J. of Supercritical Fluids 104 (2015) 1–9

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Energy recovery from effluents of supercritical water oxidation reactors

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ARTICLE INFO

Article history:
Received 18 February 2015
Received in revised form 15 May 2015
Accepted 15 May 2015
Available online 18 May 2015

Keywords:
SCWO
Shaftwork
Energy recovery
Gas turbine (GT)
Steam injection
Simulation

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 °C) 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.

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

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http://dx.doi.org/10.1016/j.supflu.2015.05.014
0896-8446/

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 °C 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 °C 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.

As a workaround, in this work we propose the injection of the top SCWO reactor effluent into the combustor or the expanding path of commercial gas turbines. We are considering, in principle, the scenario of a GT serving heat and power to a main, large facility where the SCWO reactor resides as a process unit, even though a smaller, dedicated GT can be considered. Enthalpy from the SCWO effluent would be recovered by joining it to the GT flue gases at the maximum possible pressure and temperature and following the same power recovery path through the expanding section of the GT and heat recovery path after the GT flue gases outlet. This way commercial, ready available, efficient equipment could be employed, avoiding the costs of a grass-root design of a custom turbine. Energy recovery from the effluent would take place within the GT flue gases stream. Heat and power from the GT offer also energy integration opportunities to the SCWO unit, allowing this unit to use in situ generated, less costly and perhaps autonomous energy flows for preheating and compression.

The aim of this work is to perform a theoretical analysis and assessment of energy recovery possibilities for a typical SCWO reactor effluent being injected in commercial GT. Effluent injection would take place into or after the GT combustor, and directly (if possible, and this can depend on the relative size of the GT/effluent mass flow rates) or following the needed pressure reduction. Should a pressure reduction be needed the prospect arises to take advantage of the effluent expansion to rise the pressure of a GT combustion air fraction, cutting down the power withdrawn in the GT air compressor and consequently increasing the overall power production. This option is also analyzed in combination with basic effluent injection.

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 Fig. 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.

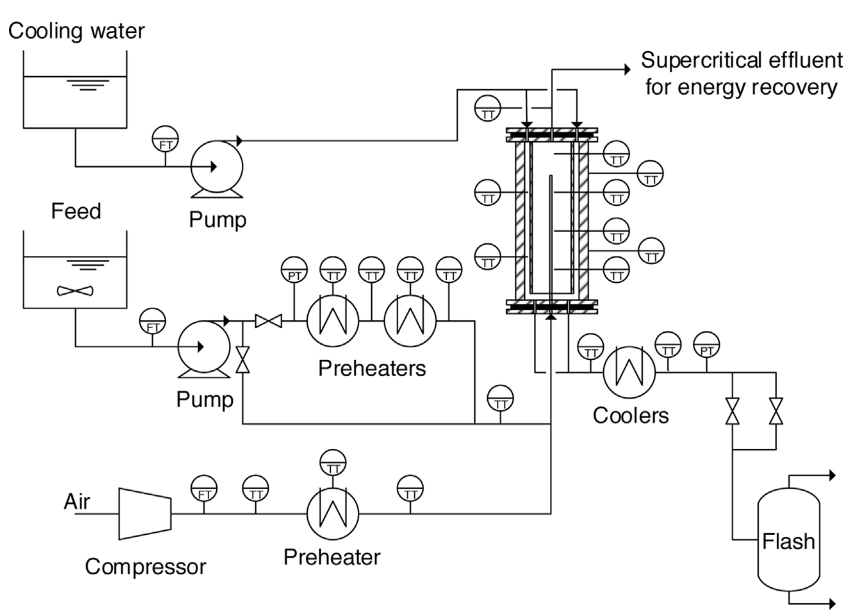

Fig. 1. Flow chart of pilot plant.