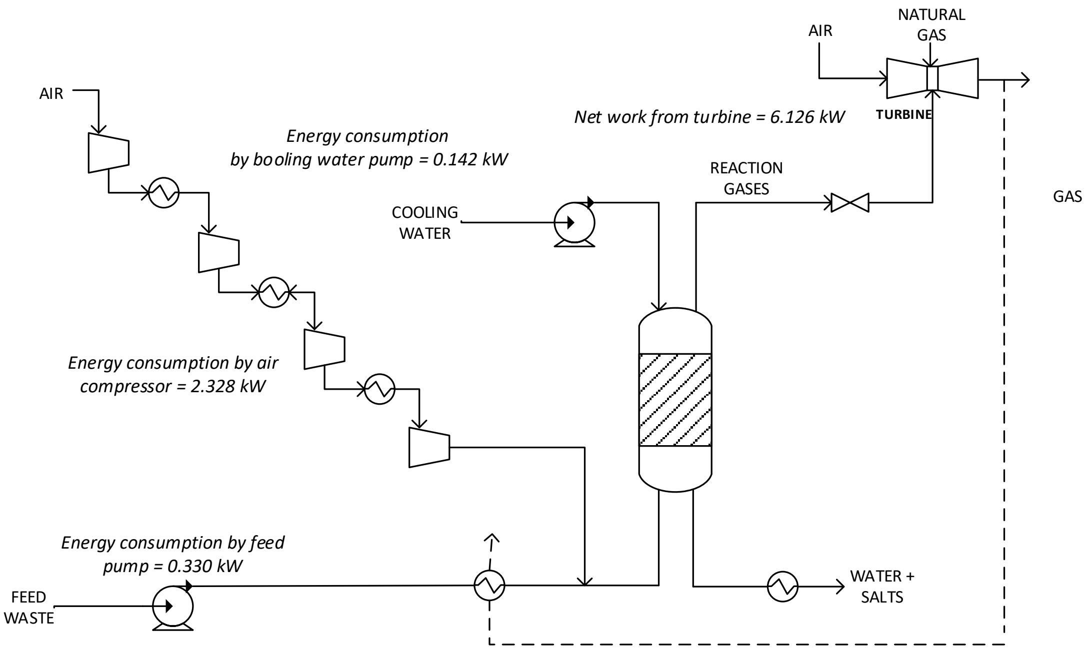

AIR
NATURAL GAS
Net work from turbine = 6.126 kW
TURBINE
AIR
Energy consumption by booling water pump = 0.142 kW
REACTION GASES
GAS
COOLING WATER
Energy consumption by air compressor = 2.328 kW
Energy consumption by feed pump = 0.330 kW
FEED WASTE
WATER + SALTS

Figure 4

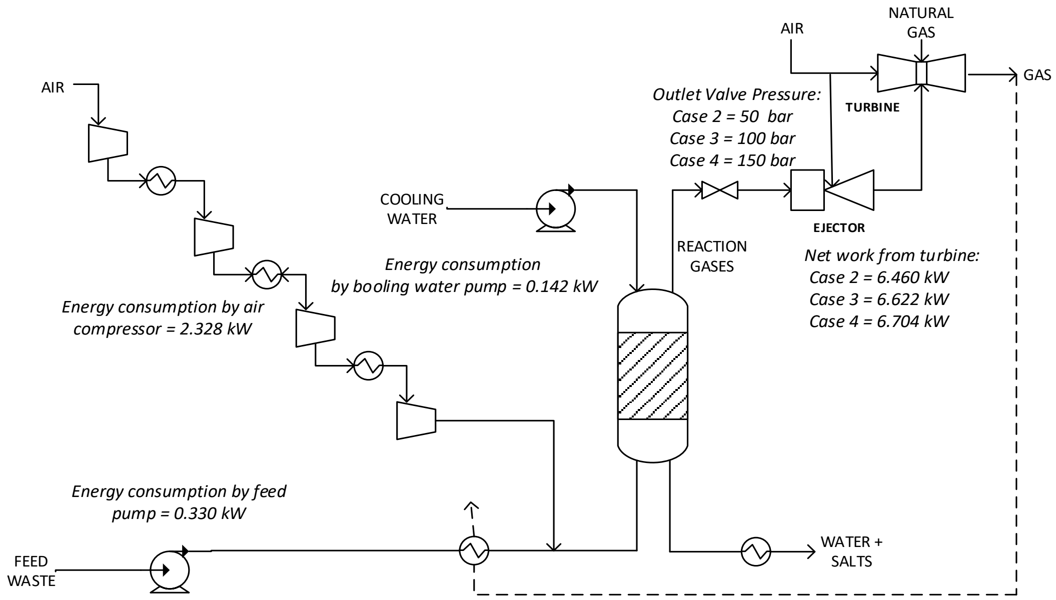
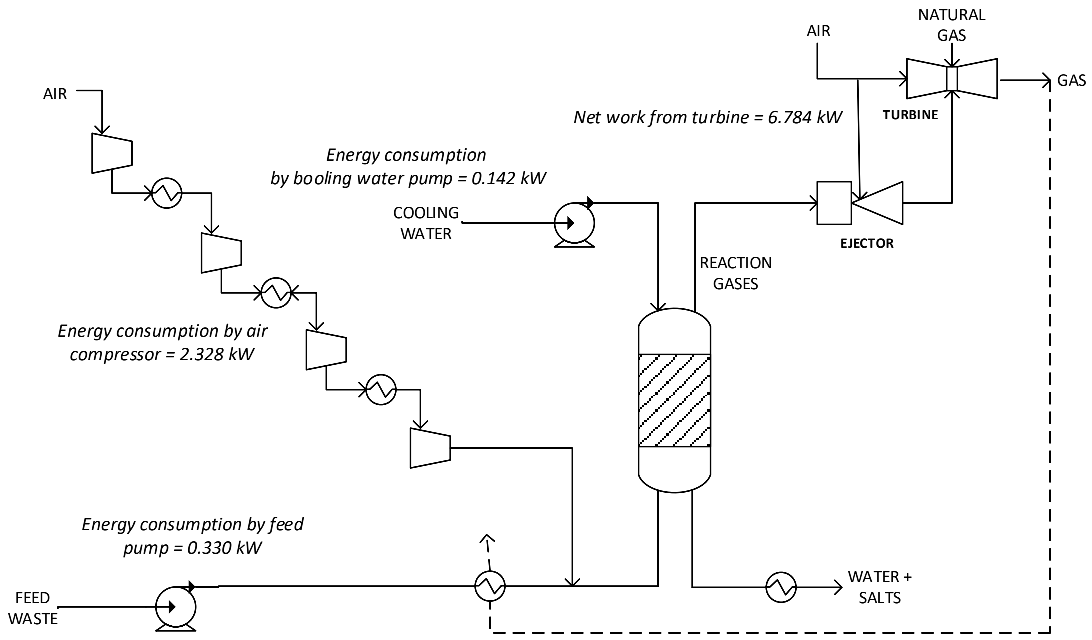

AIR
NATURAL GAS
AIR
GAS
TURBINE
Outlet Valve Pressure:
Case 2 = 50 bar
Case 3 = 100 bar
Case 4 = 150 bar
COOLING WATER
EJECTOR
REACTION GASES
Net work from turbine:
Case 2 = 6.460 kW
Case 3 = 6.622 kW
Case 4 = 6.704 kW
Energy consumption by booling water pump = 0.142 kW
Energy consumption by air compressor = 2.328 kW
Energy consumption by feed pump = 0.330 kW
FEED WASTE
WATER + SALTS

Figure 5



AIR
NATURAL GAS
AIR
GAS
TURBINE
Net work from turbine = 6.784 kW
Energy consumption by booling water pump = 0.142 kW
COOLING WATER
EJECTOR
REACTION GASES
Energy consumption by air compressor = 2.328 kW
Energy consumption by feed pump = 0.330 kW
FEED WASTE
WATER + SALTS

**Tables and Figures Captions.**

**Table 1.** Results from ASPEN simulation (Case 0, no gas injection).

**Table 2.** Results from ASPEN simulation (Case 1, effluent injection, valve decompression to 15.6 bar).

**Table 3.** Results from ASPEN simulation (Case 2, effluent injection, valve decompression to 50 bar and ejector).

**Table 4.** Results from ASPEN simulation (Case 3, effluent injection, valve decompression to 100 bar and ejector).

**Table 5.** Results from ASPEN simulation (Case 4, effluent injection, valve decompression to 150 bar and ejector).

**Table 6.** Results from ASPEN simulation (Case 5, effluent injection, no valve, ejector).

**Table 7.** Energetic results from ASPEN simulation.

**Figure 1.** Flow chart of pilot plant.

**Figure 2.** Heat integration, case 0 (flow chart).

**Figure 3.** Heat integration, case 1 (flow chart).

**Figure 4.** Heat integration, case 2, 3 and 4 (flow chart).

**Figure 5.** Heat integration, case 5 (flow chart).