ARTICLE IN PRESS

The Journal of Supercritical Fluids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Supercritical water processes: Future prospects

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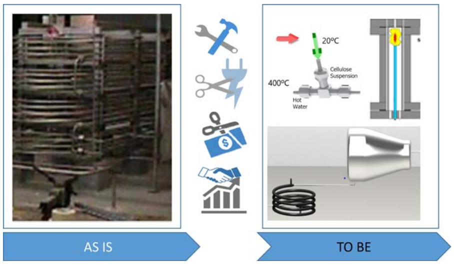
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Process intensification
Micro combustors
Oxidation
Hydrolysis
Shaft work
Energy integration

ABSTRACTS

This contribution examines the challenges faced by supercritical water processes for industrial development. As an alternative, the intensification of the supercritical water processes is presented in order to reduce the size of the equipment needed and to facilitate the scaling up of the process. The perspective of developing micro combustors using hydrothermal flames as the internal heat source could open up an alternative for the in-situ energy generation in biorefineries, for example. The fundamental studies about supercritical water hydrolysis using ultrafast reactors has enabled extremely high selectivity in the biomass fractionation processes, and in the production of C2 and C3 building blocks from key components. The high-energy consumption of this process is another issue that limit its commercialization. In the examples proposed, the energy, work recovery and energy integration allows the reduction of the total energy consumption and, in some processes, the availability of extra energy as heat and work.

1. Current state

Supercritical water (SCW) has been used as coolant in nuclear reactors for many years. In addition, geothermal studies about the water inside the earth's crust have contributed knowledge to the hydrothermal processes [1]. Modell had the vision to develop industrial processes based on the use of water at supercritical conditions after the preliminary studies about the total miscibility of hydrocarbons in SCW [2]. His companies Modar inc and Modell were a key point in the development of the supercritical water oxidation processes for environmental applications [3].

In its origin, the process aroused a great interest among the process industries or in public organisms as being a solution to recalcitrant waste treatment problems. Companies such as General Atomics or Foster and Wheeler were involved in the development of the supercritical water transpiring wall reactor. They made relevant contributions, working in projects for public USA organisms, to the development of injectors to achieve good mixing [4].

In Europe, Franck significantly improved the available information regarding SCW properties [5–7]. Companies such as Chematur built the first sludge SCWO pilot plant with a treatment capacity of 200 kg/h, in 1998 [8]. In Spain, the EMGRISA public company supported Valladolid University's research to develop the first cooled wall reactor in a pilot plant with a treatment capacity of 30 kg/h in 1994, and a demonstration plant with a treatment capacity of 200 kg/h in 2002 [9].

The main industrial development associated with sludge treatment

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https://doi.org/10.1016/j.supflu.2017.11.018
Received 9 October 2017; Received in revised form 20 November 2017; Accepted 21 November 2017

Please cite this article as: Cocero, M.J., The Journal of Supercritical Fluids (2017), https://doi.org/10.1016/j.supflu.2017.11.018

has involved tubular reactors [10–12]. Conventional reactors are thin tubes about hundred meters long, with mixing problems that force them to work with great excesses of oxygen and with evident plugging problems due to solid precipitation. In practice, industrial plants work with two reactors, one under operation and the other undertaking the cleaning of deposited solids [13–15]. In some applications, the changeover of the reactors takes over 30 min. Furthermore, cleaning is a highly energy- and time-consuming step. Its industrial development has not progressed due to the lack of control of corrosion and salt precipitation processes, the high reactor surface exposed to corrosion and the small diameter that favors plugging problems, in addition to the high processing cost [16–18].

A well-known problem of SCW oxidation is the energy requirement, which can be very high, particularly, if simple plug-flow tubular reactors are used, inasmuch as these designs require the preheating of the influent up to supercritical water temperature. The correct use of the energy produced by the oxidation is a crucial step in order to make SCWO processes economically viable [19–21].

SCW gasification is another technology to which important research efforts have been devoted, but it has not been possible to progress. Only one demonstration industrial scale plant Hydromethans AG is in Switzerland [22]. Kruse concluded in a recent review that the main reason why a SCW gasification process is not attractive for industry today is due to the high processing costs [23]. Only biomass with high disposal costs are considered to be interesting feedstock, such as sewage sludge. Kruse identified the same problems found in the SCWO: plugging, corrosion, reactor design and material selection. As possible future developments, Kruse proposed hydrothermal gasification as part of a bio-refinery. During hydrothermal liquefaction, a tarry oil and an aqueous phase are produced. So, It was then proposed to gasify the organic compounds in the aqueous effluent, and use the hydrogen to up-grade the oil [23–25].

More recently, material synthesis in SCW is a technology which is approaching the market. Adschiri has produced different materials for new industrial developments [26]. Lee had a demonstration plant under operation which synthesized nanoparticles by using SCW [27]. In recent years, Lester has coordinated the Shyman EU project for the development of a 1000 t/year demonstration plant producing nanomaterials [28,29]. Again, this technology has not reached the industrial development that it could achieve, due to the high processing cost. In addition to the energy consumption, the effluent particle concentration is very low, and the water has to be eliminated, so the downstream processing could require a lot of both, time and energy. In the cases of many materials that have been developed, the cost is much higher than the same materials that are produced by conventional technologies. The opportunity, now, lies in developing new materials that can not be produced by conventional technologies, or that would be more expensive to produce conventionally.

In this special issue, Adschiri [30] and Aymonier [31] illustrate the interest of this technology for the production of advanced nanostructured materials and for developing new nanotechnology applications.

The petrochemical companies are studying the upgrading of heavy oil by SCW. This process takes advantage of the low dielectric constant of water, which allows hydrocarbons' solubility. In addition, temperature and pressure can be manipulated to adjust the water's ionic product creating a highly ionic medium, with high $[H^+]$ concentration that could improve the hydrolysis [32]. Although many studies have not been published, relevant manuscripts about thermodynamics, kinetics, and experimental and theoretical developments on the phase equilibria of relevant water–hydrocarbon systems are available [33–35]. The advantage of this process over other upgrading technologies is the high process intensification that can be achieved by the use of SCW.

Regarding energy production, power plants with SCW steam generators as the Benson type are conventional [36,37]. Also novel SCW reactors are considered more efficient reactors for nuclear plants [38].

2. SCW processes challenges

The strong features of the supercritical water processes lie in the knowledge of the processes fundamentals supported by the abundant research SCW. Specifically: the SCW properties and its mixtures; thermodynamic and kinetic studies; thermodynamic modelling; and the computational fluid dynamic model designed to improve the hydrodynamic reactors behavior. Operation at high temperature could mean fast reaction kinetics, which could allow extremely fast processes to be developed.

The weak features include the high processing cost, in addition to the operational problems associated with plugging, corrosion, reactor design, dilution of the effluents, and high energy consumption. The processes have high costs, and this in turn has an important impact on the high cost of products.

From my point of view, the main challenges concerning SCW industrial implementation are:

- To reduce the cost of the processes, by reducing the cost of equipment.
- To reduce the operation cost by improving the heat and work recovery and the integration of the energy, to reduce the overall energy consumption.
- To improve technical issues regarding operations with solids at a high temperature and pressure, pumping highly concentrated solid suspensions, minimizing the abrasion of valve stems, and improving the solid output from SCW reactors.
- To implement downstream processes in order to achieve marketable products.

3. SCW process perspectives

One way to reduce equipment costs is to take advantage of the SCW process's fast kinetics to reduce reaction time, which will reduce the reactor size. By reducing the residence time from 10 min to milliseconds, it is possible to change conventional reactor volumes of m^3 for reactors with volumes of dm^3. That means reducing the reactor size, thus facilitating the scale-up of the process as well as the reactor control. In some applications, it is possible to improve the reactor's design to reduce the problems associated with operations involving solids at a high pressure and temperature.

It is possible to reduce the operation cost by improving the energy and work recovery, for example, by recovering the work associated with the depressurization, and implementing energy integration [39].

The processes should be focused on obtaining products that are closer to the market. As there is much information about process fundamentals, the research should be oriented to develop "products close to the market". If it is the case that the process fundamentals are not yet well known, our first step is to improve our knowledge of the process fundamentals in order to achieve a faster way of developing new processes and new products.

In this section, the perspectives of the development of three supercritical water processes are presented. These processes can operate with residence times of milliseconds, which could achieve a high level of process intensification. The energy and work recovery, as well as the energy integration, are taken into account in order to minimize energy consumption or even produce net energy as heat and shaft work.

3.1. *Micro-combustors operating on the intensification of the supercritical water oxidation process, using hydrothermal flames as the internal heat source*

In 1988, Schilling and Franck achieved the formation of a diffusion flame in homogenous supercritical aqueous fluids. The combustion of 30% methane with oxygen in the homogenous supercritical phase was investigated, and stationary diffusion flames were generated up to