Chemical Engineering Journal 343 (2018) 351–361

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

An inclined plug-flow reactor design for supercritical water oxidation

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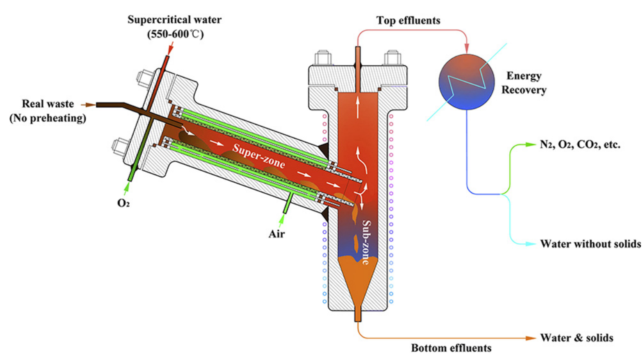
HIGHLIGHTS

- A novel reactor for continuous SCWO of real waste was designed, manufactured, and tested.
- MSS with 12% DS can be treated safely and efficiently without preheating.
- Inorganic solids from MSS can be completely separated *in situ*.
- Counter-current flow, present in traditional vertical reactors, was not observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Inner preheating
In situ solid separation
Real waste
Anti-plugging
Supercritical water oxidation

ABSTRACT

A novel reactor, combining the advantages of the MODAR reactor, horizontal stirred reactor, dynamic gas seal wall reactor, and cool wall reactor, was designed and manufactured to overcome the problems encountered in continuous supercritical water oxidation of real waste, especially in semi-solid state. It is a Y-shaped reactor consisting of an inclined reaction section on the left and a vertical separation section on the right. Nine experiments were carried out to test the performance of the reactor using municipal sewage sludge (MSS), with 12% dry solid (DS) content, as a representative sample of real waste. The results suggest that MSS, without preheating, can be safely and efficiently treated by adding 12.5% isopropyl alcohol (IPA) and pure supercritical water, the volume of which is at least 2.5 times that of the MSS. The organic carbon removal efficiency is up to 99.94%. Inorganic solid particles from the MSS are continually pushed forward in the inclined reaction section, and are completely separated and stored at the bottom of the vertical separation section. Clean effluents, comprising water and gases as the main products, are released from the top outlet. The flow regime in the inclined reaction section can be considered to be plug flow. Counter-current flow was not observed during the tests. The excellent *in situ* solid separation efficiency suggests that this reactor has potential for application in various hydrothermal processes that involve high content of inorganic solid particles.

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https://doi.org/10.1016/j.cej.2018.03.018
Received 6 January 2018; Received in revised form 2 March 2018; Accepted 3 March 2018
Available online 05 March 2018

1. Introduction

Supercritical water oxidation (SCWO) is known as an advanced oxidation process that employs supercritical water (SCW) to degrade organic pollutants in the presence of an oxidant (usually air, O_2, or H_2O_2) [1–4]. The SCW refers to water at temperature and pressure above its critical point of 373.946 °C and 22.064 MPa [5]. It exhibits several properties that are quite different from those of water at room temperature [6,7]. The most notable difference is that SCW is non-polar i.e., it is completely miscible with small organic compounds and gases, and thereby creates a homogeneous environment without inter-phase mass transfer resistance [8]. Hence, SCWO can facilitate fast reactions with high efficiencies, and the main products are H_2O and CO_2. Over the last three decades or more, SCWO has been employed with much success in end-of-pipe technologies because of its ability to destroy a wide range of organic wastes, especially some hazardous or toxic compounds that cannot be easily removed by conventional methods [8]. However, the use of SCWO entails several challenges, chief among which are corrosion, plugging, and high energy consumption, which hinder its widespread use in industrial applications [1–3,8–12].

The reactor is the key component of SCWO [13]. A well-designed reactor can be effective in minimizing the abovementioned problems. The MODAR reactor, invented by Modar, Inc. in 1987 [14], represents an original concept that has had far-reaching implications on the subsequent development of SCWO reactors [2,6,9]. As shown in Fig. 1A, it is a vertical tank reactor, consisting of an upper supercritical zone (super-zone) and a lower subcritical zone (sub-zone). Pre-heated feed is injected into the reactor through an inlet at the top, and the organic materials degrade in the super-zone. The salts in the waste are precipitated out under supercritical conditions; they then fall into the sub-zone and dissolve in subcritical water. Brine and supercritical fluid are released through outlets at the bottom and top of the reactor, respectively. Although the MODAR reactor has some drawbacks, its basic configuration of super-zone and sub-zone has been widely employed in subsequent reactor designs. A brief analysis of these reactors and reports in the literature of their performance and drawbacks follows.

1.1. Corrosion

In the absence of protection, the inner surface of the MODAR reactor is susceptible to severe corrosion due to the aggressive nature of the reaction fluid [15]. Since a 'super material' that can withstand all the conditions in SCWO is yet to be found, the most common solution is to use a substitute for the inner surface of the reactor. General Atomics improved the corrosion resistance of the MODAR reactor by using a removable liner made of either titanium or HC-276 [16,17]. Another alternative is to use a water barrier instead of a removable liner. The most popular example is that of the transpiring wall reactor (TWR) invented by Mueggenburg et al. in 1993 [18]. The concept of the TWR is based on delivery of pure water at low temperatures to fill the annulus between the outer solid pressure-bearing wall and the inner porous wall, also known as the transpiring wall, for subsequent circulation through the porous wall to form a continuous film of water on its inner surface [19]. The film of pure water removes both corrosive species and salts.

The cool wall reactor (CWR) is a variant of the TWR [20]. The porous wall in the TWR is replaced by a solid wall in the CWR. The protective film of water in the CWR is produced by the condensation of external cooling water, but not itself. Thus, significant corrosion occurs because the protective film is formed by the corrosive condensed fluid. Nevertheless, the CWR performs well in the aspect of energy recovery [21,22].

1.2. Preheating

The waste feed must be preheated to supercritical temperature before it is injected into the MODAR reactor. Corrosion and plugging often take place during preheating, especially when real waste with high organic, salt, and/or solid content is used as feed. Inner preheating is a promising technique for preparation of waste feed at subcritical or even room temperature. Hydrothermal flame [23] i.e., combustion of auxiliary fuels such as methanol, ethanol, isopropyl alcohol (IPA), etc., under supercritical conditions, is currently a popular method [19,21,22,24–27]. The technique generates substantial heat and boosts the temperature in the initial section of the reactor to values much higher than 374 °C so that the waste feed can be rapidly heated up. Pure SCW, instead of auxiliary fuel, has also been used as the source of heat for inner preheating [28,29]. In contrast to hydrothermal flames, the use of SCW entails no additional oxidant as auxiliary fuel.

1.3. Counter-current flow

As shown in Fig. 1A, both upward flowing supercritical fluid and downward flowing subcritical fluid are present in the MODAR reactor. This counter-current flow causes several problems. First, some organic material in the waste is carried by the supercritical fluid as soon as the waste is delivered into the reactor due to the proximity of the top outlet to the feed inlet. To address this issue, Xu et al. installed a central pipe

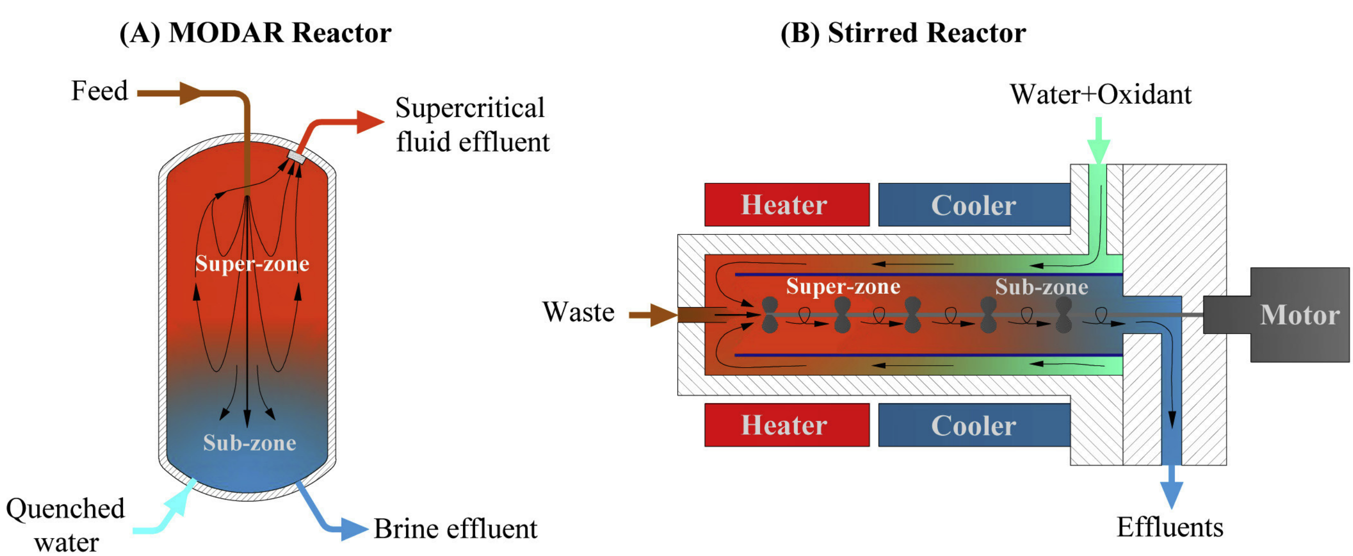

Fig. 1. Schematic diagram of the vertical MODAR reactor (adopted from Ref. [6,14]), and horizontal stirred reactor (adopted from Ref. [38,39]).