ARTICLE IN PRESS

Energy xxx (2015) 1–11

Contents lists available at ScienceDirect

Energy

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

Supercritical water oxidation for energy production by hydrothermal flame as internal heat source. Experimental results and energetic study

Pablo Cabeza, Joao Paulo Silva Queiroz [1], Manuel Criado, Cristina Jiménez, Maria Dolores Bermejo*, Fidel Mato, Maria Jose Cocero

High Pressure Process Group, Dept. of Chemical Engineering and Environmental Technology, Universidad de Valladolid, Doctor Mergelina, s/n, 47011, Valladolid, Spain

A R T I C L E I N F O

Article history:
Received 22 April 2014
Received in revised form
5 March 2015
Accepted 23 June 2015
Available online xxx

Keywords:
Supercritical water oxidation
Hydrothermal flames
Renewable energy
Reactor design

A B S T R A C T

The cooled wall reactor has been modified by adding an additional upper outlet of products at 500–700 °C to improve energy recovery and make possible energy generation with the supercritical water oxidation of different waste. Experimental and modeling results of the performance of this new reactor configuration are presented as well as a theoretical analysis of the energy recovery of the reactor compared to other supercritical water oxidation reactors. Different flow distributions were tested to find the best elimination conditions. Total organic carbon removal over 99.99% was obtained at room injection temperatures, when the fraction of products leaving the reactor in the upper effluent is lower than 70% of feed flow. The performance of the reactor was tested with the oxidation of a recalcitrant compound such as ammonia. Removals higher than 99% of $N-NH_4^+$ were achieved at temperatures near 700 °C. The behavior of the reactor working with feeds with up to 2.5% wt Na_2SO_4 could be injected in the reactor without plugging problems. Upper effluent always presented a concentration of salt lower than 30 ppm. Theoretical energetic analysis shows that the performance of this reactor is superior to other designs obtaining a maximum power efficiency of 27% (0.339 kW/kg-feed).

1. Introduction

Since Franck and coworkers discovered hydrothermal flames [1] and it could be applied to the SCWO (Supercritical Water Oxidation), new challenges came up to the study of SCWO. For flammable compounds such as methane or methanol, hydrothermal flame can occur at temperatures as low as 400 °C [2]. SCWO is the oxidation of organics in water under conditions above its critical point. In presence of hydrothermal flames the reaction times can be reduced to the order of milliseconds [3] without the production of subproducts typical of conventional combustion such as NOx [4] or dioxins [5].

SCWO with a hydrothermal flame has a number of advantages over the flameless process. Some of these advantages permit overcoming the traditional challenges that make the successful and profitable commercialization of SCWO technology difficult. The advantages include the following [3]:

- The reduced residence times (in the order of milliseconds) allows the construction of smaller reactors.
- It is possible to carry out the reaction with feed injection temperatures near to room temperature when using vessel reactors [6,7]. This avoids problems such as plugging and corrosion in a preheating system, having an advantage from the operational and energy integration perspective.
- Higher operation temperatures improve the energy recovery.

The first reactor probably working with a hydrothermal flame inside was the MODAR reactor, working in conditions of concentration, temperature and pressure above the ignition conditions of methanol and being able to work with injection temperatures of

* Corresponding author. Tel.: +34 983423166.
E-mail addresses: palabreras@gmail.com (P. Cabeza), joao.deq@gmail.com (J.P. Silva Queiroz), mcriado_sastre@hotmail.com (M. Criado), crisbaterna@gmail.com (C. Jiménez), mdbermejo@iq.uva.es (M.D. Bermejo), fidel@iq.uva.es (F. Mato), mjcocero@iq.uva.es (M.J. Cocero).
[1] Present address: Dept. of Chemical Engineering, Universidade Federal de Pernambuco, Prof. Artur de Sá, s/n, Cidade Universitária, 50740-521, Recife, PE, Brazil.

http://dx.doi.org/10.1016/j.energy.2015.06.118
0360-5442/

25 °C and injecting the air at 220 °C [7]. In the ETH of Zurich, the direct injection of the waste into a diffusion hydrothermal flame generated inside the reactor was developed as a solution to avoid the external preheating of the waste up to supercritical conditions [8,9]. Príkopský and coworkers investigated the feasibility of injecting feeds with a 3%wt of sodium sulfate (Na_2SO_4) in the TWR (transpiring wall reactor) with a diffusion hydrothermal flame as internal heat source [10]. No plugging was observed during the experiments, but salt deposits were detected in the upper hot zone of the reactor. In a previous investigation of our research group [6], it was found that using a transpiring wall reactor, a premixed hydrothermal flame inside the reaction chamber could be maintained when injecting the feed at a temperature as low as 110 °C. Using a similar reactor, feeds with up to 4.74% wt Na_2SO_4 could be injected [11]. The reactor worked without plugging, but the recovery of salts was only between 5% and 50%. Both research groups reported an increase in the temperature when salt was injected in the reactor [10,11]. Zhang et al. [12] studied the operational parameters of a TWR developed to generate thermal fluids for oil recovery. They used water-methanol as artificial fuel prior to treating oil exploration wastewater, and they found the limits of temperature of transpiring flow in order to avoid the quenching and extinction of hydrothermal flame.

It has been proved that injection of cold feeds over a hydrothermal flame is only possible when working with vessel reactors [9–11] and it is not possible when working with tubular reactors [13]. This behavior was due to the low flame front velocities in hydrothermal flames that is lower than 0.1 m/s, in comparison to the higher flame front velocities at atmospheric conditions (0.4–3 m/s). This is the reason why flow velocities lower than 0.1 m/s are necessary to keep a stable hydrothermal flame where cold reagents can be injected [14]. Our research group has succeeded in keep working continuously a vessel reactor injecting feeds at temperatures as low as 25 °C [15].

Even though the most immediate application of hydrothermal flames is in the SCWO process for waste destruction, which is the most industrially developed hydrothermal process, it is possible to move from the idea of hydrothermal flame as a technology for the destruction of wastes to consider it as a technology for the generation of clean energy, which could eventually substitute the actual technologies based on atmospheric combustion [16]. Supercritical water is already applied in energy fields through gasification processes for waste valorization Facchinetti et al. [17], Rönnlund et al. [18]. The efficiency in energy production by SCWO of coal and direct expansion of the effluent was compared to the efficiency of other conventional power plants by Bermejo et al. [19]. If the steam was produced at 650 °C and 30 MPa, efficiencies as high as 38% were obtained by SCWO. Efficiency was as high as 41% if the effluent was reheated and expanded a second time. The efficiencies at the same steam conditions for pulverized coal power plant and pressurized fluidized bed power plant were 32 and 34% respectively. Comparison is more favorable using oxygen enriched air or even using pure oxygen as the oxidant. In this last option the cost of the oxidant must be assumed. Nevertheless, it is known that in traditional combustion power plants, oxygen is used to improve efficiency. Donatini et al. [20] simulated a power plant based on direct combustion of pulverized coal in a SCWO reactor with a system for CO_2 capture. They reported net efficiencies around 27% and found that the consumption of the air separation unit for oxygen production strongly affects the viability of the plant. A similar analysis has been made by Kotowicz and Michalski [21], whom have proposed several operations in order to increase efficiency for each step in a power plant model: air separation unit, boiler (SCWO reactor burning coal) and steam turbine.

Arai et al. [22] proposed the supercritical oxidation of biomass wastes and other sustainable fuels with a hydrothermal flame as a clean energy source for reaching a sustainable society with a decentralized production based on renewable resources. Augustine and Tester [3] also propose its utilization with low grade fuels. In general, this technology can be applied to the valorization of waste such as waste water treatment plant sludge, biomass or plastic wastes or any kind of waste with high energetic content. Basic theoretical calculations indicate that feeds with an energy content of 930 kJ/kg (roughly equivalent to an aqueous solution with 2% ww of hexane) can supply enough energy to preheat the feed from room temperature up to 400 °C, and to generate electric power equivalent to that consumed by the high pressure pump and the air compressor [23]. A remarkable aspect about working with hydrothermal flames is improving energy recovery in SCWO system [19]. Hydrothermal flames allow new reactor designs that not only are able to inject feeds without preheating because of the possibility of injecting reactants at room temperature but also use the heat released by the flame for other purposes as the energetic integration of the process or for production of electricity by turbines [24]. Smith Jr. et al. [25] used exergy analysis to study the partial and total oxidation of methane in supercritical water for a heat-integrated supercritical water reactor and electrical energy production system. They assume a direct expansion of products (at 400 °C) in a turbine, followed by heat recovery of the expanded stream. It was found that the process could be energy self-sufficient and optimum flow rates were calculated in order to minimize reactor heat requirements or maximize net electrical work. The high temperature effluent can also be used as heat source in other hydrothermal processes, such as liquefaction or gasification, where the heat recovery is a critical issue [26,27]. In the case of waste with high concentration of inorganic substances, new reactor designs able to separate these salts from the effluent must be developed in order to make it possible to directly expand the effluent in an electricity production turbine.

The main goal of this work is the study of the behavior of new cooled wall reactor with the main particularity of having two outlets in order to try to keep the maximum heat released by the flame in a clean and high temperature flow leaving the reactor from the upper zone and other flow at subcritical conditions with the salts dissolved going out for the bottom of the reactor. In this way the upper/lower effluent relation was optimized taking into account the temperature profiles inside the reactor and the organic matter elimination in both streams. The performance of the reactor with recalcitrant pollutants such as ammonia was tested as well as the performance of the reactor with feeds containing salts. A CFD model is also used to describe the behavior of the reactor. Finally, a purely theoretical energy recovery study of the process with the new reactor was performed, including the possibility of direct expansion in hypothetical devices.

2. Experimental

2.1. Experimental setup

All the experiments analyzed in this research have been carried out in the SCWO facility installed in the University of Valladolid. It consists of a continuous facility working with a feed flow of 22.5 L/h, and air supplied by a four stage compressor, with a maximum feed rate of 36 kg/h is used as the oxidant. The reactor consist of a pressure vessel made of AISI 316 stainless steel able to stand a maximum pressure of 30 MPa and a maximum wall temperature of 400 °C, containing a reaction chamber made of Ni-alloy 625 where the temperature be as high as 700 °C.

Please cite this article in press as: Cabeza P, et al., Supercritical water oxidation for energy production by hydrothermal flame as internal heat source. Experimental results and energetic study, Energy (2015), http://dx.doi.org/10.1016/j.energy.2015.06.118