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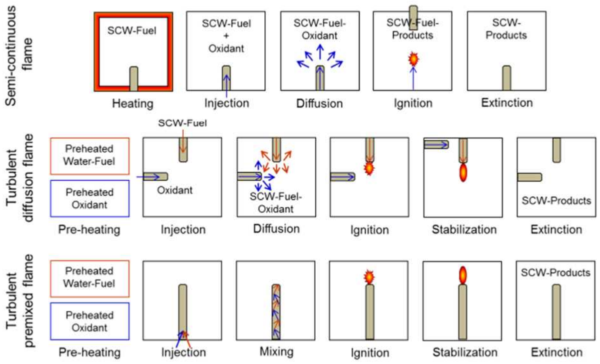

The operating parameters influence the ignition and stability of premixed and diffusion limited hydrothermal flames in continuous and semi-continuous modes.

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Ignition of Hydrothermal Flames

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Abstract:

Supercritical water oxidation is one of the most promising technologies for complete oxidation of complex organic compounds. Flames in supercritical water, often referred to as hydrothermal flames, improve the oxidation rates of reactants in an organic waste stream. The ignition and control of flames in supercritical water could potentially be used to reduce the reaction time (from seconds to milliseconds) and enhance the thermochemical decomposition rates of recalcitrant molecules without the release of any harmful intermediates. This provides a platform to design compact reactors for processing complex organic wastes followed by their conversion to valuable compounds. This paper reviews some notable work focused on the ignition and qualitative observations of hydrothermal flames as an environmentally friendly technology. More specifically, there view highlights the classification and characterization of hydrothermal flames with several demonstrations of laboratory scale (*e.g.*, visual flame cell) and pilot scale (*e.g.*, transpiring wall reactor) reactor configurations. The process parameters such as feed concentration, reaction temperature, oxidant temperature, oxidant flow rate, and transpiration flow properties (in the case of transpiring reactors) are comprehensively discussed for their influence on the ignition and stability of hydrothermal flames, and total organic carbon removal. In addition, the impact of these parameters on the performance of various flame reactors is presented. Finally, the paper also outlines some wide-ranging applications and challenges concerning the industrial utilization of hydrothermal flames.

Keywords: Supercritical water, hydrothermal flames, ignition, visual flame cell, transpiring wall reactor, transpiration flow.

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1. Introduction

There is a dramatic change in the thermo-physical properties of water beyond its critical point (*i.e.*, 374°C and 22.1 MPa) with high diffusivity, low viscosity, low ionic product and modification in its polar nature. The properties of supercritical water (SCW), particularly the high dissolution rates of organic compounds and gases, provide the basis for its wide-ranging applications such as gasification, liquefaction, particle synthesis and oxidation processes.[1-4] The complete miscibility of organic components and all involved gases (*e.g.*, N_2, O_2, CO_2, CO, CH_4 and H_2) during oxidation makes supercritical water oxidation (SCWO) a homogenous process for waste remediation without any interfacial mass transfer limitations.[5] SCWO can be in a flameless mode or in the presence of hydrothermal flames. SCWO of organics in flame mode leads to the formation of water vapor and simple gases, thus eliminating the formation of intermediate pollutants such as dioxins and furans, which are generated during incineration.[6,7]

The generation and existence of flames with higher concentrations of organics in SCW in the presence of an oxidant has been demonstrated by Schilling and Franck.[8] The flames that are produced in water with the help of an organic component and an oxidant at supercritical conditions are known as hydrothermal flames. Flames are ignited by the combustion reactions (*i.e.,* organics with oxidant) in SCW environment. The organic component along with the oxidant needs to be preheated for attaining the desired auto-ignition temperature and generating hydrothermal flames. The flames produced in SCW result in high temperatures with reactive environment favorable for the degradation of organics. The hydrothermal flames in SCW can be either continuous or semi-continuous depending on the fuel injection mode. In semi-continuous mode, the fuel is preloaded into the reactor with oxidant alone injected continuously. In order to generate hydrothermal flames continuously both SCW-fuel mixture and oxidant need to be injected in a continual mode. An organic solvent-water mixture when mixed with oxidant and maintained at supercritical temperature and pressure produces flames, which enhance the oxidation rates of components.[9] The addition of organic solvents aids to denature the complex organic wastes in various SCWO processes.[10] The feed solution corresponds to the organic fuel concentration; henceforth feed concentration refers to fuel concentration.

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The air or oxygen is generally used as the oxidant for the decomposition of organics in SCW. The oxidant is pressurized and preheated before feeding it into the reaction chamber. The reduction in ignition temperatures of the mixture at high pressures and high oxidant concentration leads to the occurrence of hydrothermal flames. When the operating conditions are maintained above the auto-ignition temperature of the mixture, oxidation takes place in the presence of hydrothermal flames.

The ignition of flames in SCW can be achieved by injecting an oxidant into a solution that contains an optimum concentration of fuel. The injected oxidant temperatures can be as low as room temperatures with the reactions occurring in an auto-thermal environment.[11] Hydrothermal flame oxidation of organics has several advantages over the conventional flameless oxidation in SCW. A few of such advantages include: (1) near-complete conversion of reactants, *i.e.* 99.999% conversion; (2) high reaction rates; (3) low reaction times, *i.e.* in milliseconds; (4) less harmful product formation; (5)flexibility in designing small reactors due to lower reaction times; (6) sustainability of auto-thermal conditions; and (7) high energy recovery.[9,12]

Hydrothermal flames are classified into two basic categories, which are premixed flames and diffusion limited flames. In premixed flames, both the feed solution (*i.e.*, SCW-fuel) and oxidant are mixed together and heated to supercritical conditions for flame generation. Conversely, diffusion limited flames are ignited by injecting preheated oxidant into supercritical feed solution. These hydrothermal flames are further subdivided into laminar and turbulent flames based on their flow rates (depending on Reynolds number, Re). In the conventional flame generation process, the fuel is injected into an oxidant-rich environment; whereas for the generation of hydrothermal flames, the oxidant is injected into fuel-rich environment. Hence, the term inverse laminar diffusion flame is in practice.[12] The feed solution (SCW-fuel) and oxidant are injected simultaneously into the reactor co-axially or radially to ignite turbulent hydrothermal flames.

In the conventional incineration, intermediate pollutants such as dioxins and furans are produced which pose serious threats to the natural ecosystem. Moreover, stable complex molecules such as phenol, acetic acid and ammonia require substantial amounts of energy for their breakdown into simple molecules.[5] Hydrothermal flame incineration of these organics could prevent the formation of intermediate pollutant molecules by breaking them

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into permanent gases (*e.g.*, CO_2, N_2 and water vapor).[5,13] Alcohols, which are flammable, are usually chosen as co-fuels to ignite hydrothermal flames. Hydrothermal flame oxidation has the potential to degrade a broad range of wastes from different application sectors including extended duration and/or extraterrestrial space missions; waste disposal from nuclear energy plants; municipal wastes (*e.g.*, sewage sludge); and biomedical wastes (particularly from the pharmaceutical industries).[14,15]

Various parameters influence the ignition of hydrothermal flames, which further impacts the SCWO process. The commercialization of SCWO technology can be attained for broad-ranging applications only when the effect of process parameters on ignition and continuous production of hydrothermal flames is well understood. Although the research on hydrothermal flames initiated three decades ago, yet this field is still in its early stages. The lack of quantitative data on hydrothermal flames is impeding their application and potential commercialization. In addition, this emerging area of research has only two comprehensive reviews so far. Recent reviews by Augustine and Tester[12] and Qian *et al.*[14] have outlined some applications and experimental investigations on hydrothermal flames. There is very little literature available on the impact of various flame parameters (*e.g.*, reactant flow rates, reactant concentration, process temperatures, etc.) on flame ignition and its characteristics. With this motivation, the current review is focused on describing hydrothermal flames along with their ignition and classification, impact of parametric studies and present scenarios for various applications of this technology as well as technical challenges.

This paper reviews the impact of different operating conditions including the influence of reactor configurations on flame ignition. It classifies hydrothermal flames depending on their mode of operation and the flow rates of reactants. The existing reactor configurations and their operation are broadly presented to understand the influence of these parameters on the ignition of hydrothermal flames in order to design the flame reactors and optimize reaction conditions for maximum conversion. This paper provides a summary of all the significant past and recent research works published in the area of hydrothermal flames.

2. Hydrothermal flames

Laminar inverse diffusion flames are semi-continuous and are generated in batch reactors while turbulent premixed and diffusion limited flames are continuously generated in

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flow reactors. The flames described in the literature until now are classified as premixed and diffusion flames. Based on the reactor configuration and operated parameters, laminar conditions are maintained mostly in semi-continuous reactor configurations to determine the characteristics of hydrothermal flames. Fig. 1a explains the mechanism of generation of laminar diffusion flames.

The semi-continuous laminar diffusion flames can be achieved in about five stages. In the first stage, *i.e.* heating stage, the organic component (fuel) is mixed with water and heated up to supercritical water conditions (> 374°C and 22.1 MPa). An oxidant, which needs to be injected, is also heated close to the critical temperature of water (374°C) in a preheater. The heating stage is followed by injection of high-temperature oxidant into SCW-fuel rich environment (injection stage). The third stage is the diffusion stage which is the limiting step of diffusion flames. Upon the injection of the high-temperature oxidant, it diffuses into the SCW-fuel environment and an interface is developed where the combustion reactions are initiated (diffusion stage). Due to thermal gradients (density difference) inside the system, the components interact with each other forming a flame front. The flame front is the interface where the combustion reactions occur following the ignition of flame. The delay in the ignition of the flames depends on the diffusion process to attain the SCW-fuel-oxidant mixture into an auto-thermal condition. Diffusion process initiates the ignition process; hence ignition stage follows after diffusion stage. With the attainment of auto-thermal conditions for SCW-fuel-oxidant mixture, the ignition of hydrothermal flames occurs (ignition stage). Free radical mechanism prevails during the combustion process providing the scope for complete conversion of organics. With the continuous depletion of fuel loaded into the reactor, the flames finally become extinct (extinction phase).

Hydrothermal flames (*i.e.*, premixed and diffusion limited) can also be generated continuously. The flow reactor configurations are intended to study the stability of hydrothermal flames, flow patterns and temperature profiles (*i.e.*, radial and axial) and conversion efficiencies. The process of interaction between the fuel and oxidant differentiates the premixed and diffusion flames. The diffusion of the components is predominant in turbulent diffusion flames. Hydrothermal diffusion flames follow six stages right from preheating to extinction as shown in Fig. 1b. The first stage is preheating stage that heats up the pressurized feed solution (*i.e.*, water-fuel) and oxidant in individual

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preheaters to the desired supercritical temperatures (~400°C). In the injection stage, both heated fuel and oxidant are injected into the reaction chamber. The next crucial step is diffusion stage, where the components diffuse and an interface is developed at the contact forming a flame front. The components interact through the convective diffusion due to high feed and oxidant flow rates. The sooner the flame front is developed, the lesser will be the ignition delay. Once the flame front is developed, the ignition of diffusion flame is attained (ignition stage). Stabilization is an additional stage usually observed in flow reactors. Unlike semi-continuous flames, the continuous flames are stabilized in the stabilization stage where the flow of the components (products) inside the reactor gets stabilized (stabilization stage). With the hydrothermal flame as a source inside the reactor, it is essential to determine the lowest temperature with which the feed can be injected into the reactor to sustain the flame environment that can be known during the extinction phase. In order to determine the extinction temperature, the feed temperature is reduced in regular steps and introduced into the reactor. The minimum temperature at which the stable flame is sustained is noted as the extinction temperature for that concentration (extinction stage).

In premixed flames, the contact between oxidant and fuel is through turbulent mixing. Similar stages to that of the continuous diffusion flames are applied for continuous premixed flames. All the stages observed in turbulent diffusion flames are also noticed with turbulent premixed flames. The diffusion stage in diffusion flames is replaced by mixing stage in premixed flames. Fig. 1c represents the steps involved in turbulent premixed flames. Both the fuel and oxidant physically mix and the flame front is developed in the mixing zone of the oxidant and fuel.

3. Reactor configurations for hydrothermal flames

The reactor configurations, which have been implemented for hydrothermal flames, can be categorized based on their mode of flame generation. There are two types of reactor configurations, namely semi-continuous and continuous. Semi-continuous reactors include visual flame cells (VFC), whereas continuous reactors comprise of water-cooled hydrothermal burner (WCHB), tubular reactor and transpiring wall reactor (TWR). The semi-continuous configurations are mostly developed for laboratory scale set-ups, while the continuous configurations represent scaled-up or industrial scale configurations for the

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ignition of hydrothermal flames. Laminar inverse diffusion flames are produced in a semi-continuous flame set-up mostly to understand the behavior of hydrothermal flames. Since the oxidant is injected constantly but not the fuel, the reactor configurations implemented to understand the behavior of hydrothermal flames are semi-continuous. A set of flexible parameters for these reactor configurations includes oxidant temperature and flow rate, while fuel concentration depends on the initial process conditions. Almost all the reactor configurations employed to ignite laminar inverse diffusion flames are similar and follow the below-mentioned operating procedure.

Fig. 2 represents a typical schematic of inverse diffusion flame set-up. The operation of the semi-continuous configurations for laminar inverse diffusion flames has been described by Augustine and Tester.[12] The components of this semi-continuous reactor include high-pressure liquid pump, piston accumulator or back pressure regulator, visible flame cell, thermocouples, preheaters, oxidant injection nozzle, compressor, CCD camera and analytical instruments for in-situ product gas analysis. Water mixed with fuel can be loaded into the reactor vessel with a high-pressure liquid pump until the operating pressure is attained. A heater is used to heat the fuel mixture to the desired temperature (normally around 400°C). A compressor draws the oxidant from the reservoir where it is pressurized and further heated with a preheater before it is injected into the reaction chamber. The heated oxidant is then injected from the bottom of the reactor through a specially designed nozzle. If the operating conditions are above the auto-ignition conditions of the mixture, then the ignition takes place in the reaction cell. Thermocouples are fixed along the axis of the reactor to record the temperature of the SCW environment. In-situ analysis of flames in SCW is achieved via Raman spectroscopy. The flame images are captured and recorded by near-infrared camera. An abrupt increase in the temperature inside the reaction chamber indicates the onset of ignition. Due to combustion, the concentration of fuel in the reactor chamber is depleted with time indicating the progress of oxidation reactions. The product gases are analyzed with analytical instruments, *e.g.* gas chromatography or gas analyzers.

Different reactor configurations have been applied for continuous generation of hydrothermal flames. Several research groups implemented different configurations such as tubular, transpiring and wall-cooled hydrothermal burner for turbulent diffusion hydrothermal flames. The review by Augustine and Tester[12] explains the details concerned

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to WCHB. Tubular and transpiring wall reactors are other flexible configurations used in investigations related to turbulent diffusion flames.

Tubular reactors have been employed in SCWO of organics for their simple and easy construction with short residence times. The design and operation of tubular configurations for hydrothermal systems have been described by Cabeza *et al*.[5] The materials employed for the construction of tubular reactor are made up of stainless steel SS316 or nickel-alloy 625. Turbulent jets of preheated fuel and oxidant with appropriate operating conditions are injected continuously to achieve ignition of hydrothermal flames. The turbulent flames are sustained as long as the fuel mixture and oxidant are injected into the reactor. The effects of feed concentration, feed injection temperature, oxidant temperature, total organic carbon (TOC) and product gas composition can be investigated for the stability of turbulent flames.

Most of the accessories involved in the tubular reactor are similar to continuous configurations except the additional preheaters and a sophisticated reaction vessel with an active cooling system. A high-pressure pump pressurizes the feed with suitable concentration of organic compound (*i.e.*, fuel) for heating to supercritical temperatures in the preheater. Based on the concentration of fuel mixture, an appropriate feed injection temperature is chosen for the ignition of flames. The oxidant (usually the air or oxygen) from a reservoir is pressurized by high-pressure pumps and heated to the desired operating conditions in a separate preheater. The heated oxidant is then mixed with the feed in a mixer (injector) finally reaching the tubular reactor. A sharp increase in temperatures along the reactor during the process corresponds to the flame ignition. High-temperature thermocouples are placed in various positions inside the reactor to determine the temperature profile of the combustion system. The back pressure regulator controls the excess pressure in the combustion system. The products and exhaust gases are cooled with cooling water system and analyzed with chromatographic techniques.

Fig. 3 shows a flow diagram of a continuous set-up for the generation of turbulent hydrothermal flames. The extreme reaction environments and precipitation of inorganic salts usually lead to reactor plugging and corrosion. New reactor designs are being developed to overcome such limitations of SCWO reactions. Moreover, high reaction temperatures (~1200°C) demand an active cooling mechanism for continuous generation of turbulent flames.[12] TWR with varying designs provides the protection to the walls of the combustion

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reaction chamber. TWR are advantageous for the continuous generation of hydrothermal flames.[16] Transpiring wall is a design that differentiates itself from the conventional tubular reactor configurations. The materials involved in building of transpiring walls are stainless steel, Ni-alloys and alumina ceramics. Both upper and lower ends of the transpiring wall are made non-porous for protection from high temperatures along with durability. The non-transpiring wall reactor is made up of Ni-alloy 625 while the porous wall is made up of Ni-alloy 600.

The accessories involved in the tubular reactors could be used for developing a TWR. In TWR, cold water forms a thin protective film which protects the reactor walls from corrosively reactive species and plugging salts. The TWR consists of a reaction chamber which is surrounded by a porous wall. The feed solution and oxidant are pumped with high-pressure pump into the TWR chamber. Transpiring water is pumped into the TWR where it flows through the porous wall and mixes with hot products. The transpiring water flows outside the transpiring wall to remove the precipitated salts during the process and thereby reduces any chance of reactor plugging. With this advanced reactor, high temperature of hydrothermal flames could be confined to the central zone of the reactor with an advantage of complete oxidation of the organics. The research group at ETH Zurich in Switzerland performed the injection of feed and oxidant from reactor's top, while injecting transpiring water radially to cool the walls of hydrothermal burner.[17]

Conversely, the High Pressure Processes (HPP) group in Spain performed experiments by injecting feed and oxidant from the bottom of the reaction chamber through the static mixer.[18] TWR is engineered to facilitate ignition in the reaction chamber instead of the static mixer chamber. The static mixer is filled with particles of either alumina or Ni-alloy of different sizes with smallest particles settled on top. The feed enters the reaction chamber where the conditions are supercritical due to the hydrothermal flames. The dissolved salts precipitate in the reaction chamber rather than in the static mixer, thereby avoiding plugging in the static mixer lines. The sudden increase in temperatures in the reaction chamber near the exit of the static mixer indicates the generation of flames. The reaction products flow down along with the transpiring water and are collected at the bottom for analysis.

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The selection of parameters such as dimensions of hydrothermal flame burner, transpiration ratio and temperature have a great impact on the performance of TWR. The performance of TWR has been tested for hydrothermal flame oxidation of organics, mostly alcohols. Useful length (UL) and useful residence time (URT) decide the performance of a TWR. UL is defined as the length of the reactor over the supercritical temperature, and URT is defined as the time within which the reagents are in supercritical environment. Various parameters influence the overall efficiency of the process in TWR configurations.

The flexibility to alter the feed composition, feed flow rate, oxidant flow rate and temperature provides the opportunity to explore the impact of these parameters on hydrothermal flames. Transpiring flow is an additional parameter which needs to be optimized to enhance the performance of TWR. Stable hydrothermal flames are continuously generated with TWR by optimizing the above-mentioned parameters for various applications. With no limitation on tuning feed, oxidant and transpiring water flow rate, this advanced TWR configuration has been used to explore the continuous generation and stability of hydrothermal flames. Unlike semi-continuous reactors, these continuous reactors are used to investigate the feasibility of flame generation along with their stability for a variety of waste remediation processes. Further details about TWR design and operation for SCWO can be found elsewhere.[16]

4. Past and present research on hydrothermal flames

Notable research investigations of hydrothermal flames have been conducted by several groups including the HPP group at University of Valladolid in Spain and Swiss Federal Institute of Technology in Zurich (ETHZ) in Switzerland. In addition, other research groups that have attempted significant research on hydrothermal flames are Ebara Research Company(Japan), Shandong University (China), Xi'an Jiaotong University (China), McGill University (Canada) and NASA Glenn Research Center (USA). Although with different research objectives, these groups have been exploring hydrothermal flames from ignition to stability. This section provides the up-to-date research work conducted by various groups across the world on hydrothermal flames. Table 1 presents several research groups and identifies their objectives.

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The group at ETHZ in Switzerland has focused on the continuous generation of flames and their stability.[12] The group has investigated characterization of continuous hydrothermal diffusion flames in TWR.[20] Moreover, a pilot plant has been developed to study continuous generation of hydrothermal flames and their application towards hydrothermal spallation of hard rocks.[22] Researchers have used methanol and ethanol as fuel with oxygen as an oxidant in different configurations of WCHB. The HPP group in Spain has published both experimental and modeling research papers on premixed hydrothermal flames. The performance and behavior of various reactor configurations for generation of stable and continuous hydrothermal flames have also been studied. They have also investigated the oxidation of recalcitrant molecules in the presence of hydrothermal flames.[5] The HPP group has used isopropanol as a fuel and both air/oxygen as an oxidant in tubular and transpiring wall reactors.

The configurations used by ETHZ and HPP groups have active cooling mechanisms to overcome the problems associated with reactor plugging and corrosion. Both these groups have concentrated on continuous hydrothermal turbulent flames implemented with various reactor configurations for different applications. Hydrothermal flames are typically generated in a vertical reactor where fuel and water are initially mixed by HPP and ETHZ research groups. In the vertical reactor configuration by Ebara Research Company in Japan, the oxidant was mixed with SCW to form SCW-oxidant mixture rather than the usual SCW-fuel mixture.[13] The fuel was co-axially injected into the reactor through the nozzle where the upper section was heated to desired operating conditions to attain flames in SCW. The ignition of hydrothermal flames was achieved by controlling fuel concentration and temperatures, which were maintained to be within the design limits for mechanical safety of the reactor. The group in Shandong University, China has investigated the application of transpiring wall for SCWO.[31] The impact of operating parameters on characteristics and performance of transpiring wall for SCWO has been recently explored by this group.[32] Methanol and oxygen have been used as fuel and oxidant, respectively. Researchers from Xi'an Jiaotong University in China have investigated the oxidizing effects of methanol on the refractory molecules in the presence of hydrothermal flames.[37]

Laminar diffusion flames mostly deal with the characteristics of hydrothermal flames. The combustion group at McGill University, Canada has implemented visible flame

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set-up for ignition of hydrothermal flames.[9] The group at McGill University in Canada used methanol as a fuel and the air as an oxidant to investigate the impact of operating parameters on hydrothermal flames. National Aeronautics Space Administration (NASA) in USA has examined the ignition conditions in SCW using a portable SCWO drop-rig set-up. They explored the impacts of buoyancy forces on the ignition and thermal distribution (*i.e.*, heating and cooling rates) of flames in the presence and absence of gravity. The primary targets of NASA are finding application of hydrothermal flames for the oxidation of wastes generated in space shuttles such as human metabolic wastes (*e.g.*, feces and urine), plastics and food residues in the presence of salts, salt precipitation and transport mechanisms in zero gravity environments.[15]

4.1. Laminar inverse diffusion hydrothermal flames

The first breakthrough work of Schilling and Franck[8] to ignite flames in SCW has led to exploring the advantages of such highly reactive environments and confinement of energy for remediation of various components. Stationary diffusion flames were ignited with methane as a fuel and oxygen as an oxidant up to 500°C at 30-200 MPa. A cone-shaped flame was observed at 30:70 mol% ratio of methane-to-water using a camera with emission spectra in the UV region. Since this initial work, the research on hydrothermal flames has continued using various organic solvents (*e.g.*, hydrocarbons and alcohols) as fuels.

The ignition of flames has been achieved by introducing oxygen into SCW-methane and SCW-methanol mixtures at 1-50 mol% for temperatures of 380-510°C and pressure of 27.5 MPa.[30] The behavior of hydrothermal flames has been characterized into various flame zones based on the sensitivity and mass diffusivities at high temperatures and pressures.[38] A wide range of hydrocarbons has also been examined for their oxidation and hydrolysis in the presence of N_2 and SCW. It has been reported that SCW reduced soot formation and increased CO conversion.[24] Hydrothermal diffusion flames were produced with CH_4 and H_2 by injecting O_2 at temperatures around 500°C and pressure range of 5-100 MPa.[25] Further research on the combustion of organics (*e.g.*, methane, higher alkanes and toluene) in SCW with hydrothermal flames has been published by Steinle and Franck[26] and Franck and Wiegand.[27]

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The characteristics of hydrothermal flames were further explored in downstream continuous reactor with isopropanol and the air at 30 MPa and 600°C.[39] Sobhy *et al*. took the advantage of low reaction time to develop a small bench-scale VFC reactor for investigation of hydrothermal flames.[9] Methanol with varying concentrations (18-46 wt%) in the presence of air has been studied for the generation of flames at different ignition temperatures. Fig. 4 shows the photographs of methanol-air flames generated in SCW in a VFC reactor. Sobhy *et al*. have determined the minimum fuel concentration required for SCW-methanol mixture to ignite in the VFC reactor and attain a maximum flame temperature above 1000°C.[9] They further explored the combustion of naphthalene in the presence of hydrothermal flames with VFC reactor.[28] They suggested that the oxidant should be injected into the fuel mixture at an optimized temperature and flow rate for the generation of stable flames.

Table 2 summarizes the latest findings of semi-continuous and continuous hydrothermal flames. As mentioned earlier, NASA at Glenn Research Centre, USA has built SCWO reactor to investigate hydrothermal flames in zero gravity environments for space applications.[29] The heating and cooling rates are found to be different at ground level and zero gravity due to the differences in buoyancy forces. They have developed various reactor configurations to generate hydrothermal flames and investigate the impact of parameters on the flame generation, stability and propagation for applied extraterrestrial research.[15]

4.2. Turbulent hydrothermal flames

Serikawa *et al*. have generated weak but continuous hydrothermal flames with isopropanol and air in SCW.[13] They investigated the effect of parameters (*e.g.*, isopropanol concentration, air ratio and reaction temperature) on reactant decomposition and flue gas composition. Complete oxidation of dioxins in the presence of hydrothermal flames has been achieved in a continuous reactor with isopropanol as the fuel.[13] Flame temperatures around 1100°C have been obtained with 2 vol% of isopropanol, air ratio of 1.8, pressure of 25 MPa and temperature ranging from 400-600°C. Fig. 5 shows the images of the continuous ignition of hydrothermal flames with isopropanol-air mixture.

The search for new reactor configurations to overcome problems of plugging and corrosion has led to the development of TWR set-ups. Wellig *et al*. studied the hydrothermal flame as an internal source to determine the axial and radial temperature profiles, dynamics

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of the fluid flow as a function of temperature and transpiration intensity with methanol as fuel and oxygen as oxidant at 25 MPa.[19] At these conditions, the hydrothermal flames were generated in the presence and absence of salts in feed solution without any problems of plugging and reactor corrosion. Wellig *et al*. inferred that transpiration water temperature influences temperature profiles in the reactor.[19]

In order to avoid plugging and corrosion in the preheater, it is necessary to inject the feed at room temperature into an internal heat source of hydrothermal flame. For the oxidation of organics (*e.g.*, alcohols), the possibility of introducing low-temperature waste streams has been made possible. Wellig *et al*. further studied the feasibility of hydrothermal flames in this configuration, with feed (SCW-methanol) solution containing salts, and reported that 65% of salts introduced were recovered.[19] Prikopsky *et al*. performed experiments on the generation of hydrothermal flame with methanol in artificial wastewater containing 3% salts at 25 MPa.[20] Upon studying the different porosities of TWR, transpiration intensities and temperature of transpiration water, they found negligible effect of salt deposition in TWR. Transpiring water was introduced at various sections of TWR (*i.e.*, top, middle and bottom). They observed that although the upper section (*i.e.*, the hot zone of the reactor) was prone to corrosion and salt deposition; yet it did not plug the reactor for 500 hours of operation. In addition, Wellig *et al*. performed experiments with hydrothermal flame source inside TWR to determine the stability of methanol-oxygen diffusion flames at 25 MPa in a co-axial burner.[17] The experimental results indicated that the feed temperatures can be less than 100°C for higher feed concentrations (> 27 wt%) with an internal hydrothermal flame source. Furthermore, the conversion efficiencies reached up to 99.99% with a residence time of 0.1 s.

The HPP group in Spain has also tested various designs and performance of TWR for SCWO process. They have used isopropanol as fuel and the air as oxidant to study the impact of operating parameters on TOC removal and temperature distribution inside the reactor.[33,34] It was concluded that the ignition of flames depends not only on the fuel and oxidant but also on the geometry (*i.e.*, dimensions of static mixture and injector along with the reactor).Vessel reactors were used for continuous generation of flames and require an injector to produce an internal heat source. Bermejo *et al*. have investigated various static injectors with isopropanol and air stream at different operating conditions.[35] They

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determined the auto-ignition conditions for various mixers (*e.g.*, 1/4 inch, 1/8 inch, 1/4 inch with reverse and mixing flows, and 1/4 inch with upward and downward flow connected by horizontal tram) and found that ignition occurred at lower temperature of 450°C in a 1/4 inch tubular mixer.

The impact of parameters on the generation of premixed hydrothermal flames in a refrigerated reactor chamber with isopropanol and air has also been evaluated with different tubular injector configurations by Bermejo *et al.*[18] Feed solution containing 2.5% Na_2SO_4 was introduced into this configuration with only 10% of introduced salt being recovered without any plugging issues with TOC removal of 99.7%. The abovementioned reactor configurations (*i.e.*, tubular and transpiring wall) were applied for generation of hydrothermal flames and degradation of organic compounds. The outcomes of experimental investigations on tubular and TWR with hydrothermal flames were analyzed thoroughly for scaling-up these reactors.[11] Hydrothermal flames were obtained with isopropanol and oxygen for denaturation of acetic acid and ammonia revealing 99% TOC and 94% N_2 removal at temperatures above 710°C in 0.7 s.[5] SCWO of sludge in the presence of hydrothermal flames has been performed in TWR with 99.99% TOC and 99.9% N_2 removal.[36]

The researchers from ETHZ have investigated hydrothermal spallation of rocks with ethanol and oxygen.[21] They have determined the heat transfer coefficient of the ternary mixture in SCW for designing and optimizing conditions for continuous generation of hydrothermal flames. Stathopoulos *et al.* have further explored hot-wire ignition characteristics of SCW-ethanol fuel mixtures with oxygen as oxidant along with heat transfer mechanisms at 26 MPa.[22] Flame impingement experiments were conducted in a pilot plant at ETHZ for hydrothermal spallation of rocks. Various nozzle designs have been investigated for water entrainment in flame jets with the aim for underwater welding and cutting metals.[23]

5. Process parameters affecting hydrothermal flames

5.1. Feed (fuel)

Various organics (*e.g.*, alcohols and flammable hydrocarbons) are chosen as the fuel for generation of flames in SCW. Non-polar organic components that are normally insoluble

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in water at room temperature are easily soluble in SCW providing access to the solubility limitations.[1,2] The organic compounds such as methane, hydrocarbons and solvents have been investigated to produce hydrothermal flames.[12] Among all organics investigated, methanol and isopropanol have received most attention.[14] The choice of the fuel for hydrothermal flame depends on its solubility with water at room temperature, flammability, optimal auto-ignition conditions, high heating value, low cost, and safety to handle. The organic component should be soluble in water to avoid two-phase pumping of fluids into the reactor.

The organic component should be flammable making it easy for the ignition in SCW. Although being water-soluble, certain organics such as acids, aldehydes and ketones are non-flammable, which limits their use as fuels in SCW. Moreover, the auto-ignition temperature of the fuel should be near or higher than its critical temperature at the operated pressure. The ignition takes place with the injection of oxidant into SCW-fuel environment, which are above its auto-ignition conditions. The organic component should have high heating value for generating higher energy for potential recovery to preheat the feed mixture. The cumulative combustion reactions and heating values for the most widely used organic fuels in SCW are mentioned below. Unlike methanol, isopropanol does not undergo pyrolysis and gasification at SCW conditions to a large extent. Nonetheless, the heating value of isopropanol makes it as a preferable fuel compared to any other organic compound.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_c = -890 \text{ KJ/mol}$$

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_c = -726 \text{ KJ/mol}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad \Delta H_c = -1368 \text{ KJ/mol}$$

$$C_3H_7OH + 4.5O_2 \rightarrow 6CO_2 + 8H_2O \qquad \Delta H_c = -2006 \text{ KJ/mol}$$

5.2. Feed (or fuel) concentration

Irrespective of the type of flames (premixed or diffusion limited), the feed concentration is one of the crucial parameters for hydrothermal flame ignition. The ignition studies of organics in SCW suggest that there should be an optimum concentration for ignition. The ignition limits of methanol in SCW with oxygen are presented in Fig. 6. Steeper *et al*. studied the effect of fuel concentration on the ignition of flames.[30] They have

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evaluated the fuel concentration-temperature ignition limit maps for methanol and methane in SCW. Flames were not observed below a certain concentration of methanol and methane. It was suggested that the organic components have a chance to undergo pyrolysis and hydrolysis during the preheating and reactor heating. For a feed temperature of 380°C, the minimum concentration of 12 mol% (*i.e.*, 10.8 wt%) of methane and 36 mol% (*i.e.*, 50 wt%) of methanol is required for flame ignition in SCW. Diffusion limited flames in SCW were produced at concentrations as low as 6 mol% at 500°C with methane and methanol at 27 MPa.[30]

The increase in feed concentration reduces the feed temperature for the hydrothermal flame ignition. Varying isopropanol concentrations of 1-6 vol% (*i.e.*, 2.5 to 7.5 wt%) were used by Serikawa *et al.*[13] to ignite the flames in a vertical down-flow reactor. With no flames observed below 2 vol%, unstable sporadic flames appeared between 2 and 5 vol% at 25 MPa. The experimental investigations confirmed that the formation of continuous stable flames depends on other process parameters such as the air flow rate, feed flow rate and reactor configuration.

Laminar inverse diffusion flames have been ignited with a VFC set-up.[9] The variation of organic concentration (*i.e.*, 15-40 vol% or 18.3-45.9 wt%) has been tested for the ignition of flames in fuel-rich environment. Flames are readily ignited with air injection, and the ignition of the flames has been confirmed with near-infrared camera. Over the investigated concentration range, hydrothermal flames were ignited between 21 and 35 vol%. Moreover, the strongest flame luminosity has been observed with 23 vol% at 400°C and 23 MPa. Unlike the flames in down-flow reactor, the flames generated by Sobhy *et al.* in VFC were stable for less than 10 s.[9]

In the continuous flame set-ups, the ignition of hydrothermal flames greatly depends on nozzle and reactor configurations along with process parameters. The researchers from ETHZ reported different ignition conditions for several configurations using methanol as the fuel.[12] Flames were produced with methanol concentration of 10 mol% (*i.e.*, 16.5 wt%) in WCHB-1 (*i.e.*, radial burner) at feed temperature of 520°C.[40] Hydrothermal flame ignition with methanol concentration ranging from 15 to 22.1 wt% in a TWR has been investigated by Wellig *et al.*[17] They observed the ignition temperature is between 465 and 490°C. The lowest concentration of 6.1 wt% required a feed temperature of around 440°C. Furthermore,

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in the third generation WCHB-3 (*i.e.*, co-axial burner with four sapphire windows), methanol concentration as low as 7.1 mol% (*i.e.*, 11.8 wt%) was sufficient enough to generate flames at low feed temperature of 452°C at 25 MPa.[42] Although high feed temperature of 550°C is employed for 15.8 mol% (*i.e.*, 25 wt%) of methanol, hydrothermal flames failed to ignite with the same nozzle configuration that ignited in WCHB-1.

The HPP group in Spain has employed isopropanol as a fuel to ignite hydrothermal flames in TWR. The ignition of premixed flames was achieved with 6.5 wt% of isopropanol above 420°C at 23 MPa.[33] The energy generated from the flames was used to maintain high temperatures for sustaining the flame, thereby reducing the feed inlet temperature. The flames were stable for feed temperatures as low as 110°C for the same feed concentration. Bermejo *et al*. have investigated ignition of isopropanol in different mixer configurations for determining their auto-ignition conditions.[35] The continuous generation of premixed flames can be achieved with concentration of 4 wt% for isopropanol. Their results indicated that 1/4 inch tubular mixer resulted in the lowest auto-ignition temperature of 450°C.

Several experiments have been performed in tubular and TWR reactors with the air or oxygen as oxidants and isopropanol as fuel for ignition of hydrothermal flames.[11] The flame ignition was attained with the air and oxygen at 4 wt% isopropanol concentration. Concentrations ranging from 8 to 10 wt% of isopropanol have been tested to generate a stable hydrothermal flame in TWR. With an increase in isopropanol concentration by 1 wt%, a temperature increase of 150°C was observed. The temperature profiles for different concentrations of isopropanol have been established with oxygen as an oxidant in tubular reactors.[5] The maximum temperature attained in the reactor increased with the increase in fuel concentration at the similar injection temperature. Fig. 7 shows the variation of maximum temperature attained with change in isopropanol concentration. The ignition was achieved with as low as 1.5 wt% isopropanol.

The previous investigations indicate that the generation of stable hydrothermal flames was possible with 4 wt% of isopropanol. Taking this as a reference, premixed hydrothermal flames were generated in a refrigerated reactor(room temperature water is passed through the annulus of transpiring wall and reactor shell) with different injectors, and isopropanol as fuel and air as oxidant.[18] The concentrations varying from 6.5 and 12.5 wt% were used for the stable generation of hydrothermal flames. In order to maintain the

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temperature in the reactor around 700°C, the fuel concentration was increased up to 12.5 wt% for the lowest feed temperature employed in this configuration. Various injectors used in this investigation were Injector-1 (outer diameter: 1/4 inch, length: 95 cm); Injector-2 (outer diameter: 1/8 inch, length: 95 cm); and Injector-3 (outer diameter: 1/4 inch, length: 55 cm). Among all injectors implemented for ignition experiments, Injector-1 used a maximum of 9 wt% fuel concentration, while the other two injectors required 12.5 wt% fuel concentration for stable hydrothermal flames. With different heat transmissions taking place in TWR, the optimum organic concentration for the ignition of stable hydrothermal flames also depends on the flow parameters.

High concentrations of isopropanol have been applied for the generation of stable premixed hydrothermal flames to degrade sewage sludge in cooled wall reactor.[36] To maintain ignition and required reaction temperature, the concentration of the fuel has been increased from 8.5 to 13 wt%. Hydrothermal flames were ignited with ethanol and oxygen by means of hot wire ignition.[22] A minimum concentration of 12.5 wt% was required to ignite flames with oxygen at 26 MPa. With an increase in the fuel concentration, the ignition power was found to decrease. In the study by Stathopoulos *et al*., when the concentration of ethanol was increased from 12.5 to 17.5 wt%, the ignition power almost halved.[22] From the experimental data, it was inferred that with the increase in carbon chain length of the alcohol, the minimum concentration required to ignite hydrothermal flames decreased under the same operating conditions. Table 3 presents the optimum concentration for the ignition of flames in different reactor configurations for various organic fuels employed.

5.3. Feed temperature

Feed temperature is another important parameter affecting the ignition of hydrothermal flames. The lowest feed temperature injected into the reactor to maintain a stable hydrothermal flame is known as the extinction temperature. It is evident that feed temperature should be above the critical temperature (*i.e.*, 374°C) of the water for ignition. Furthermore to ignite flames, the decrease in feed temperature is compensated by an increase in feed concentration in the ignition regime. Using methanol in SCW, the minimum temperatures for ignition of diffusion flames were found to be 380°C and 440°C at 27.5 MPa and 25 MPa, respectively with oxygen.[12] For 4 wt% isopropanol, the premixed flames

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were attained at 450°C and 23 MPa,[11] while diffusion flames were attained at 470°C and 27.5 MPa.[13]

Due to the reactor configurations, the existence of the hydrothermal flame source inside the reactor has paved the path to introduce the feed at room temperature. It is essential to introduce the feed at lower temperature to prevent the corrosion and plugging problems in the preheater. Once the ignition has been achieved, the hydrothermal flames canbe used as the internal heat source to lower the inlet feed temperatures and explore extinction of the diffusion flames.[17] In addition, Wellig *et al*. attempted to determine the extinction limits for different concentrations of methanol.[17] With the hydrothermal flame serving as an internal heat source for SCWO of methanol, feed temperatures can be lowered to 100°C for a feed (*i.e.*, methanol) concentration of 27 wt% at 25 MPa.

The increase in the concentration reduces the fuel injection temperature when there is an internal heat source. Feed temperature can be as low as 90°C for methanol concentration of 28.1 wt%.[17] Stable hydrothermal flames were generated at feed temperature of 170°C for isopropanol concentrations of 8-10 wt%.[11] Using an internal hydrothermal flame source, the feed temperature can be lowered still maintaining stable flames in the reactor. The introduction of low-temperature feed has been implemented for temperatures as low as 40°C. This was compensated with an increase in the fuel concentration.[18] The presence of hydrothermal flame source resulted in the decrease in the feed temperature down to 20°C.[36]

5.4. Feed flow rate

In order to generate inverse diffusion flames, the feed is loaded into the reactor, which rules out the effect of feed flow rate. The stability and effluent organic concentration depend on the feed process parameters (*e.g.*, concentration, flow rate and temperature) in continuous hydrothermal flames. An optimum flow rate is required to ignite hydrothermal flames along with efficient removal of TOC in the feed. Lower flow rates have higher residence times and high temperatures but the UL in TWR also get lower resulting in lower TOC removal. Higher flow rates reduce the URT that leads to high TOC in the effluent with less flame stability. Various feed flow rates ranging from 8.7 to 24.2 kg/h have been studied to test the performance of TWR for efficient TOC removal.[33] It was observed that with high and low flow rates the UL and URT were insufficient for complete oxidation of organics. It

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was also demonstrated that feed flow rates between 16 to 20 kg/h were able to achieve high reaction temperatures sufficient enough to completely oxidize isopropanol. The ignition of methanol-oxygen hydrothermal flames was attained with 5.4 kg/h in TWR.[17]

The effect of feed flow rate ranging from 6 to 18 kg/h on ignition of isopropanol in different mixers was investigated by Bermejo *et al*.[35] With the increase in flow rate, the time for hydrothermal flame ignition decreases. In addition, it was observed that the fuel mixture ignited at lower temperatures for the low feed flow rates of 6 and 7.5 kg/h. For higher feed flow rates of 13 and 18 kg/h, the ignition was possible in the mixer's entrance zone at temperatures around 400°C. Flow rates ranging from 20 to 40 kg/h in a pilot plant and feed flow of 60 kg/h was used in demonstration plant for generation of flames in presence of air and oxygen.[11] It has been reported that the extinction temperature is lowered with the decrease in feed flow rate. With the decline in feed flow rates from 14 to 6 kg/h, the extinction temperatures reduced from 388 to 354°C for 4 wt% of isopropanol.[11]

The ignition of stable hydrothermal flames depends on fluid velocity and injection temperature. From the experimental results by Bermejo *et al*., it was confirmed that stable hydrothermal flames are not possible with lower feed flow rate and temperature in tubular reactors.[11] The increase in feed flow rate from 7.4 to 32 kg/h resulted in a decrease of injection temperature in scale-up TWR with an internal hydrothermal flame source with TOC removal of 99%. TOC removal of around 90% was obtained at the feed flow rate of 20-60 kg/h in scale-up TWR demonstration plant in the presence of oxygen even though the maximum temperatures in the reactor were in the range of 610-810°C.[11] Three different flow rates (*i.e.*, 13, 20 and 25 kg/h) were employed for SCWO of organics with a tubular injector in a refrigerated reaction chamber.[18] The experimental results by Bermejo *et al*. inferred that stable hydrothermal flames can be generated and maintained by the operated flow with the lower injection temperature of 50°C for about 99.95% TOC removal.[18]

The higher feed flow rates result in improper mixing of the reactants leading to lower TOC removal. The increase in feed flow rate from 8 to 14 kg/h increases the reaction temperature in a pilot-scale TWR.[31] With the rise in feed flow rate from 8 to 17 kg/h, UL increased at the expense of URT demanding an optimum flow rate for efficient TOC removal. Zhang *et al*. have reported that an optimum flow rate of 14 kg/h was required for the effective performance of TWR for methanol-oxygen mixture with > 99% TOC removal

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in a pilot-scale set-up.[31] High temperatures were achieved at higher flow rates resulting in greater TOC removals for methanol-oxygen mixtures.[32] Reaction temperature around 760°C was obtained with a TWR reactor for a feed flow rate of 4.21 kg/h without considering auxiliary water heat source flow. The results confirmed that an optimum feed flow rate of 4 kg/h was effective for the pilot-scale TWR operation with maximum TOC removal.

5.5. Oxidant temperature

Required oxidant for SCWO of organics is usually supplied in the form of pure oxygen or the air. The complete miscibility of the air or oxygen at supercritical conditions makes SCWO a homogenous process with higher TOC removal rates. The flame ignition is achieved quickly with oxygen at lower operating temperatures rather than with the air.[11] An insufficient air supply for SCWO leads to the formation of significant amounts of CO as an indication of incomplete combustion. Spontaneous ignition of flames has been achieved with injection of oxidant into SCW-fuel mixture. For practical applications, the air is preferred over oxygen for eliminating any complications associated with high temperature and pressure.[9] The temperature and flow rate of the oxidant play prominent roles in the generation of flames in SCW.[17]

The temperature of the injected oxidant should be near or beyond the critical temperature of water to avoid delay in the ignition of the fuel mixture. Upon introduction of oxidant into the fuel mixture, the system temperature decreases, and the ignition occurs when the mixture attains auto-ignition conditions. The ignition delay time for SCW-fuel mixtures can be reduced by introducing high-temperature oxidant.[12,13] Sobhy *et al*. did not observe any spontaneous ignition at temperatures below 300°C for methanol-air diffusion flames.[9] However, with an increase in the oxidant temperature by 50°C, they observed a reduction in ignition delay by 1 to 2 s.

Similar behavior has been observed in the ignition delays for continuous generation of flames in flow reactors.[35] Upon injection of low-temperature oxidant (*i.e.*, air) with high-temperature feed into the reactor, the temperature of the mixture decreases before it reaches auto-ignition conditions. Wellig *et al*. investigated the impact of oxidant temperature at constant flow rate and fuel composition.[17] They reported that a minimum oxidant temperature of 400°C was required for ignition of methanol-oxygen flames. In tubular

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reactors, the influence of excess air has a significant impact on the oxidant temperature in ignition delays for premixed flames.[35] Experiments were performed by increasing both excess air and temperature for ignition of isopropanol mixture at 465°C with a feed flow rate of 7.5 kg/h. Bermejo *et al.* suggested that ignition of the fuel mixture was delayed by increasing the excess air at different temperatures.[35] However, no significant difference was observed in the ignition for a temperature difference of 40°C with excess air of 11% and 15%. The delay in ignition increased with higher temperature difference between the fuel and oxidant mixture.

5.6. Oxidant flow rate

An optimum flow rate is required for the ignition of stable continuous hydrothermal flames. High flow rates might extinguish the flame or move it away from the injector while low flow rates limit the feed-oxidant mixing to reach auto-ignition temperature. For the ignition of methane and methanol in SCW with oxygen, a flow rate in the range of 1-3 mL/min was employed for inverse diffusion flames.[30] Sobhy *et al.* did not notice any ignition below and above certain flow rate for methanol-air hydrothermal flames.[9] With no flames observed below 0.5 mL/min, the flames extinction occurred at flow rates higher than 1.5 mL/min.

Different oxidant flow rates have been examined for the ignition of flames in WCHB-3 using methanol-oxygen mixture by Wellig *et al.*[17] Their experimental results suggested that in the oxidant flow rate from 0.76-2.5 kg/h, methanol flames were ignited at oxidant temperature of 400°C. Lower extinction temperatures were observed with oxygen compared to the air for 4 wt% isopropanol in a tubular injector.[11] In addition, the flame extinction can be lowered with lower oxidant flow rates for premixed flames in tubular reactors. For 6 wt% isopropanol, hydrothermal flames were ignited at 354°C with 0.5 kg/h of oxygen and 370°C with 2.8 kg/h of the air.

5.7. Flame temperature and stability

The flame temperature depends on fuel concentration and fuel temperature. Flame temperatures of around 1000°C have been recorded with methanol-air mixture in inverse diffusion flames by Sobhy *et al.*[9] Serikawa *et al.* have measured flame temperatures from

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800 to 1100°C with the increase in air-to-fuel ratio from 1.1 to 2.2 in turbulent diffusion flames.[13] Flame temperatures around 1200°C with 16 wt% of methanol have been achieved in turbulent diffusion flames in WCHB-3/TWR.[17] In TWR experiments by the HPP group, the flame temperature was maintained below 850°C for oxidation of organics to maximize the durability of the porous tube along with the pressure shell.[11,36] Temperatures around 900°C have been attained in TWR with auxiliary water as a heat source with methanol-oxygen mixture.[32]

Stability of the flame depends on the fluid velocity, injection temperature and flow patterns inside the reactor. The fluid velocity inside the reactor should be at par with the flame velocity for a stable hydrothermal flame. Furthermore, the injection temperature for generation of stable hydrothermal flames depends on the fluid velocity in the reactor. If the flame front velocities are greater than the fluid velocities, then the flame front shifts towards the injector.[11] The flame might also be extinguished if the flame velocity is less than the fluid velocity in the reactor. The experimental investigations revealed that hydrothermal flames are stabilized in vessel reactors compared to the tubular reactors. The results by Bermejo *et al*. indicated that the flame front velocities (*i.e.*, 0.01-0.1 m/s) were lower than normal air combustion velocities (*i.e.*, 0.4-3m/s).[11] The velocities inside the tubular reactors (*i.e.*, 2 to 12 m/s) are higher than the flame front velocities at operating conditions resulting in the extinction of hydrothermal flames. In vessel reactors, where hydrothermal flames act as an internal heat source, the velocities are around 0.04 m/s leading to flame stability.

6. Transpiration flow

Transpiration flow comes into the picture in the case of WCHB and TWR to cool the walls of the reactor. Transpiration flow has a major impact on the temperature profiles inside the reactor resulting in variations for UL and URT. Higher transpiration flow reduces the temperature in the reactor, thereby reducing UL, which further reduces URT. Lower transpiration flow increases the temperature inside the reactor that might lead to the failure of transpiring wall. Transpiring water intensity is the parameter related to transpiring flow in the reactor. Transpiration water ratio or transpiration water intensity (R) is defined as transpiration flow to the total flow (*i.e.*, feed-oxidant). An optimized valve of transpiring flow is required since the high transpiration water intensity gives high protection. However,

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this may also result in dilution of the feedstock, thereby decreasing the residence time, reaction temperature and overall performance of TWR.[31] As long as transpiration water intensity is enough to avoid flooding in the reactor (thus extinguishing reactions) its impact on TOC removal is negligible.

Wellig *et al.* investigated different transpiration intensities and evaluated the performance of TWR.[19] They used a second stream of waste water (*i.e.*, water-methanol) and oxygen for oxidation along with transpiring flow at different sections. The set-up also has cold water flows at the bottom for the safety and enhanced performance. Transpiring water flow rates in the range of 1.5-3.2 kg/h and cold-water flow rates in the range of 230-266 kg/h were employed in their experimental studies. The elimination of high pressure and high-temperature zones at the walls of the reactor ruled out the problems of corrosion and plugging. The salt that was precipitated at the supercritical environment was found to be dissolved in the cold film of transpiring wall. In another investigation by Wellig *et al.* transpiring flow rates of 1.8-32.4 kg/h and cold flow rates of 234-270 kg/h were employed at temperatures between 28 and 35°C.[17] They reported that with the maximum temperature attained in the reactor, the cooling of reaction products with transpiring water provided solutions for corrosion and plugging.

A linear relation exists between the temperature of the reactor and transpiration flow. The experimental results revealed that higher transpiration flow reduces the reaction temperature. For example, an increase in transpiration ratio from 0.16 to 0.46 led to temperature decrease from 630 to 600°C.[33] Furthermore, the transpiration flow temperature has the least impact on TOC removal. Any reduction in transpiring flow temperatures reduces the temperatures inside the reactor, thereby decreasing both UL and URT. As the transpiring temperature reduced from 250 to 25°C, both UL and URT decreased by 0.4 m and 10 s, respectively along with TOC removal approaching 99.9%.[33] Bermejo *et al.* observed similar results in another study without salts employing different reactor designs.[34] The experiments were performed with feeds containing Na_2SO_4 salt at concentrations of 4.74 and 2.44 wt%. With a TOC removal of 90%, Bermejo *et al.* indicated that lower TOC removal was attributed to phase changes at the injected salt concentration.[34] They recommended that in order to achieve high TOC removal, the feed with high salt concentration should be injected at the top of the reactor near the hydrothermal flame.

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Fouling and scaling were observed while operating with feeds containing salts, especially at the top section of reactor where temperatures are high requiring periodic cleaning.

With an internal hydrothermal flame source in TWR, an optimum transpiration water intensity value has been chosen to make the reaction products in subcritical state so that the precipitating salts can leave the reactor to avoid plugging and fouling.[11] Transpiring flows affect both reactor temperature and URT. Experimental studies were done with tubular injectors to generate hydrothermal flames in a refrigerated chamber with feeds containing Na_2SO_4 to achieve better TOC removal compared to the previous designs by the HPP group.[18] The HPP group employed cooling water with different flow rates of 5-20 kg/h to maintain the temperature below 400°C. It was reported that TOC removal of 99.7% was achieved with injected salts recovery of only 10%. Furthermore, it is also suggested that the salts could act as flame retardant at the injector outlet.

Transpiring flow has been introduced into the reactor at three sections with the performance of the reactor being evaluated.[31] Transpiration ratio of 0.04 to 0.08 has been varied, which reflected a decrease in UL from 0.349 to 0.331 m and URT from 18.7 to 13.7 s. With the increase in transpiring water temperature from 200 to 340°C in the upper section of the reactor, UL increased from 0.271 to 0.351 m, while URT increased from 10.2 to 15.9 s with TOC removal being higher than 99%. A negligible effect was observed with the rise in temperature of transpiring water at the middle section of the reactor. The transpiring water temperature can be as low as 100°C.

Zhang *et al*. explored the impact of transpiring flow and temperatures on the performance of TWR.[32] Higher transpiration flow leads to increase in cooling effect along with enhanced mixing due to convection effect. UL decreased from 0.395 to 0.187 m and URT dropped from 12.45 to 6.26 s with the increase in transpiration ratio from 0.75 to 1.55. They observed that with a reduction in transpiration water temperature from 350 to 35°C, the reaction temperature increased from 740 to 825°C. This also decreased the UL from 0.377 to 0.261 m and URT from 10.94 to 7.86 s with TOC removal being reduced to 98.7%. The increase in reaction temperature with decrease in the transpiration temperature is attributed to the density differences between hot reactive fluid and cold transpiring water. Further details about the impact of transpiration flow on reactor temperature and TWR performance can be found elsewhere.[16]

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7. Applications and technical challenges

The advent of hydrothermal flames accompanying oxidation processes provides the pathway for the destruction of recalcitrant molecules. Alcohols are introduced as fuels for the generation of hydrothermal flames, and such a flame environment can enhance the degradation rates of complex molecules. Hirth and Franck investigated heptane and toluene as fuels for the soot formation revealing that soot formation was suppressed in the presence of SCW.[24] Dioxins and its isomers are decomposed completely (*i.e.*, 99.9%) in less than a minute with isopropanol as fuel in turbulent diffusion flames.[13] Naphthalene at a concentration of 75 ppm was found to be degraded by 99.9% with methanol as a fuel in a VFC reactor by Sobhy *et al.*[28]

Acetic acid and ammonia are the most recalcitrant molecules produced in many of chemical oxidation processes including flameless SCWO.[43] These compounds are degraded in tubular reactors with isopropanol as co-fuel with a residence time of 0.7 s.[5] The disposal of sludge is complicated with the presence of ammonium nitrogen. Hydrothermal flame generated with isopropanol and air has been applied for denaturation of actual and synthetic sludge.[36] Conversion efficiencies for NH_3 to N_2 have reached 99.9% with TOC removal of 99.99% resulting in no by-product formation. The effluent concentrations of ammonium nitrogen are less than 40 ppm and nitrate concentrates less than 20 ppm. The application of hydrothermal flames for treatment of municipal wastes can also be extended to biomedical wastes.

A current innovative application exploiting the presence of hydrothermal flames is the hydrothermal spallation of rocks for the extraction of oil and gas in deep well drillings.[12] Thermal spallation drilling of rocks in deep wells requires high-pressure thermal energy. Spallation of hard rocks, mainly granite in deep waters demands high confinement of energy to break them into smaller fractions or spalls. The introduction of hydrothermal flames in the form of thermal jets instantaneously heats the rock surface. This tremendous temperature gradient and thermal stresses due to localized thermal expansion of rocks result in their quick fragmentation. The impact of hydrothermal flames leads to high heat transfer fluxes at moderate temperatures making hydrothermal spallation drilling a very attractive option in the current drilling technologies for geothermal systems.[23] The deeper boreholes filled with

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high-pressure aqueous water need to impart forced ignition of hydrothermal flames to generate high thermal stress. This results in the entrainment of high-pressure aqueous water during thermal jet spallation showing a significant impact on the efficiency of spallation drilling technology. The various parameters involved in ignition and controlling of hydrothermal flames need to be understood thoroughly in order to apply thermal spallation technology efficiently for drilling through hard rocks in deep wells.

Spallation and rock drilling are new alternative methods to the conventional rotary drilling for recovering geothermal energy.[12] Spallation or drilling of hard rocks in deep waters is usually applied for the extraction of crude oil from deep oceans beds. Due to the underwater construction, the metallic structures (usually steel and titanium alloys) with maximum strength are used for this application. Even minute failures in the structures result in considerable damage. A high confinement of energy is required for underwater cutting of high strength metals, which can be provided with hydrothermal flames. Heat transfer mechanisms are outlined in forced ignition of SCW-ethanol-oxygen mixtures for hydrothermal spallation drilling.[22]

Nuclear power plants generate numerous toxic and radioactive wastes that are robust to neutralize or remediate by the conventional methods (*e.g.*, biological, chemical and incineration treatments). Liquid-liquid extraction involved in spent nuclear fuel processing products [*e.g.*, kerosene, tributyl phosphate, chlorinated solvents (trichloroethylene and perchloroethylene), silicone oil and mineral oils] generates a combination of organic and chlorinated or fluorinated oils.[44] Liquid organic solvents mixed with chlorinated solvents have major challenges for their disposal. SCWO of nuclear waste heteroatoms such as chlorine, sulfur and phosphorous present in nuclear wastes form acids that make the harsh environment leading to corrosion.[45] Water has considerable amounts of inorganic salts, which results in salt precipitation at supercritical conditions. It receives understanding of the solubility and precipitation mechanisms of salt/acids along with their transport and deposition on the surfaces with large temperature gradients.[15]

Spent organic ion exchange resins (*e.g.*, styrene-divinylbenzene copolymers) are other radioactive wastes which need to be disposed. SCWO of these spent organic ion exchange resins in the presence of isopropanol as a co-fuel has been demonstrated to achieve destruction efficiency higher than 99%.[46] Hydrothermal flame oxidation of these resins

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provides a perfect platform which can be decomposed into simple gases eliminating NO_x and SO_x emissions with conversions reaching up to 100% without any catalyst addition. Some persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzofurans/dioxins are difficult to degrade through conventional incineration processes. SCWO of these pollutants, mineral oil and transformer oil denaturation seems to be promising with TOC removal efficiency reaching 99.7%.[47] Furthermore, the application of hydrothermal flames to degrade these harmful pollutants along with lubricants, greases, polycarbonates, tires and rubber wastes into permanent gases seems to be a new-age environmentally friendly waste remediation technology. In addition, ship wastes and space shuttle wastes are other kinds of waste where hydrothermal flames can find promising applications.[15,48]

High-temperature and high-pressure systems are often prone to technical problems arising from pumping of feed to product collection. The immiscibility of organics limits the exploration of other hydrocarbons and flammable compounds to use as fuel for generation of hydrothermal flames. In order to understand in-situ hydrothermal flame characteristics, it is important to measure the local flame temperatures and feed concentrations. Although, spectral/optical techniques are employed to determine flame characteristics, yet there are significant challenges in the measurements of temperature and other flame characteristics at extreme SCW conditions. Although metal-sheathed thermocouples are capable of determining the high temperatures of hydrothermal flame at SCW conditions, yet their durability is questionable and limited. Moreover, the introduction of analytical probes into the reaction chambers has chances of disrupting the feed/oxidant flow patterns, flame size/shape and temperature profiles inside the reactors. Lack of advanced materials and techniques to measure the high-temperature hydrothermal flames is a major limitation for determining the concentration of organics.[12]

Corrosion is a major problem when dissociation reactions, solubility of corrosive products and solubility of gases are higher in the water. It is difficult to find a material that can withstand the range of operating conditions employed in SCWO processes.[49] Corrosion of materials occurs in preheaters, reactor, porous tube and heat exchanger in the hydrothermal flame oxidation process. High probability of corrosion is possible at the critical point where high temperature promotes corrosion reactions enhancing the kinetics of

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corrosive species such as halides and dissolved oxygen. Hot reaction zones in the reactor lead to the formation of red hot spots where the material gets brittle and results in cracking or failure. Implication of highly resistant materials (*e.g.*, Inconel 625, Haste alloy 600, Nickel-based alloys 600, 625, 718 and C-276 as well as stainless steel alloys) in accessories can prevent corrosion in SCWO processes.[50] For further protection, liners are employed mostly in the materials exposed to temperature gradients, especially in heat exchangers and preheaters. The metallic, ceramic, fixed and removable liners are suitable for vessel reactors rather than tubular reactors. Coatings have a similar function to that of liners and can be applied to smaller surface areas and intricate geometries (*e.g.*, thermocouples, nozzle tips etc.). These coatings are made of metallic or ceramic fillers that form a protective oxide layer, thus protecting the material.[51]

Due to the lower solubility of the inorganic salts in SCW, it is essential to avoid the plugging in preheaters. Vadillo *et al*. provide the limits of the salts and corrosive species to avoid plugging and corrosion in tubular configurations.[52] Chloride concentrations should be less than 2 ppm to prevent the formation of acids and reduce the corrosion and plugging problems. Advanced reactor configurations such as TWR provide a way to overcome the problems of plugging and corrosion with internal heat source where feed can be injected into the reactor at room temperatures.[11,17,32] The exposure of the top section of TWR to high temperatures leads to the failure of transpiring wall. Recent experimental investigations on methanol-oxygen flames in TWR reported failures of the porous tube after 80 h of operation due to high temperature (> 600°C).[32] Fig. 8 presents a photo of the damaged porous tubes initially employed in TWR systems.

Nonetheless, feeds containing inorganic salts are one of the biggest challenges in SCWO experiments. Most of the existing reactor configurations lack the ability to recover salts in the decomposed products. Significant research efforts are being focused to demonstrate the solubility and phase constraints of inorganic salts-organics-gases mixture to improve the efficiency of the overall SCWO process.[15]

8. Conclusions and recommendations

A first attempt in this review has been undertaken towards a comprehensive and systematic analysis of the behavior of hydrothermal flames. Special emphasis was placed on

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the understanding of a hydrothermal flame ignition, which is the first step to stabilizing and controlling flames in SCW. Some recent data has been presented on the possibility for complete degradation of complex organic molecules and toxic products. Although the subtleties of some steps involved in this evolution mechanism are still unanswered at the present state of analysis, the observations and arguments presented in this paper offer a key to understanding a number of phenomena connected with the behavior of a variety of organics in hydrothermal flame environments. In particular, the development of different by-products and phase homogeneity are addressed.

In order to achieve a maximum efficiency and performance of hydrothermal flames, one has to consider an SCW-flame reactor configuration, a set of optimal operating conditions, as well as the overall system design. Advanced knowledge of chemical processes and influence of combustion chamber size or configuration are critical for advancing SCW-flame development. The present study systematically characterized the impact of various parameters such as feed concentration, feed flow, oxidant temperature, oxidant flow rate and transpiring flow on the stability and duration of hydrothermal flames.

Premixed and diffusion limited hydrothermal flames in several reactor configurations have been discussed offering an insight into various applications. They were explained in the proposed evolution mechanism, which is based on the time-resolved profiles of intermediates formed during the SCW combustion. Experimental results suggest that complex organics can be completely burned in hydrothermal flames and that the SCW combustion of different hydrocarbons in the supercritical region could be alike.

We anticipate, however, some practical problems. For example, a fraction of salts may precipitate at the optimal operating conditions. The growth of salt-based solids in SCW-combustion and oxidation chambers is detrimental, and its prediction may be complicated due to irregular morphology of particles. Certainly, we realize the potential pitfalls on the pathway from the current small-scale experimental observation to a large-scale application. Clearly, further engineering improvements will be needed.

Thermal gradients in vessel reactors result in dissolving the precipitated salts with the flexibility to protect the walls without affecting the performance of the reactors. Understanding the thermal and mass transfer mechanisms beyond supercritical temperatures is critical for detailed analysis and modeling of hydrothermal flames. It could be done using

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organic liquids with low auto-ignition temperature, which are miscible with water. It was also shown that, in general, a continuous generation of a stable hydrothermal flame is not possible in tubular reactors due to their high velocities. However, transpiring wall reactors employ a hydrothermal flame as an internal heat source, providing an option to introduce the feed at room temperature into the reactor and eliminate potential plugging in preheaters.

The areas of interest described above are important for the design of the next generation of SCW-flame reactors. Observed hydrothermal flame behavior may have significance in designing practical SCWO reactors tailoring their geometry and conditions to different stages of the combustion process. For example, future applications of hydrothermal flames for underwater cutting and welding require a thorough understanding of hydrodynamics of the configurations of pre-selected nozzles. In addition, determination of temperature profiles (*i.e.*, axial and radial) of hydrothermal flames provides a direction for in-situ breakdown of tar and heavy oils upon their injection into the hydrothermal flame environment.

Since possible industrial applications of hydrothermal flames would involve treatment of complex organics in an uninterrupted manner, the next logical step would be a series of experiments in a tailor-designed SCW reactor. Namely, a design that would allow for the initially formed intermediates and salt particles to reside longer times in the hydrothermal flame zone of the reactor. The ultimate goal would be the development of a salt-free SCW-based combustion where energy would be generated and hydrothermal flame properties would be controlled. Such a new reactor design would contribute significantly to progressing towards industrial and commercial applications of hydrothermal flames.

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Table 1: Worldwide research groups and their significant objectives on hydrothermal flames investigation

Institutes/research centers	Types of flame	Objectives	References
Ebara Research Company, Japan – Serikawa Research Group	Diffusion limited; Turbulent	Visual capturing of hydrothermal flames. Application of these flames for oxidation of pollutants (*i.e.*, stock native dioxins).	Serikawa *et al.*[13]
Institute of Process Engineering, ETH Zurich, Switzerland	Diffusion limited; Turbulent	Ignition, stability and extinction limits of hydrothermal flames. Application for spallation of rocks in deep waters.	Wellig *et al.*[17,19]; Prikopsky *et al.*[20]; Stathopoulos *et al.*[21-23]
Karlsruhe University, Germany – Franck Research Group	Diffusion limited; Laminar	Ignition of hydrothermal flames and impact of process variables on soot formation.	Schilling and Franck[8]; Hirth and Franck[24]; Pohsner and Franck[25]; Steinle and Franck[26]; Franck and Weigand[27]
McGill University, Canada – Kozinski Research Group	Diffusion limited; Laminar	Recording of ignition of methanol-air flames and extending it for destruction of naphthalene.	Sobhy *et al.*[9,28]
National Aeronautics and Space Administration, USA – Glenn Research Center	Diffusion limited; Laminar	Ignition of flames for destruction of space generated wastes in zero gravity.	Hicks *et al.*[15,29]
Sandia National Laboratories, USA – Combustion Research Group	Diffusion limited; Laminar	Ignition of flames in SCW with methanol and methane.	Steeper *et al.*[30]
Shandong University, China – National Engineering Laboratory for Coal-fired Pollutants Emission Reduction	Premixed; Turbulent	Performance study of a transpiring wall reactor for oxidation of organics	Zhang *et al.*[31,32]
University of Valladolid, Spain – High Pressure Processes Group	Premixed; Turbulent	Ignition of hydrothermal flames and performance of reactor configurations. SCW oxidation of recalcitrant molecules.	Bermejo *et al.*[11,18,33-35]; Cabeza *et al.*[5,36]

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Table 2: Semi-continuous and continuous ignition of hydrothermal flames with various fuel mixtures and oxidants

Fuel (Organic solvent)	Oxidant	Types of flames	Process parameters			Reactor configuration	References
			Feed concentration	Feed flow rate	Oxidant flow rate		
Methane	Oxygen	Semi-continuous; laminar diffusion flames	27.6 wt%	-	1-6 mm^3/s	High pressure flame reactor	Schilling and Franck[8]
		Continuous; turbulent diffusion flames	4-25 wt%	2.1 g/s	1.1 g/s	water-cooled hydrothermal burner (WCHB-1)	Weber[40]
Methanol	Air	Semi-continuous; laminar diffusion flames	18.3-45.9 wt%	-	0.5-1.5 mL/min	Visual flame cell	Sobhy *et al.*[9]
	Oxygen	Semi-continuous; laminar diffusion flames	1.8-64 wt%	-	1-3 mL/min	Hydrothermal flame visual reactor	Steeper *et al.*[30]
		Continuous; turbulent diffusion flames	16.5-30 wt%	3.2 g/s	1.5 g/s	water-cooled hydrothermal burner (WCHB-2)	Weber *et al.*[41]
		Continuous; turbulent diffusion flames	16 -22 wt%	1.5 g/s	0.43-0.63 g/s	Transpiring wall reactor	Wellig *et al.*[19]
		Continuous; turbulent diffusion flames	15.8 wt%	1.25-1.5 g/s	1.5 × stoich.	water-cooled hydrothermal burner (WCHB-1)	Augustine and Tester[12]
		Continuous; turbulent diffusion flames	15-22.1 wt%	1.5-1.6 g/s	0.4-0.63 g/s	Transpiring wall reactor	Wellig *et al.*[17]
		Continuous;	2-6 wt%	8-17 kg/h	0.05-4 kg/h	Transpiring wall	Zhang *et al.*[31]

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		turbulent diffusion flames				reactor	
		Continuous; turbulent diffusion flames	30-35 wt%	2-4.95 kg/h	1.68-3.93 kg/h	Transpiring wall reactor	Zhang *et al.*[32]
Ethanol	Oxygen	Continuous; turbulent diffusion flames	7.5-20 wt%	20-30 kg/h	1.2 mass ratio of ethanol:oxygen	Hydrothermal spallation drilling pilot plant	Stathopoulos *et al.*[22]
Isopropanol	Air	Continuous; premixed flames	2.5-7.5 wt%	0.83 g/s	1.1-2.2× stoich.	Vertical SCWO tower	Serikawa *et al.*[13]
		Continuous; turbulent premixed flames	6.5-8 wt%	8.7-24.2 kg/h	1.15 × stoich.	Transpiring wall reactor	Bermejo *et al.*[33]
		Continuous; turbulent premixed flames	6.5-8 wt%	16-24 kg/h	-	Transpiring wall reactor	Bermejo *et al.*[34]
		Continuous; turbulent premixed flames	4-5 wt%	6-18 kg/h	0.24-26.4%excess air	Tubular mixer	Bermejo *et al.*[35]
		Continuous; turbulent premixed flames	4 wt%	6-14 kg/h	2.8-5.1 kg/h	Tubular reactor	Bermejo *et al.*[11]
		Continuous; turbulent premixed flames	8-10 wt%	7.4-36.7 kg/h	6.9-22.9 kg/h	SCWO Pilot Plant	Bermejo *et al.*[11]
		Continuous; turbulent premixed flames	8-12.5 wt%	13-25 kg/h	-	Tubular injector with reaction chamber	Bermejo *et al.*[18]
		Continuous; turbulent premixed	8-14 wt%	13.6 kg/h	0.5-15% excess air	Cooled wall reactor	Cabeza *et al.*[36]

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		flames					
	Oxygen	Continuous; turbulent premixed flames	4 wt%	6-10 kg/h	0.5-1.4 kg/h	Tubular reactor	Bermejo *et al.*[11]
		Continuous; turbulent premixed flames	8 wt%	21-65.6 kg/h	6.4-11.2 kg/h	Demonstration SCWO plant	Bermejo *et al.*[11]
		Continuous; turbulent premixed flames	1-4.5 wt%	9 kg/h	6-57% excess oxygen	Tubular reactor	Cabeza *et al.*[5]

Table 3: Optimal process parameters for ignition of hydrothermal flame from most widely used fuels

Fuel	Feed concentration	Feed temperature	Oxidant parameters	Reactor configuration	References
Methanol	28 wt%	400°C	1-3 mL/min of O_2	Semi-continuous; Visual flame cell reactor	Steeper *et al.*[30]
	15 wt%	465°C	0.4-0.63 g/s	Continuous; Transpiring wall reactor	Wellig *et al.*[17]
Ethanol	12.5 wt%	390°C	1.2 mass ratio of ethanol:oxygen	Hydrothermal spallation drilling pilot plant	Stathopoulos *et al.*[22]
Isopropanol	2 wt%	400°C	6-57 % excess O_2	Tubular reactor	Cabeza *et al.*[5]

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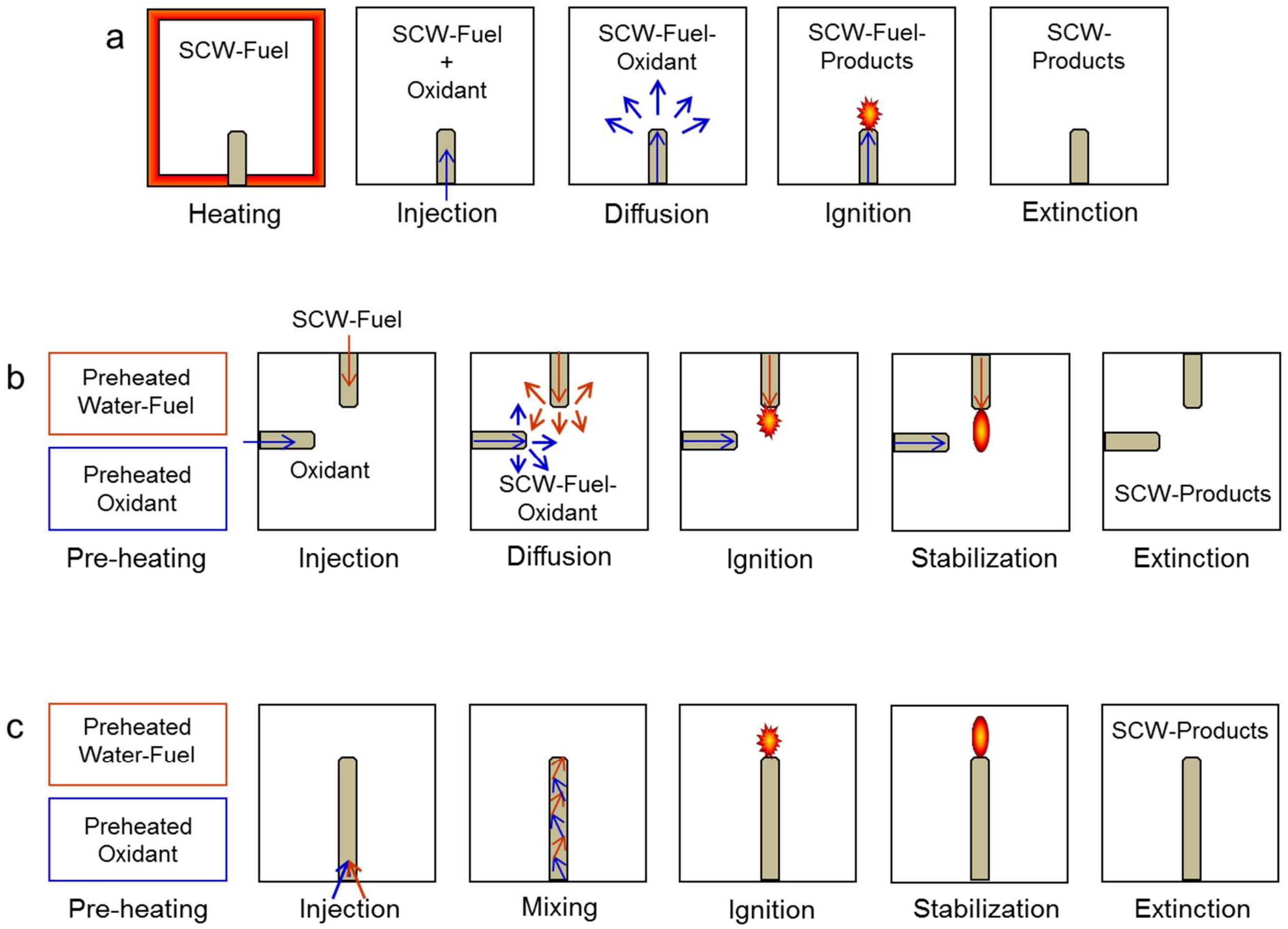

Fig. 1: The stages during ignition ofhydrothermal flames in different modes: (a) semi-continuous, (b) turbulent diffusion, and (c) turbulent premixed

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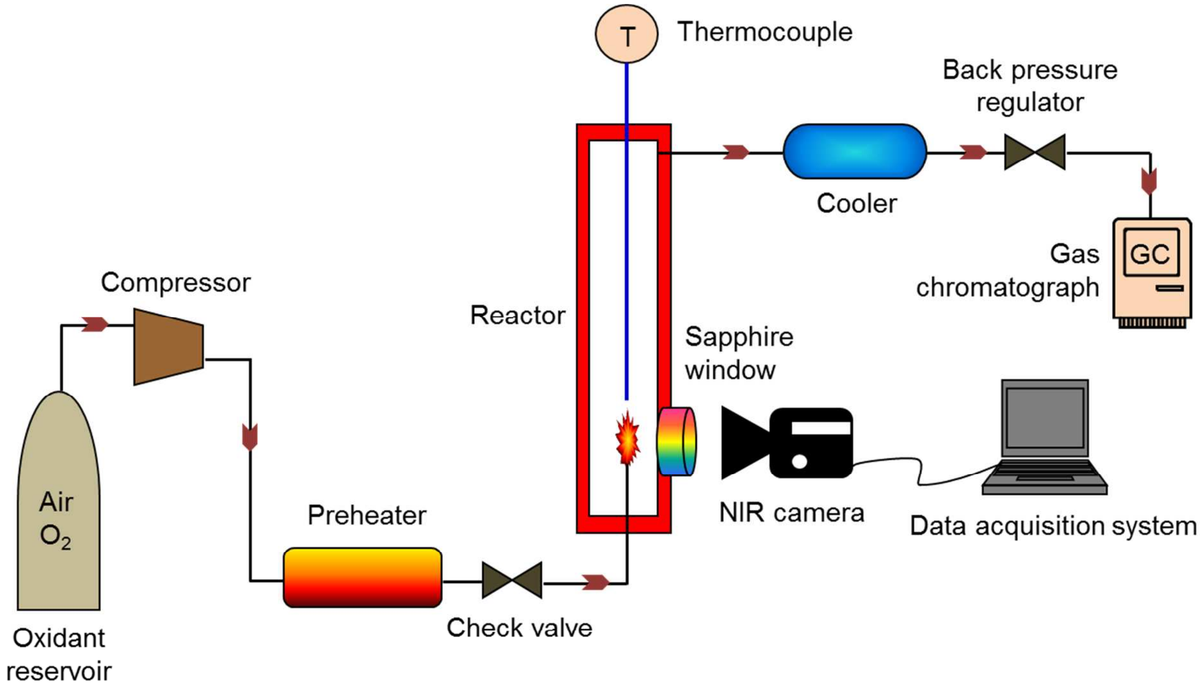

Fig. 2: Schematics of a visual semi-continuous mode flame set-up for laminar inverse diffusion flames

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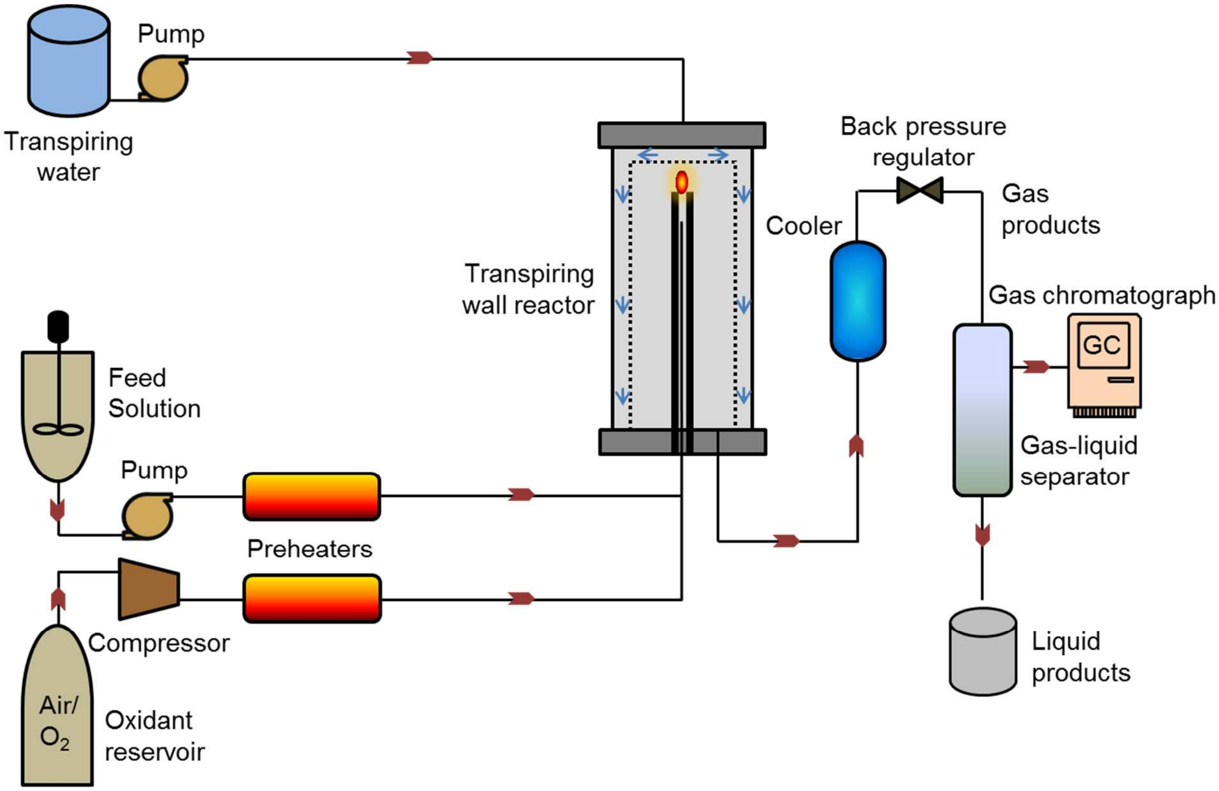

Fig. 3: Schematics of a continuous mode flame set-up

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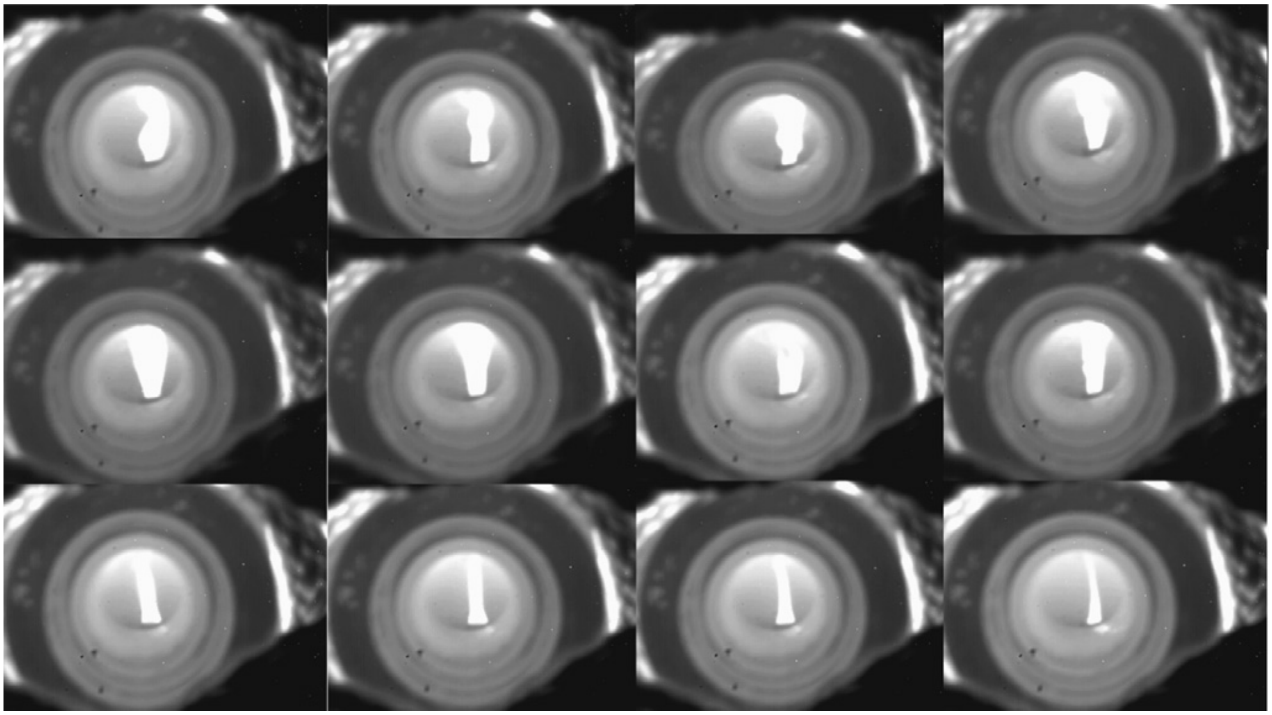

Fig. 4: Semi-continuous methanol-air hydrothermal flames (Reprinted with permission from Sobhy *et al.*[9])

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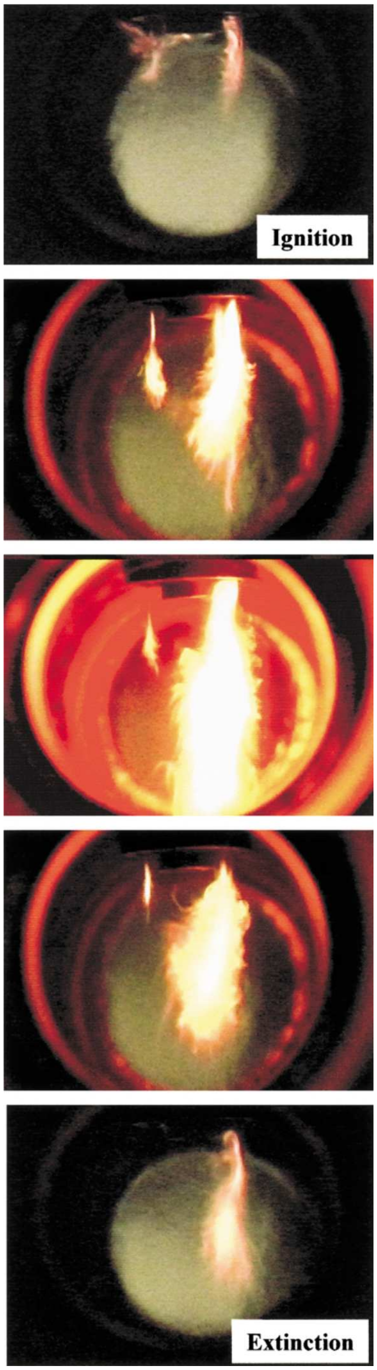

Fig. 5: Continuous hydrothermal flames with isopropanol-air mixture (Reprinted with permission from Serikawa *et al.*[13])

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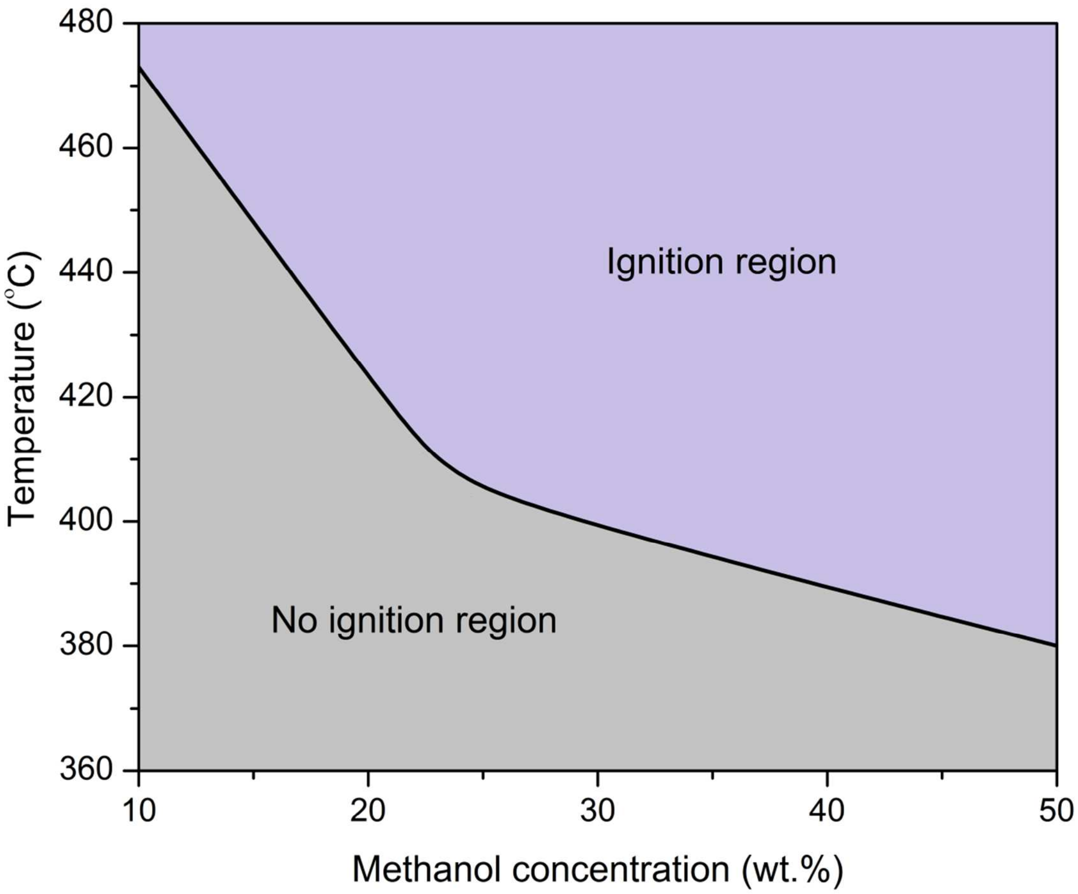

Fig. 6: Ignition limits of methanol-oxygen hydrothermal flames (Data extracted from Steeper *et al.*[30])

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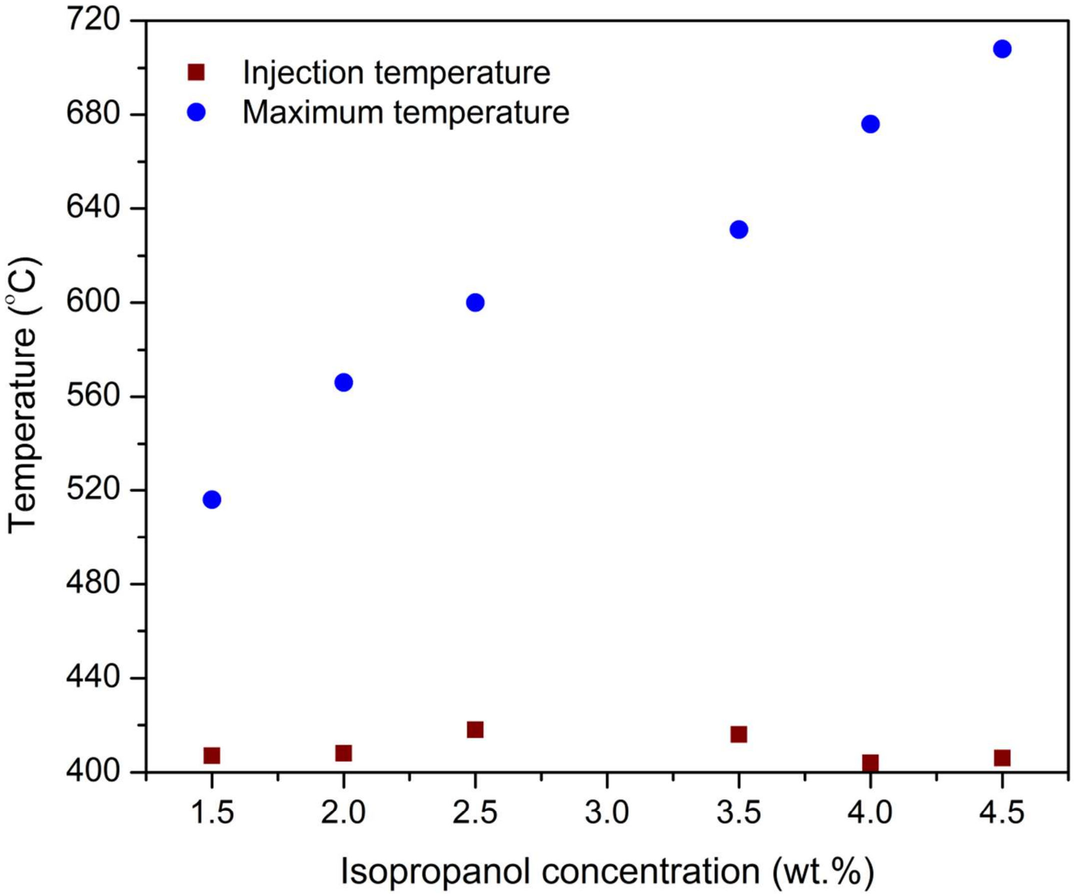

Fig. 7: Variation in maximum temperatures attained with changes in isopropanol concentration (Data extracted from Cabeza *et al.*[5])

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(a)

(b)

Fig. 8: Pictures of the damaged porous tubes employed in hydrothermal flame experiments (a) Reprinted with permission from Bermejo *et al*.[34] Copyrights 2006 American Chemical Society. (b) Reprinted with permission from Zhang *et al*.[32]

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