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Pseudo fluid modelling used in the design of continuous flow supercritical water oxidation reactors with improved corrosion resistance

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ABSTRACT

Supercritical water oxidation (SCWO) is considered to be a green technology, providing an effective route to convert waste materials into simpler, less hazardous products. This article reports the use of a physical modelling approach to assess mixing dynamics inside three different types of reactor where supercritical water (water above 374 °C and 218 atmospheres) is mixed with a second colder, waste containing, effluent flow. Physical or 'pseudo' modelling was used to simulate the general flow patterns and mixing regimes in transparent pseudo reactors (to allow visualization). Towns water was used to simulate the supercritical water flow (density 998 kg/m^3 and viscosity 1.0×10^{-3} kg/m s at 25 °C and 1 bar respectively) and 40% w/w aqueous sucrose solution to simulate the cold aqueous effluent flow (density 1176 kg/m^3, viscosity 6.16×10^{-3} kg/m s at 25 °C and 1 bar respectively). Flow rates of 100's ml min^{-1}–1000's ml min^{-1} were used to create a range of Reynolds numbers experienced during mixing at supercritical conditions (in laminar and turbulent regimes). Three types of vertical pipe-in-pipe reactor were simulated using this method (counter current and co-current arrangements). This visual technique allowed the quantification of mixing efficiency, as well as identification of issues such as flow recycling, stagnant zones, and other inconsistencies in the mixing dynamics. An upwards co-current arrangement provided the 'best' mixing i.e. with minimal wall contact during the downstream oxidation process.

1. Introduction

Under supercritical conditions ($T_c = 374$ °C, $P_c = 22.1$ MPa) [1] water offers many favorable characteristics including increased dissociation [2] (and thus increased basicity and acidity) and decreased polarity leading to an increased solubility of organic substances [3]. These properties present water as an excellent medium for the oxidation of organic waste. The process, known as *supercritical water oxidation* (SCWO), is a destructive treatment of organic waste in an aqueous medium in the presence of an oxidizing agent [2–5]. The process has numerous advantages including higher destruction efficiency and lower retention time [6] and is as a promising alternative to other treatment technologies such as incineration [7] and wet air oxidation [8].

SCWO does however suffer from a number of technical problems including corrosion [9], salt deposition [10], and high opex if not run autothermally [11]. These issues have all hindered general industrial implementation of the process [12]. Variation in the composition of the process flow can exacerbate corrosion issues [13]. The presence of halogens in the contaminant stream is a particularly problematic issue [14]. A considerable amount of research has been published on the reduction of corrosion in SCWO reactors [15]. These corrosion mitigation studies include use of high corrosion resistance materials [16], applying of liners/coatings [17], employing transpiring/cooled wall reactors [18,19], pre-neutralization [20], and optimization of process operating conditions [21]. Wellig et al. [22] claimed that the development of a sophisticated reactor design may be able to solve problems that arise during SCWO processes. Hodes et al. [23] also discussed how an appropriate reactor design and/or operational procedures would be the most effective approach to overcoming such problems. The most likely regions of the reactor to suffer from corrosion and salt deposition are the mixing areas, where the fluid temperatures are near-critical [24] and

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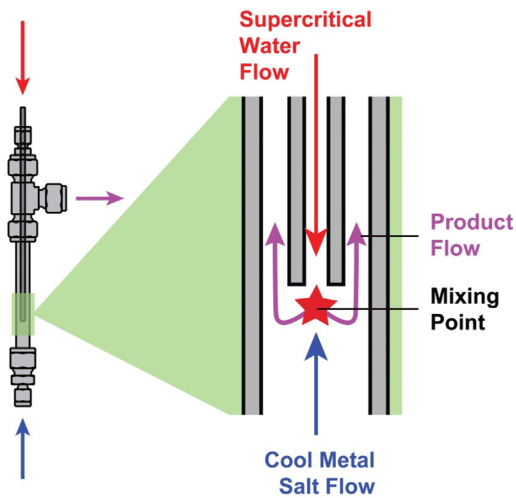

Fig. 1. Diagram of the counter-current mixing reactor used for the synthesis of nanoparticles. The cold aqueous metal salt flows upwards from the base of the reactor and mixes counter currently with a superheated water stream [32].

recirculation and disorderly mixing patterns can lead to increased salt deposition [23].

Clearly knowledge of the fluid dynamics and mixing regimes inside the reactor are fundamentally important [25]. Supercritical water cannot be directly visualized easily, because the process conditions do not easily permit transparent reactors, although research groups at Tohoku research group have had some success probing stainless steel reactors using neutron beams [26] and there are examples of visualization within sapphire micro reactors [27].

Pseudo fluid modelling can successfully recreate the mixing patterns inside actual reactors at supercritical fluid conditions [28]. Whilst this technique operates at ambient temperatures and pressures, it has been validated by recent studies using CFD modelling [29] where close agreement was found between the techniques. More recently, good correlation has been demonstrated between pseudo fluid modelling, CFD and neutron beam measurement techniques [30,31]. Advances in processing hardware, improvement in camera resolutions and greater capability of image analysis functionality have all served to improve the potential of pseudo fluids modelling as a technique. The technique has also be validated by empirical studies with reactors operating at supercritical conditions [32].

This article reports the use of pseudo fluids for identification the relative merits of three different reactor geometries that could potentially be used for continuous supercritical water oxidation. The purpose of this study is the development of useful color contour concentration maps, which simplify success to a ‘traffic light system’, clearly indicating desirable flow conditions through use of artificial color mapping.Initial visualization experiments are based on the counter current reactor design [32] which has been extensively used for nanoparticle formation through supercritical water hydrothermal synthesis. A schematic diagram for this model is shown in Fig. 1. This is a tube-in-tube configuration where the superheated water stream is flowed downward through the inner pipe (1/8″ outer diameter), and a cool metal salt stream is fed counter-currently in the outer pipe (3/8″ outer diameter) [32]. Mixing and particle formation occurs at the interface and the product travels upwards and leaves via the side branch of the reactor before being cooled at the heat exchanger. The two subsequent reactor geometries use a vertical co-current arrangement to mix the supercritical water with the cold stream containing the contaminants.

2. Experimental

2.1. Modified pseudo fluids modelling

In 2004, Blood et al. developed a physical modelling technique to quantify the mixing patterns for two fluids in an acrylic pseudo reactor at ambient conditions [28]. These studies used cylindrical channels drilled into Perspex blocks and used methanol (density 791 kg/m^3 and viscosity 5.9×10^{-4} kg/m.s at 25 °C and 1 bar respectively) and 40% w/w aqueous sucrose solution (density 1176.4 kg/m^3 and viscosity 6.16×10^{-3} kg/m s at 25 °C and 1 bar respectively) to simulate the behavior of the supercritical and cold flow streams [28]. The selection of these two fluids created a ratio of inertia to viscous forces similar to that expected between supercritical and cold water flows [33].

Five specific developments have been made to the modelling process beyond this original work.

1. The flows in the original studies were effectively 3D as the drilled channels were cylindrical. Although this closely replicates the actual reactor geometry, the variable (variable chord lengths across the width the cylindrical channel) and relatively large path lengths through the channel significantly limited the potential to observe mixing detail. The new approach uses sheets of Perspex clamped together with a custom crafted rubber spacing layer to create a “slice” of the 3 dimensional reactor offering the same mixing geometries, but with a restricted path length relative to the camera viewpoint (see Fig. 2).
2. The original images acquired in 2001 were relatively low definition, at 512 by 512 pixels and 24 frames per second with 8 bit color. The new images are captured at a resolution of 1080 by 1960 pixels 50 frames per second, in 24 bit color, using a Panasonic video camera (HC-700) recorder.
3. Initial trials investigated whether an alternative to methanol could be employed for the studies, in order to reduce testing costs and hazards associated with methanol toxicity. These initial tests indicated identical mixing regimes where water (containing no sucrose) was used in place of methanol and the flow rate was adjusted correspondingly in order to match the Reynolds numbers of the flows. Fig. 3 compares the results from methanol-sugar water and town water-sugar water (using an increased flow rate to compensate for the increased density and viscosity) for the pseudo supercritical water stream. A series of comparative experiments indicated negligible differences between the use of methanol and water as the pseudo supercritical water feed. Hence, town water/40% w/w dyed aqueous sucrose solution combination were being used to simulate the properties of SCWO streams. Town water (‘pseudo supercritical water’) was chosen to represent hydrothermal solution whereas the aqueous wastewater stream was modelled by a 40% w/w dyed aqueous sucrose solution (‘pseudo-wastewater’). This modification enabled a greater range of longer duration experiments to be conducted, giving a vast increase in data acquisition volume, while enhancing process safety, repeatability and reducing experimental cost (Table 1).

Table 1
The properties of pseudo fluids at 25 °C and 1 bar.

Pseudo fluid	Density, Kg/m^3	Viscosity, Kg/m s
Methanol liquid	791.01	0.00059
Town water	998.21	0.00100
Aqueous sucrose 40% w/w	1176.4	0.00617

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