

## HYDROTHERMAL OXIDATION PROCESS

### FIELD OF THE INVENTION

The present invention relates to a hydrothermal oxidation process and in particular to a  
5 continuous process for the hydrothermal oxidation of organic matter. The present  
invention also relates to a hydrothermal oxidation reactor.

### BACKGROUND

Wet oxidation is an industrial process applied to organic matter that is suspended in a  
largely aqueous environment. Generally, the conversion is an oxidative one, whereby the  
10 organic matter is subjected to chemical reaction with an oxidant such as oxygen ( $O_2$ ). The  
conversion occurs at temperatures below the critical point of water ( $373^\circ C$ ); thus, the  
process is also termed subcritical wet oxidation. During wet oxidation, system pressures  
are maintained above the vapour saturation point of water at a given process temperature,  
accommodating an overpressure of oxidant, which is often applied in gaseous form (e.g.  
15 air or pure oxygen). Oxidation reactions result in degradation of the organic matter, with  
ultimate end products being carbon dioxide and water. Depending on the system  
temperature and processing time, a range of intermediate components may form,  
including short chain fatty acids such as acetic and formic acids.

Wet oxidation is deployed industrially to remediate problems with wet organic waste, which  
20 contains contaminants such as micro-plastics and pathogens. The conversions destroy  
the suspended organic solids present in the waste, yielding a final product that contains  
an inorganic ash fraction, and an aqueous fraction that can be readily processed using  
conventional biological wastewater treatment systems. The benefits of successful  
processing of wet organic waste include reduction of organic solids that need to be  
25 disposed of in landfills or land application, plus extraction of value from the end-products.  
One example of such value extraction may be in utilisation of the aqueous fraction to  
generate methane gas as an energy product. As such, wet oxidation enhances  
sustainable waste management practices and opportunities for a biobased economy.

There are problems associated with wet oxidation. Wet oxidation and hydrothermal  
30 oxidation processes are generally operated at high temperatures and pressures in highly  
turbulent conditions. However, it has been observed that even in such conditions, wet

oxidation is not a fast process. Some components of organic matter are more recalcitrant to oxidation than others, and there can be multiple reaction pathways such reactions follow before breaking down organic matter into small carbon molecules. This can depend on the feedstock, and the type of mineral ash and nitrogen species utilised.

- 5 Oxygen is the most common oxidant for wet oxidation, which is usually added as purified oxygen or air. Under these conditions, the process is characterised as a gas-liquid system. Due to the poor solubility of oxygen in water, gas-liquid mass transfer is potentially a rate limiting step in the oxidation reactions. Gas-liquid mass transfer is controlled by, amongst other factors, the intensity of mixing interaction occurring within a given system.
- 10 Thus, the mixing turbulence of the fluids within the system is an important consideration in wet oxidation system design.

- Reaction cycles in wet oxidation typically take 10-120 minutes, with the reaction kinetics being relatively slow when compared with supercritical water oxidation. Supercritical water oxidation is another hydrothermal process used for organic waste destruction, which has
- 15 reaction times measured in seconds.

- Current wet oxidation practice usually involves large-scale deployments of continuous flow reactors, using completely mixed reactor system configurations, such as continuous stirred tanks reactors (CSTR) or bubble columns. Because they are completely mixed, such reactors operate at a single rate, controlled by the reactant concentrations in the
- 20 mixed vessel. Coupled with the potential for reaction limitation through gas-liquid mass transfer, these reactor designs are characterised by aggressive mechanical or hydraulic mixing to ensure good interface between the gaseous oxidant and the liquid phase environment where reactions take place.

- Mixing is an energy-consuming process and also comes with considerable operational
- 25 challenges encountered within the high temperature and pressure system (for example, wear and tear on mechanical seals of mixing elements). Reducing this energy and operational cost demand would provide new impetus for deployment of the technology. As such, there remains a need for innovation in hydrothermal oxidation processes and apparatus.

- 30 One possible option might involve the use of plug flow reactor configurations. Plug flow reactors (PFRs) can be deployed in tubular reactor configurations. They offer advantages

in reaction kinetics, and thus require smaller processing volumes. Further, the primary construction element, namely tubes or pipes, offers the possibility for construction efficiencies through procurement of the pipes or tubes as standardised materials.

However, tubular PFRs can struggle to provide the turbulent environment of CSTR or bubble columns. The primary means to improve mixing in tubes is to reduce the diameter of the tube. If the overall PFR volume is to be retained, which is important for effecting completion of the wet oxidation reaction, a reduction in diameter requires tube length increase. Given the square law relationship between diameter reduction and length increase, this can lead to logistical and cost challenges for tubular PFR design. This may be a reason for the almost complete dominance of CSTR and bubble column in wet oxidation system designs.

Improvement of turbulent mixing within tubular PFR design could also be achieved by means such as addition of static mixers which disrupt the flow pattern through the tube. However, these means involve additional elements to the reactor design, thus increasing capital and maintenance costs for the system.

The present invention provides useful alternatives to known wet oxidation processes and reactors.

#### SUMMARY OF THE INVENTION

The present disclosure provides a continuous process for the hydrothermal oxidation of organic matter comprising:

- pumping organic matter in an aqueous stream into a first section of a reactor,
- pumping a gaseous oxidant into the first section of the reactor,
- maintaining conditions in the reactor at pressures in the range of about 2 to about 250 bar and temperatures in the range of about 100 to about 373°C,
- subjecting the organic matter in an aqueous stream and the gaseous oxidant to high intensity mixing in the first section of the reactor,
- transferring the organic matter in the aqueous stream and the gaseous oxidant into a second or subsequent substantially horizontally arranged tubular section of the

reactor, where at least some of the organic matter containing aqueous stream is in a liquid phase and at least some of the gaseous oxidant is in a gas phase,

and

maintaining the rate of travel of the liquid phase through at least part of the  
5 second or subsequent section of the reactor at a maximum velocity of about 0.1m/s, or

maintaining the Reynolds number of the liquid phase travelling through at least part of the second or subsequent section of the reactor between about 0 and about 10000.

In one aspect the liquid phase containing the organic matter travels through the tubular reactor section at a maximum velocity of about 0.05m/s.

10 In one aspect the liquid phase containing the organic matter travels through the tubular reactor section at a maximum velocity of about 0.02m/s.

In one aspect, the Reynolds number of the liquid phase in the tubular reactor section is between about 0 and about 4000.

The Reynolds number of the liquid phase in the tubular reactor section may also be  
15 between about 0 and about 400.

In one aspect pressures in the reactor are maintained in the range of about 10 to about 200 bar and temperatures in the range of about 160 to about 350°C.

In one aspect pressures in the reactor are maintained in the range of about 20 to about 200 bar and temperatures in the range of about 200 to about 350°C.

20 In one aspect pressures in the reactor are maintained in the range of about 30 to about 120 bar and temperatures in the range of about 220 to about 300°C.

In one aspect the liquid and gaseous phases exist as distinct or segregated layers in at least part of the tubular reactor section. In another aspect, the liquid and gaseous phases exist as sequences of slugs of liquid separated by slugs of gas. In a still further aspect,  
25 the liquid and gaseous phases exist as a mixture of layered flow and slug flow.

In one aspect the bulk of the gaseous phase moves at a speed equal to or greater than the velocity of the bulk of the liquid phase.

In one aspect the ratio of the gaseous phase velocity to the liquid phase velocity is in the range of about 1.01:1.00 to about 10:1.

In one aspect the ratio of gaseous phase velocity to liquid phase velocity is in the range of about 1.1:1 to about 10:1.

- 5 In one aspect the ratio of the gaseous phase velocity to the liquid phase velocity is about 3:1 to about 6:1.

In one aspect, the ratio of the gaseous phase velocity to the liquid phase velocity is about 2:1 to about 5:1.

In one aspect the gaseous oxidant is oxygen gas.

- 10 In one aspect the gaseous oxidant is air.

In one aspect the gaseous oxidant is enriched air, for example about 40% O<sub>2</sub>.

In one aspect the gaseous oxidant is oxygen gas and the ratio of the gaseous phase velocity to the liquid phase velocity is about 1.1:1 to about 10:1.

- 15 In one aspect the gaseous oxidant is oxygen gas and the ratio of the gaseous phase velocity to the liquid phase velocity is about 2:1 to about 5:1.

In one aspect a highly soluble supplementary oxidant is added. Optionally, the highly soluble supplementary oxidant is added to the reactor in proximity to an aqueous stream inlet of the reactor.

In one aspect the highly soluble supplementary oxidant is a peroxide.

- 20 In one aspect the highly soluble supplementary oxidant is a nitrogen oxide.

In one aspect the direction of flow of the gaseous phase in the reactor is in counter-current to the flow of the liquid phase.

In one aspect the aqueous stream comprises an organic content of between about 0 and about 15% weight to volume.

- 25 In one aspect the aqueous stream comprises an organic content of between about 0 and

about 10% weight to volume.

In one aspect the aqueous stream comprises an organic content of between about 0 and about 8% weight to volume.

In one aspect the volume of the liquid phase equates to between about 40 and about 70%  
5 of the interior volume of a tubular section of the reactor.

In one aspect the organic matter comprises or consists of dissolved organic molecules.

In one aspect the organic matter comprises or consists of suspended solids.

In one aspect the organic matter comprises or consists of both dissolved organic molecules and suspended solids.

10 In one aspect the organic matter is one or more of wastewater, industrial effluent, farm effluent, food waste, packaging materials, and plant residues.

In one aspect the continuous hydrothermal oxidation process is followed by a settling stage to allow the settling out and separation of inorganic ash particles.

In one aspect the liquid outputs of the process are fed to an anaerobic digester for the  
15 production of biogas.

In one aspect the aqueous stream is pre-heated before being injected into the tubular reactor.

In one aspect the residence time and processing conditions are engineered to optimise the yield of C1 to C5 short chain fatty acids.

20 The present disclosure also provides a hydrothermal oxidation reactor comprising a first section and a second or subsequent substantially horizontally arranged tubular section, an aqueous stream inlet port, a gaseous oxidant input port, an aqueous stream outlet port, a gaseous stream outlet port.

In one aspect the first section comprises a tubular section.

25 In one aspect the first section comprises a stirred tank reactor.

In one aspect the second or subsequent substantially horizontally arranged tubular section

comprises a plurality of tubular sections.

In one aspect the first section comprises a tubular section and the second or subsequent substantially horizontally arranged tubular section has a larger diameter than the first section.

- 5 In one aspect the second or subsequent substantially horizontally arranged tubular section comprises one or more bends.

In one aspect the axes of tubular reactor section(s) of the second or subsequent substantially horizontally arranged tubular section are level or have less than about a 15-degree incline or decline relative to level.

- 10 In one aspect the axes of tubular reactor section(s) of the second or subsequent substantially horizontally arranged tubular section are level or have less than about a 5-degree incline or decline relative to level.

In one aspect the axes of tubular reactor section(s) of the second or subsequent substantially horizontally arranged tubular section are level or have less than about a 1-

- 15 degree incline or decline relative to level.

In one aspect, the bend sections of the second or subsequent substantially horizontally arranged tubular section are adapted to receive a liquid phase and a gaseous phase and to deliver an aqueous layer and a gaseous layer flowing in substantially parallel flow to an adjacent tubular section.

- 20 In one aspect the reactor or parts of the reactor are contained within a thermal envelope.

In one aspect the reactor comprises additional oxidant ports.

Other embodiments of the invention will be evident from the following detailed description of various aspects of the disclosure.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- 25 The summary, as well as the following detailed description, is further understood when read in conjunction with the appended drawings. To illustrate the disclosed process and apparatus, exemplary embodiments of the process and apparatus are described with

reference to the drawings. However, the process and apparatus are not limited to the specific embodiments disclosed.

Figure 1: shows a schematic representation of different reaction zones during the course of a wet oxidation reaction.

- 5 Figure 2: shows Chemical Oxygen Demand (COD), (Figure 2a)) Volatile Suspended Solids (VSS) (Figure 2b)) and Acetic Acid concentration profile (Figure 2c)) along time-course of wet oxidation reaction.

Figure 3: shows alternative arrangements for combining Mass Transfer (MT) Limited and Kinetically Limited Zones in a tubular PFR.

- 10 FIGURE 4: shows a tubular reactor with substantially horizontal sections and bend sections.

Figure 5: shows a process flow diagram.

Figure 6: shows a schematic view of a reactor according to one aspect of the present disclosure.

- 15 Figure 7: shows a representative temperature profile across the length of the reactor.

Figure 8: shows the total chemical oxygen demand (COD) concentration across the reactor.

Figure 9: shows the total COD removal across the reactor.

## DETAILED DESCRIPTION

### 20 Definitions

The 'Reynolds number' is a dimensionless quantity that is used to categorise the type of flow pattern in a system as either laminar (smooth) or turbulent while flowing through a pipe. It is defined by the ratio of inertial forces to that of viscous forces as determined by the formula:

25 
$$Re = v_i d \rho_i / \mu_i$$
, where

$Re$  = Reynolds number (-)

$v_i$  = fluid velocity (m/s)

$d$  = pipe diameter (m)

$\rho_i$  = fluid density (kg/m<sup>3</sup>)

5  $\mu_i$  = fluid viscosity (Pa.s)

subscript  $i$  = fluid  $i$  (in this case the gas or liquid phase, or the entire mixed multiphase).

The 'fluid velocity' is determined by the formula:  $v_i = Q_i/A_{\text{pipe}}$ , where

$Q_i$  = volumetric flow of fluid (m<sup>3</sup>/s)

$A_{\text{pipe}}$  = pipe internal diameter (m<sup>2</sup>).

10 In this description, it should be noted that velocity and /or Reynolds numbers are used as proxies for laminar vs turbulent flow, with numbers appropriate for practical reactor diameters. The true measure is one that cannot be described simply as it is dependent on many variables.

The terms 'comprise', 'comprises', 'comprised' or 'comprising', 'including' or 'having' and  
15 the like in the present specification are used in an inclusive sense, that is to specify the presence of the stated features but not preclude the presence of additional or further features.

The use of examples, or exemplary language (for example, 'such as') is intended merely to better illuminate the invention and does not pose a limitation on the scope of the  
20 invention.

Except where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification are to be understood as being modified in all instances by the term 'about'. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following description are approximations that  
25 may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, each numerical parameter should be construed in light of the number of significant digits and ordinary rounding conventions.

Recitation of ranges of values is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated, each individual value is incorporated into the specification as if it was individually recited. For example, if a range is from about 1 to about 50, it is deemed to include, for  
5 example, 1, 7, 34, 46.1, 23.7, or any other value or range within the range.

#### Description

In response to limitations of currently available hydrothermal oxidation processes and apparatus, the present disclosure provides a means for hydrothermal oxidation which allows for relatively less demanding engineering requirements, improved efficiency and/or  
10 cost effectiveness.

The present disclosure provides a hydrothermal oxidation process and in particular a continuous process for the hydrothermal oxidation of organic matter. The present disclosure also provides to a hydrothermal oxidation reactor within which the process of the present disclosure is carried out.

15 In this specification, the terms 'hydrothermal oxidation' and 'wet oxidation' are used interchangeably.

Full bibliographic details of references cited are collected at the end of the specification.

As noted above, it is generally accepted that elevated turbulence is beneficial during wet oxidation to ensure sufficiently efficient processing through enhancing the gas-liquid mass transfer rate. Implicit in this approach is the concept that the gas-liquid mass transfer rate  
20 is limiting the oxidation process. Contrary to this, the process of the present disclosure makes use of reactors that provide low mixing intensity environments during certain stages of the process. The process allows hydrothermal oxidation to progress successfully even though certain stages of the oxidation are conducted under conditions of low mixing  
25 intensity.

Without being bound by theory, it has been found that oxygen transport demand may not be completely dominant throughout the entire wet oxidation reaction cycle. The reaction, when considered as occurring along the progression of a tubular reactor, can be separated into distinct zones, characterised by the type of reaction rate limitation that exists. The  
30 progression of wet oxidation reveals an initial transitional heat-up zone, followed by a zone

characterised by high oxygen demand, followed by a transition to a zone of significantly lowered oxidation rate – and hence lowered oxygen demand (see Figure 1). The identified zones are:

5 Transition Zone 1 - Heat-up: in this zone, reactor contents are taken from ambient to reaction temperature. Reaction rate limitations move from kinetic to mass transfer limited.

Mass Transfer Limited Zone: in this zone, the hydrothermal oxidation reactions are underway, and oxygen transport from gas to liquid phase is critical. Sufficiently high mixing intensity or turbulence is required to minimise the gas-liquid mass transfer rate limitation  
10 on the overall process reactions.

Transition Zone 2: this zone occurs between the two major zones (Mass Transfer Limited and Kinetically Limited Zones) and is characterised by a mix of limitations between these two zones.

15 Kinetically Limited Zone: in this zone, the oxygen consuming hydrothermal oxidation reaction rates have slowed, and reaction rates are limited by the fundamental kinetics and stoichiometry. Here, oxygen transport from gas to liquid phase is not a major rate limiting factor, and the absolute requirement for mixing intensity or turbulence is significantly lower than in the Mass Transfer Limited Zone.

The process of the present disclosure utilises these different rate-limiting stages.

20 Experimental data supports this analysis. For the purposes of illustration only, Figure 2 provides an analysis of batch wet oxidation of biomass at a temperature setpoint of 230°C. The use of batch data is relevant, as the reaction kinetics are equivalent to those of a plug flow reactor, which is a reasonable representation of a tubular reactor. The oxidation of organic components, represented by the total COD (total Chemical Oxygen Demand) data  
25 is initially rapid, up to 0.2hrs. The suspended solids, as Volatile Suspended Solids (VSS), diminish by approximately 0.1hrs. The Kinetically Limited Zone is represented in the time period from 0.3hrs onwards, showing slow but non-zero rates of change of the key parameters. The benefit of the Kinetically Limited Zone is shown from the ongoing decrease in total and soluble COD and VSS during this zone, through to the conclusion of

this reaction ( $t=1\text{hr}$ ), and the ongoing increase in acetic acid concentration throughout the entire reaction period.

The process and reactor of the present disclosure are now further described.

As already noted, the process and apparatus of the present disclosure incorporate low  
5 mixing intensity in at least part of a wet oxidation reactor, compared with the relatively and  
consistently high turbulent mixing intensity conditions of conventional wet oxidation  
reactors. This is achieved by a combination of gas and liquid flowrates, combined with  
tubular reactor geometry (such as diameter) and operating temperature and pressure,  
which results in low liquid phase turbulence within at least part of the reactor where the  
10 requirement for oxygen transport into the liquid phase through gas-liquid mass transport  
is relatively low.

#### *Process*

The process of the present disclosure is continuous, and comprises:

- pumping organic matter in an aqueous stream into a first section of a reactor,
- 15 pumping a gaseous oxidant into the first section of the reactor,
- maintaining conditions in the reactor at pressures in the range of about 2 to about  
250 bar and temperatures in the range of about 100 to about 373°C,
- subjecting the organic matter in an aqueous stream and the gaseous oxidant to  
high intensity mixing in the first section of the reactor,
- 20 transferring the organic matter in the aqueous stream and the gaseous oxidant  
into a second or subsequent substantially horizontally arranged tubular section of the  
reactor, where at least some of the organic matter containing aqueous stream is in a liquid  
phase and at least some of the gaseous oxidant is in a gas phase,
- and
- 25 maintaining the rate of travel of the liquid phase through at least part of the  
second or subsequent section of the reactor at a maximum velocity of about 0.1m/s, or
- maintaining the Reynolds number of the liquid phase travelling through at least

part of the second or subsequent section of the reactor between about 0 and about 10000.

In one aspect distinct liquid and gaseous phases exist in at least part of the tubular reactor section. Preferably, the gaseous phase moves at a speed equal to or greater than the velocity of the liquid phase. This is achieved through management of reactor temperature  
5 and pressure, and reactor geometry (such as diameter) combined with the relative mass flowrates of liquid and gaseous materials entering the reactor.

Providing a relatively low velocity liquid phase in the second or subsequent section of the reactor results in increased residence time relative to the length of the tubular reactor section, which allows for relatively shorter and lower cost reactors.

10 Typical tubular reactors operating hydrothermal oxidation, characterised as having significant reaction rate limitation by oxygen transfer from gas to liquid phase, operate using highly mixed turbulent flows in order to increase this oxygen transfer rate. To achieve highly turbulent flows in a tubular wet oxidation reactor, having residence times of 30 to 120 minutes would normally manifest as extremely long reactor lengths of narrow  
15 diameter tubular sections. This becomes logistically challenging to fit into a spatial footprint, and the resultant high pressure drops across the reactor length will result in elevated pumping costs.

Conventional implementation of hydrothermal oxidation uses highly mixed tubular systems with a long reactor length, or highly mixed continuous stirred tank reactors (Continuous  
20 Stirred Tank Reactor (CSTR), such as bubble columns) requiring high residence times to match tubular kinetics. The low velocity tubular process of the present disclosure is lower cost than highly mixed tubular and CSTR systems.

In one aspect the liquid phase containing the organic matter preferably travels through the reactor at a maximum velocity of about 0.1m/s, for example at a maximum velocity of  
25 about 0.05m/s or at a maximum velocity of about 0.02m/s. This will be controlled by selection of tube diameter, relative to the pumped flowrate of the liquid phase. The velocity is a function of these parameters and is also controlled by the temperature and pressure environment of the reactor, the gaseous phase flowrate and the orientation of the reactor itself, which dictates the relative distribution of gas and liquid phases within the tube. The  
30 flow velocity for this complex mixed phase system can be predicted by empirical correlations such as that given by Beggs and Brill.

In one aspect the process of the present disclosure produces relatively low turbulence in the second or subsequent reactor section through selection of reactor pipe/tube diameter on the basis of the desired volumetric fluid flow through the pipe. One measure of this is the Reynolds number. This dimensionless number provides a ratio of inertial to viscous  
5 fluid forces. For a given fluid in a pipe, higher Reynolds numbers are associated with greater turbulence, which is in turn representative of mixing energy. Low values of the Reynolds number, usually below about 2000, are consistent with observations of laminar fluid flow, while higher numbers, often higher than 4000, but ranging to higher than 10000, are consistent with observations of turbulent flow.

10 In one aspect the Reynolds number of the liquid phase is between 0 and about 10000, for example between 0 and about 4000. Alternatively, the Reynolds number is between 0 and about 400.

In one aspect pressures in the reactor are maintained in the range of about 10 to about 200 bar, for example in the range of about 20 to about 200 bar or in the range of about 30  
15 to about 120 bar. Pressure will be maintained through control of system back pressure.

In one aspect temperatures in the reactor are maintained in the range of about 160 to about 350°C, preferably in the range of about 220 to about 300°C. Temperature will be maintained and controlled through feedback control of the system heat exchange and/or any external heating methods which may be applied to the reactor (for example, electrical  
20 heating elements).

In one aspect pressures in the reactor are maintained in the range of about 20 to about 200 bar and temperatures in the range of about 200 to about 350°C.

In another aspect pressures in the reactor are maintained in the range of about 30 to about 120 bar and temperatures in the range of about 220 to about 300°C.

25 In one aspect the ratio of the gaseous phase velocity to the liquid phase velocity is in the range of about 1.01:1.00 to about 10:1, preferably in the range of about 1.0:1 to about 10:1, or in the range of about 3:1 to about 6:1.

In one embodiment, the ratio of the gaseous phase velocity to the liquid phase velocity is about 2:1 to about 5:1.

In one aspect the gaseous oxidant is oxygen gas, air or enriched air (air comprising 40% oxygen).

In one embodiment, the gaseous oxidant is oxygen gas and the ratio of the gaseous phase velocity to the liquid phase velocity is about 1.01:1 to about 10:1.

- 5 In another embodiment, the gaseous oxidant is oxygen gas and the ratio of the gaseous phase velocity to the liquid phase velocity is about 2:1 to about 5:1.

Gaseous oxidant can be supplied to the reactor and moderated through either total system pressure (more mass of oxygen at high pressures) and/or gas flowrate (higher flow equals more oxygen).

- 10 Oxygen can be delivered using air instead of more expensive oxygen or chemical oxidants and at lower pressures which may reduce safety and engineering demands on the reactor.

In one aspect a highly soluble supplementary oxidant is added to the reactor in proximity to an aqueous stream inlet. Optionally, the highly soluble supplementary oxidant is a peroxide or a nitrogen oxide.

- 15 Highly soluble supplementary oxidants are known in the art and can be selected depending on the organic matter and desired output. Examples include air, enriched air (that is, air with nitrogen removed such that the oxygen concentration has been enhanced), oxygen, ozone, hydrogen peroxide, sodium percarbonate, Fenton's reagent, nitrous oxide, sodium peroxide, potassium persulfate, sodium hypochlorite, peracetic acid.

- 20 In one aspect the direction of flow of the gaseous phase in the reactor is in counter-current to the flow of the liquid phase. Counter-current air flow may be used as an additional means of retarding velocity of the liquid phase.

In one aspect the volume of the liquid phase in the reactor equates to between about 40 and about 70% of the interior volume of a tubular section of the reactor.

- 25 In one aspect the aqueous stream may be pre-heated before being injected into the reactor, via heat recovery from the material that is discharged from the reactor at high temperature.

*Reactor*

In one aspect, the hydrothermal oxidation reactor of the present disclosure comprises a first section and a second or subsequent substantially horizontally arranged tubular section, an aqueous stream inlet port, a gaseous oxidant input port, an aqueous stream outlet port, a gaseous stream outlet port.

- 5 The process of the present disclosure makes use of a reactor comprising a tubular reactor section. Optionally the tubular section forms part of a hybrid reactor.

- The axes of tubular reactor sections are preferably level or have less than about a 15-degree incline or decline relative to level. For example, the axes of tubular sections of the reactor are level or have less than about a 5-degree incline or decline relative to level or  
10 the axes of tubular sections of the reactor are level or have less than about a 1-degree incline or decline relative to level.

In one embodiment, the tubular reactor section(s) of the second or subsequent reactor section may be coiled. Optionally, the coiled section(s) are substantially horizontal.

- In one embodiment, the tubular reactor sections immediately following the inlet ports are  
15 of lesser internal diameter than subsequent tubular sections.

In one embodiment, the second or subsequent substantially horizontally arranged tubular section comprises the bend sections that are adapted to receive the liquid phase and a gaseous phase and to deliver an aqueous phase and a gaseous phase flowing in substantially parallel flow to an adjacent tubular section. This is a highly stratified system.

- 20 In one aspect, the reactor or parts of the reactor are contained within a thermal envelope to minimise energy loss to the external environment. This thermal envelope allows the heat added and heat generated to be used for attaining and retaining the desired temperature setpoint or set points along the course of the tubular reactor length, preferably without addition of any external heating source. This thermal envelope may be exemplified  
25 by lagging or external insulation around the pipe with materials of poor heat conductivity, and/or by the use of a thermal storage medium, by which thermal energy is stored within a mass (such as silicone-based sand) in order to buffer against temperature changes in the system.

- In one aspect, the reactor comprises additional oxidant ports along the length of the tubular  
30 reactor section. This adds control options to the reactor, avoiding the risk of oxygen

depletion from the initial inlet port, and allows potential manipulation of the end products through control of the oxidation along the reactor.

As already note, the reactor of the present disclosure is configured to provide high intensity mixing or turbulence areas, particularly at the front end of the reactor, in the Mass Transfer Limited Zone. This high turbulence zone may or may not be conducted in a tubular reactor element. If it is not, the reactor is considered to be a hybrid reactor.

The reactor is configured to also provide low turbulence areas, particularly at the section subsequent to the high turbulence areas, in the Kinetically Limited Zone.

In one aspect, the reactor of the present disclosure provides physical elements where high turbulent mixing intensity is induced, followed by physical elements where turbulent mixing intensity is minimised. These elements may include, for example, the provision of a stirred tank forming the first section of the reactor, larger tube diameter in second or subsequent section of the reactor and surface texturing of baffles inside the reactor.

Embodiments of suitable arrangements are illustrated in Figure 3. The embodiments shown in Figure 3 allow for high mixing intensity or turbulence in part of the reactor, and low mixing intensity in another part of the reactor.

Figure 3a) shows an arrangement in which the first section is a small diameter tube. This is followed by a large diameter tube. The two tube sizes will be characterised by high turbulence (the Mass Transfer Limited Zone, small diameter tube) and low turbulence (the Kinetically Limited Zone, large diameter tube).

An alternative hybrid reactor, presented in Figure 3b), shows coupling of a stirred tank to a horizontally arranged tubular reactor section. The stirred tank is demonstrated as a mechanically mixed reactor but may also be in the form of a bubble column.

In this embodiment, a high level of turbulence is induced in the system during the Mass Transfer Limited Zone (this time not relying on a tubular reactor section). The Kinetically Limited Zone is accomplished in a tubular section. An advantage of this configuration is the highly specific control of turbulent mixing intensity, temperature and reaction rate enabled within the first mechanically mixed stage.

Figure 3c) shows flow through a tube which includes an internal recirculation loop. Fluid

is recirculated back to the front of the reactor providing enhanced mixing intensity in the first Mass Transfer Limited Zone. Beyond the recirculating zone, the latter part of the tubular reactor has lower mixing intensity, representing the Kinetically Limited Zone. In this embodiment, the pipe diameter could be the same for both the Mass Transfer Limited  
5 Zone and the Kinetically Limited Zone, the internal recirculation of fluid providing for enhanced mixing intensity in the Mass Transfer Limited Zone.

*Material for processing*

The organic matter may be one or more of wastewater, industrial effluent, agricultural effluent, food waste, packaging materials, and plant residues. However, it will be  
10 appreciated that any suitable organic matter may be used.

In one aspect the aqueous stream comprises an organic content of between 0 and about 15% weight to weight, preferably between 0 and about 10% weight to weight, and more preferably between 0 and about 8% weight to weight.

In one aspect the organic matter comprises or consists of dissolved organic molecules,  
15 suspended solids or both dissolved organic molecules and suspended solids.

The outputs of the reactor consist of gas, liquid and solid phases. In the liquid phase, water is the carrying fluid, within which is contained a range of soluble organic components, generated as reaction product. Amongst these are typically a range of short chain fatty acids, ketones and aldehydes, the largest contributor typically being acetic acid.

20 In the gas phase, residual unreacted oxygen, water vapour, carbon dioxide, inert gases such as nitrogen, and some low levels of carbon monoxide and volatile organic compounds are typical.

The process may be followed by a settling stage to allow the settling out and separation of inorganic ash particles.

25 Liquid outputs of the process are fed to an anaerobic digester for the production of biogas.

In one aspect the residence time and processing conditions are engineered to optimise the yield of C1 to C5 short chain fatty acids.

Acetic acid is quite recalcitrant to wet oxidation making it an effective end point for a

hydrothermal oxidation process.

The end product can be used as a chemical feedstock and value can be recovered from the carbon component of the organic feedstock.

### Exemplification

- 5 Figure 4 shows an exemplification of the second or subsequent tubular reactor section of a reactor according to the present disclosure Figure 5 shows a process diagram.

The second or subsequent tubular reactor section comprises horizontal sections of pipes (1) that are connected by bend sections (2). The liquid and gas inlets are located at the bottom of the reactor (3) and (4), the outlet of the reactor is located at the top end (5) of the reactor. Straight pipe pieces are connected by multiple L- or U- shaped sections (6).  
10 There is at least one sampling point along the reactor (7), a thermocouple (8) and a valve (9).

The process is carried out as follows:

- First, the appropriate organic matter is introduced via pumping into a front end of the reactor (not shown in Figure 4). This organic matter is substantially within a water matrix,  
15 typically comprising 90-98% water, with the balance being the organic material to be treated.

The pump is a high-pressure pump, capable of reaching the reaction pressures of, for example, 50-100bar.

- 20 The feed material is heated in a primary heating stage, to a temperature that is typically between 50-300°C. This heating may be derived from heat exchange with the exiting reactor contents or from an external heating source (for example, electrical or hot oil). Gaseous oxidant is added separately, either prior to heating or after the primary heating stage. The mass of oxygen added is calculated as proportional to the organic content of the feed, in terms of Chemical Oxygen Demand (COD). Typical proportions would be  
25 Oxygen/COD ratio (termed Lambda factor) of 0.6-2. The oxidant may or may not be preheated prior to addition to the feed.

The gas-liquid feed matrix passes through the reactor, with its various reaction zones. The

- heat of oxidation reaction, coupled with the heating provided to the contents, acts to bring the reactor contents to the desired system temperature. The pressure of the system is set via back-pressure control, ensuring that the liquid water does not boil, which would make a penalty of the entire latent heat of vaporisation of the water. The pressure of the system
- 5 also ensure sufficient liquid phase is retained to sustain the oxidation reactions, pass the materials through the reactor sections without adhering to the walls of the tubes, and limit the vaporisation of the water to desired levels. Typical system pressures are 5-50bar above the vapour pressure of the liquid matrix, at the desired temperature setpoint. The temperature setpoint is typically 200-300°C.
- 10 The reactor contents, on passing through the various sections of the tubular reactor, are brought back to ambient temperature and pressure via various means, including heat exchange and back pressure regulator arrangements. Preferably, these arrangements are organised so as to recover energy from the reactor discharges, to maximise the work efficiency of the reactor system as a whole. As part of this, solids may be separated from
- 15 the fluids before or after gas-liquid separation, which may itself occur before or after temperature and pressure reduction. The cooled liquid discharge consists of the final treated materials, available for further processing for value recovery.

- In embodiments where the flow of the gaseous oxidant is counter current flow relative to the liquid phase, the counter current air transfers heat back towards the beginning of the reactor; surface ripples are caused by slip velocity which introduces turbulence; counter
- 20 current flow increases the surface area of the liquid - gas interface; and the residence time of the liquid phase is slowed down by friction.

### Experimental Example

- This Example provides results of hydrothermal processing of soluble substances in the tubular reactor of the present disclosure.
- 25

#### Materials and Methods

##### Starting material

- The starting material comprised solutions of organic materials that were substantially soluble in water. The material was an aqueous mixture of molasses and hydrolysed fish
- 30 material, providing a synthesised representation of a waste sample containing high levels

of organic pollutants. Typical pollutant biomass is characterised by major chemical classes that can be defined as fibrous, carbohydrate, protein across, fat or oil based, or cellular DNA/RNA fragmentation. The chosen mixture represented a biomass with high carbohydrate and proteinaceous characteristics.

- 5 Mixtures were made up in water, and adjusted to pH7, prior to feeding into a serpentine tubular reactor as shown in Figure 6.

The reactor length was 22.4m, with internal diameter of 15.748 mm.

Aqueous feed rates were either 5 or 10L/hr.

- 10 The organic fraction concentration in the aqueous feed was measured via chemical oxygen demand (COD) units. COD is defined as the amount of oxygen that would be theoretically required to completely oxidise a particular sample, thus providing a measure of organic pollutant concentration without having to measure individual components. The feed COD was measured as 7900 mg/L.

- 15 Heating was provided by electrical coils, mounted externally to the first three run lengths of the reactor. For the given experiment, the reactor temperature was set at 250°C.

The oxidant pumped into the reactor was oxygen delivered as air from high pressure cylinders. Gaseous air flow was controlled via thermal mass flow controller, with flows between 7.65 and 15.31 nL/min (normal litres per minute, volumetric flow normalised to 101300Pa and 0°C).

- 20 The oxygen to COD ratio, a critical parameter for hydrothermal oxidation, was set between 1.1 and 2 gO<sub>2</sub>/gCOD.

Reactor pressure was controlled via a back pressure controller. For this experiment, two reactor pressures were trialled – 70 and 90bar.

Four trials were completed, as outlined in Table 1.

- 25 Table 1: Trial matrix

| Trial | System pressure (bar) | Aqueous flowrate (kg/hr) |
|-------|-----------------------|--------------------------|
|-------|-----------------------|--------------------------|

|              |    |    |
|--------------|----|----|
| 1 (P90, Q5)  | 90 | 5  |
| 2 (P90, Q10) | 90 | 10 |
| 3 (P70, Q5)  | 70 | 5  |
| 4 (P70, Q10) | 70 | 10 |

## Results

Temperature profile across the reactor length is presented in Figure 7.

### Flow conditions within reactor

The reactor conditions are defined as multiphase flow – a mix of gas and liquid. The nature of this multiphase flow facilitates transport of oxygen from the gas phase into the liquid where it is involved in the oxidative reactions. In general, the greater the interphase mixing, the greater the transport of oxygen between gas and liquid phases. This mass transport is a function of mixing or turbulence, which can be defined by the dimensionless Reynolds number correlation, as defined above.

The volumetric flow is a function of the mass flow, material characteristics and environmental conditions of the system (temperature and pressure). For this work, the liquid phase was modelled as water, containing amounts of dissolved components – acetic acid (a product of the oxidation process), oxygen, nitrogen, carbon dioxide), whilst the gas was considered as a mixture of gases – oxygen, nitrogen, carbon dioxide and water (derived from evaporation from the liquid phase).

Values were generated based on volumetric flow at reaction temperature (240°C) and pressure (70 and 90 bar), allowing for evaporation of water into the gas phase. The results were generated using a publicly available chemical process simulator DWSIM (<https://dwsim.org/>), applied using the NRTL thermodynamic property package (Renon and Prausnitz 1968).

Parameters used in the analysis are provided in Table 2, with flow description in terms of fluid volumetric flow, fluid velocity and Reynolds number.

Table 2: Key parameters and derived flow characteristics for trials

|                                 | Trial 1<br>(P90, Q5)  | Trial 2 (P90,<br>Q10) | Trial 3 (P70,<br>Q5)  | Trial 4 (P70,<br>Q10) | Units             |
|---------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------------------|
| Density – gas                   | 52.0                  | 52.0                  | 38.4                  | 38.4                  | kg/m <sup>3</sup> |
| Density – Liquid                | 817                   | 817                   | 817                   | 817                   | kg/m <sup>3</sup> |
| Kinematic<br>Viscosity – gas    | 4.77x10 <sup>-7</sup> | 4.77x10 <sup>-7</sup> | 6.15x10 <sup>-7</sup> | 6.15x10 <sup>-7</sup> | m <sup>2</sup> /s |
| Kinematic<br>Viscosity - Liquid | 1.41x10 <sup>-7</sup> | 1.41x10 <sup>-7</sup> | 1.40x10 <sup>-7</sup> | 1.40x10 <sup>-7</sup> | m <sup>2</sup> /s |
| Liquid Holdup                   | 0.75                  | 0.67                  | 0.59                  | 0.52                  | -                 |
| Volumetric Flow<br>- Liquid     | 0.0016                | 0.0032                | 0.0015                | 0.0031                | L/s               |
| Volumetric Flow<br>– gas        | 0.0050                | 0.010                 | 0.0078                | 0.016                 | L/s               |
| Velocity - Liquid               | 0.0082                | 0.017                 | 0.0079                | 0.016                 | m/s               |
| Velocity – gas                  | 0.026                 | 0.052                 | 0.040                 | 0.081                 | m/s               |
| Reynolds<br>Number - Liquid     | 914                   | 1850                  | 89                    | 1800                  | -                 |
| Reynolds<br>Number – gas        | 850                   | 1720                  | 1030                  | 2080                  | -                 |
| Flow Regime                     | Segregated            | Segregated            | Segregated            | Segregated            | -                 |

Table 2 reveals Reynolds numbers for liquid phase are less than 2000. A generally accepted ‘rule of thumb’ is that laminar flow is present at Reynolds values less than 2000,

with transition to turbulent flow happening above 2000 (Perry and Green, 1984). The gas phase Reynolds numbers are also low, with all having Reynolds numbers below 2050.

Included in Table 2 is a description of the Flow Regime. This is derived from a correlation developed for describing multiphase flow – the Beggs and Brill correlation (Beggs and Brill, 1973). Its calculation is built into the pipe tool calculators within a number of process  
5 simulators, including DWSIM, where it was applied in this example.

Applying this correlation identifies the flow regime as ‘segregated’ for each trial. Segregated flow is described as a condition where the gas and liquid phases are present in substantially distinct layers within the pipe. Segregated flow is present where gas and  
10 liquid flows are low.

#### Reaction performance

Reactor performance is measured in terms of COD removal across the reactor. One of the attributes of the serpentine reactor is that it is an example of a plug flow reactor. Once temperature is reached, the length of the reactor reflects the reaction time, and thus  
15 reaction progression. Hence sampling along the length of reactor can be taken to represent performance of a reactor of differing length, or retention time of the materials within the system.

The three sample points each represent a particular time that the fluid has spent in the reactor. This liquid retention time can be calculated from the ratio of reactor length at each  
20 specific sampling point, to the predicted liquid velocity through the reactor (from Table 2).

Calculating the liquid retention time allows a plot of COD concentration as a response to this parameter as shown in Figure 8. Also plotted is the COD removal, as a percentage of the original COD, against liquid retention time (shown in Figure 9).

COD diminishes from the original 7900mg/L, down to 4000mg/L after approximately 50  
25 minutes of reaction time. This represents 50% COD removal across this time period, a robust performance at the given reaction temperature.

All data fits on a consistent curve, indicating that whilst the 5 and 10L/hr samples represent different input flowrates, the reactor performed consistently when response was normalised to liquid residence time.

Changes in pressure had minimal effect on the COD removal, under the conditions chosen for the current trials.

The results of the Example show that wet oxidation is occurring to a practical level under low turbulence conditions.

- 5 While illustrative embodiments have been illustrated and described, including the best mode known to the inventors for carrying out the invention, those skilled in the art will recognise that the disclosure may be practiced with variations on the disclosed structures, materials, compositions and processes, and such variations are regarded as within the ambit of the disclosure.

## References

Beggs, D. H.; Brill, J. P. (1973). A Study of Two-Phase Flow in Inclined Pipes. *Journal of Petroleum Technology* 1973, 25 (05), 607–617.

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Renon, H.; Prausnitz, J. M. (1968). Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE Journal* 14 (1), 135–144.  
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**What is claimed is:**

1. A continuous process for the hydrothermal oxidation of organic matter comprising:
  - pumping organic matter in an aqueous stream into a first section of a reactor,
  - pumping a gaseous oxidant into the first section of the reactor,
  - maintaining conditions in the reactor at pressures in the range of about 2 to about 250 bar and temperatures in the range of about 100 to about 373°C,
  - subjecting the organic matter in an aqueous stream and the gaseous oxidant to high intensity mixing in the first section of the reactor,
  - transferring the organic matter in the aqueous stream and the gaseous oxidant into a second or subsequent substantially horizontally arranged tubular section of the reactor, where at least some of the organic matter containing aqueous stream is in a liquid phase and at least some of the gaseous oxidant is in a gas phase,
  - and
  - maintaining the rate of travel of the liquid phase through at least part of the second or subsequent section of the reactor at a maximum velocity of about 0.1m/s, or
  - maintaining the Reynolds number of the liquid phase travelling through at least part of the second or subsequent section of the reactor between about 0 and about 10000.
2. The process of claim 1, wherein the liquid phase containing the organic matter travels through the reactor at a maximum velocity of about 0.05m/s.
3. The process of claim 1, wherein the liquid phase containing the organic matter travels through the reactor at a maximum velocity of about 0.02m/s.
4. The process of claim 1, wherein the Reynolds number of the liquid phase in the tubular reactor section is between about 0 and about 4000.
5. The process of claim 1, wherein the Reynolds number of the liquid phase in the tubular

reactor section may also be between about 0 and about 400.

6. The process of claim 1, wherein pressures in the reactor are maintained in the range of about 10 to about 200 bar and temperatures in the range of about 160 to about 350°C.
7. The process of claim 1, wherein pressures in the reactor are maintained in the range of about 20 to about 200 bar and temperatures in the range of about 200 to about 350°C.
8. The process of claim 1, wherein pressures in the reactor are maintained in the range of about 30 to about 120 bar and temperatures in the range of about 220 to about 300°C.
9. The process of claim 1, wherein the liquid and gaseous phases exist as distinct or segregated layers in at least part of the tubular reactor section.
10. The process of claim 1, wherein the liquid and gaseous phases exist as sequences of slugs of liquid separated by slugs of gas.
11. The process if claim 9 or clam 10 wherein the liquid and gaseous phases exist as a mixture of layered flow and slug flow.
12. The process of claim 1, wherein the bulk of gaseous phase moves at a speed equal to or greater than the velocity of the liquid phase.
13. The process of claim 1, wherein the ratio of the gaseous phase velocity to liquid phase velocity is in the range of about 1.01:1.00 to about 10:1.
14. The process of claim 1, wherein the ratio of the gaseous phase velocity to the liquid phase velocity is in the range of about 1.1:1 to about 10:1.
15. The process of claim 1, wherein the ratio of the gaseous phase velocity to the liquid phase velocity is about 3:1 to about 6:1.
16. The process of claim 1, wherein the ratio of the gaseous phase velocity to the liquid phase velocity is about 2:1 to about 5:1.
17. The process of claim 1, wherein the gaseous oxidant is oxygen gas.
18. The process of claim 1, wherein the gaseous oxidant is air.

19. The process of claim 1, wherein the gaseous oxidant is enriched air, for example about 40% O<sub>2</sub>.
20. The process of claim 1, wherein the gaseous oxidant is oxygen gas and the ratio of the gaseous phase velocity to the liquid phase velocity is about 1.1:1 to about 10:1.
21. The process of claim 1, wherein the gaseous oxidant is oxygen gas and the ratio of the gaseous phase velocity to the liquid phase velocity is about 2:1 to about 5:1.
22. The process of claim 1, wherein a highly soluble supplementary oxidant is added.
23. The process of claim 22, wherein the the highly soluble supplementary oxidant is added to the reactor in proximity to an aqueous stream inlet of the reactor.
24. The process of claim 22 or claim 23, wherein the highly soluble supplementary oxidant is a peroxide or nitrogen oxide.
25. The process of claim 1, wherein the direction of flow of the gaseous phase in the reactor is in counter-current to the flow of the liquid phase.
26. The process of claim 1, wherein the aqueous stream comprises an organic content of between about 0 and about 15% weight to volume.
27. The process of claim 1, wherein the aqueous stream comprises an organic content of between about 0 and about 10% weight to volume.
28. The process of claim 1, wherein the aqueous stream comprises an organic content of between about 0 and about 8% weight to volume.
29. The process of claim 1, wherein bend sections of the reactor are adapted to receive an aqueous layer and a gaseous layer and to deliver the aqueous layer and the gaseous layer flowing in substantially parallel flow to an adjacent tubular section.
30. The process of claim 1, wherein the volume of the liquid phase in the reactor equates to between about 40 and about 70% of the interior volume of a tubular section of the reactor.
31. The process of claim 1, wherein residence time and processing conditions are adapted to optimise the yield of C1 to C5 short chain fatty acids.

32. A reactor for hydrothermal oxidation of organic matter comprising:
- a first section,
  - a second or subsequent substantially horizontally arranged tubular section,
  - an aqueous stream inlet port,
  - a gaseous oxidant input port,
  - an aqueous stream outlet port, and
  - a gaseous stream outlet port.
33. The reactor of claim 32, wherein the first section comprises a tubular section.
34. The reactor of claim 33, wherein the tubular section is of lesser internal diameter than the second or subsequent tubular section.
35. The reactor of claim 32, wherein the first section comprises a stirred tank reactor.
36. The reactor of claim 32, wherein the second or subsequent substantially horizontally arranged tubular section comprises a plurality of tubular sections.
37. The reactor of claim 32, wherein the first section comprises a tubular section and the second or subsequent substantially horizontally arranged tubular section has a larger diameter than the first section.
38. A reactor of claim 32, wherein the axes of tubular reactor section are level or have less than about a 15-degree incline or decline relative to level.
39. A reactor of claim 32, wherein the axes of tubular reactor section are level or have less than about a 5-degree incline or decline relative to level.
40. A reactor of claim 32, wherein the axes of tubular sections of the reactor are level or have less than about a 1-degree incline or decline relative to level.
41. The reactor of claim 32, wherein the second or subsequent substantially horizontally arranged tubular section comprises one or more bends.
42. The reactor of claim 41, wherein the bend sections of the second or subsequent substantially horizontally arranged tubular section are adapted to receive a liquid phase

and a gaseous phase and to deliver an aqueous layer and a gaseous layer flowing in substantially parallel flow to an adjacent tubular section.

43. The reactor of claim 32, comprising additional oxidant injection ports.