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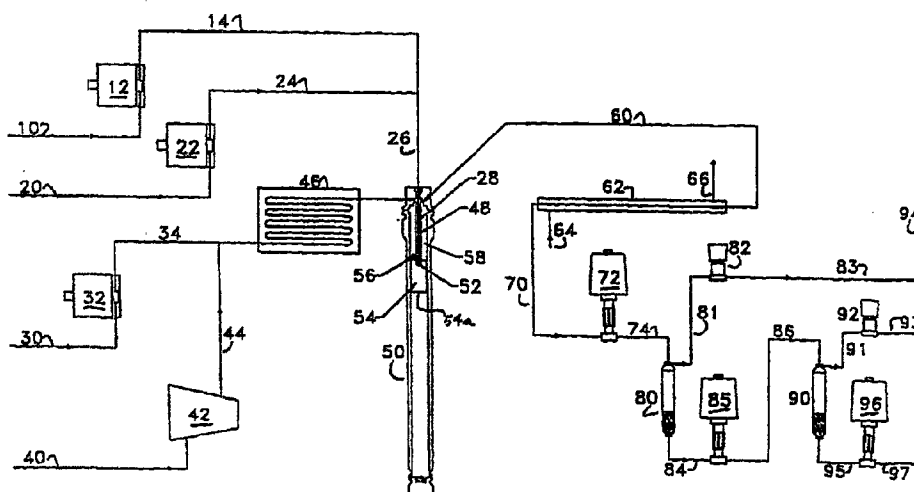
(71) MODAR, INC., US

(51) Int.Cl.^{6} C02F 1/72

(30) 1995/07/28 (08/509,504) US

(54) **PROCEDE D'OXYDATION HYDROTHERMALE**

(54) **METHOD FOR HYDROTHERMAL OXIDATION**

(57) Procédé d'oxydation hydrothermale en flux continu, constituant un moyen peu coûteux de déclenchement et de propagation d'une réaction. La charge aqueuse-organique et l'agent oxydant sont introduits dans une petite chambre de réaction (2) où ils se mélangent avec le contenu échauffé et ayant partiellement réagi. Ce rétro-mélange permet de déclencher la réaction de la charge arrivante. De manière facultative, le contenu de la chambre (2) peut être admis dans un deuxième réacteur (4) situé en aval, pour permettre l'achèvement de la réaction d'oxydation.

(57) A method of continuous flow hydrothermal oxidation which provides for a low cost means of reaction initiation and propagation. The aqueous-organic feedstock and oxidant are introduced to a small reaction chamber (2) and allowed to mix with the hot, partially reacted contents thereof. This backmixing serves to initiate the reaction of the incoming feedstock. Optionally, the contents of the chamber (2) then pass to a second reactor (4) located downstream, in order to allow for completion of the oxidation reaction.

PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C02F 1/72	**A1**	(11) International Publication Number: **WO 97/05069**
		(43) International Publication Date: 13 February 1997 (13.02.97)

(21) International Application Number: PCT/US96/12228

(22) International Filing Date: 24 July 1996 (24.07.96)

(30) Priority Data:
08/509,504   28 July 1995 (28.07.95)   US

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(81) Designated States: AU, BR, CA, CN, CZ, FI, JP, KP, MX, NO, NZ, PL, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD FOR HYDROTHERMAL OXIDATION
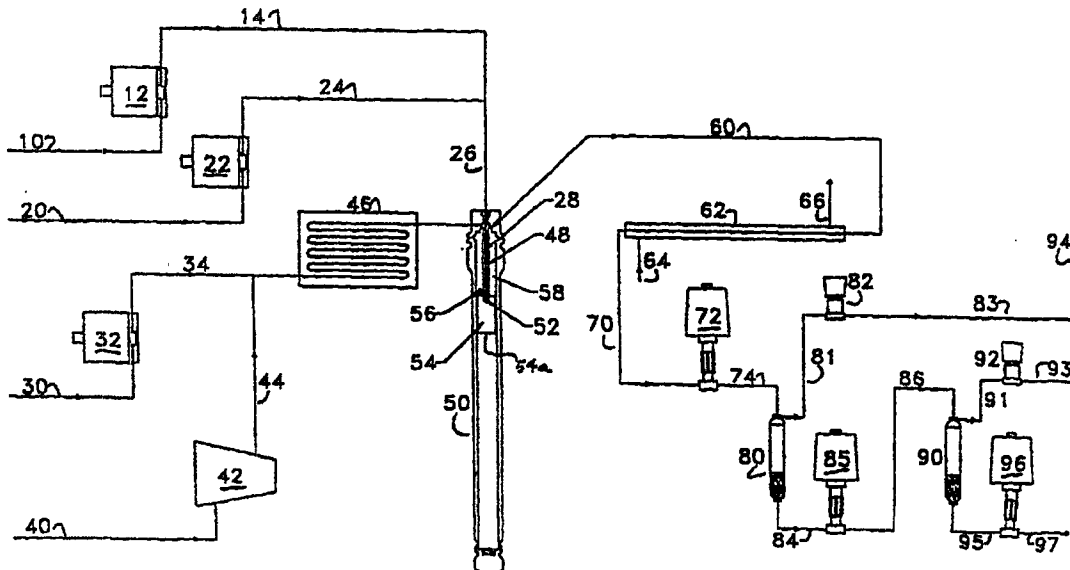
(57) Abstract

A method of continuous flow hydrothermal oxidation which provides for a low cost means of reaction initiation and propagation. The aqueous-organic feedstock and oxidant are introduced to a small reaction chamber (2) and allowed to mix with the hot, partially reacted contents thereof. This backmixing serves to initiate the reaction of the incoming feedstock. Optionally, the contents of the chamber (2) then pass to a second reactor (4) located downstream, in order to allow for completion of the oxidation reaction.

Title: Method for Hydrothermal Oxidation

SPECIFICATION

Background

The process of wet oxidation has been used for the
treatment of aqueous streams for over thirty years. It
involves the addition of an oxidizing agent, typically
air or oxygen, to an aqueous stream at elevated
temperatures and pressures, with the resultant
"combustion" of oxidizable materials directly within
the aqueous phase. The wet oxidation process is
characterized by operating pressures of 30 to 250 bar
(440 to 3630 psia) and operating temperatures of 150°
to 370°C. Since gas phase oxidation is quite slow at
these temperatures, reaction is primarily carried out
in the liquid phase. Thus, the reactor operating
pressure is typically maintained at or above the
saturated water vapor pressure, so that at least part
of the water is present in liquid form. Even in the
liquid phase, however, reaction times are on the order
of 1 hour.

Conventional wet oxidation is limited by the
degree of oxidation attainable, an inability to
adequately handle refractory compounds, slow reaction
times, and lack of usefulness for power recovery due to
the low temperature of the process. For these reasons,
there has been considerable interest in extending wet

oxidation to higher temperatures and pressures. In
U.S. Pat. No. 2,944,396, issued July 12, 1960 to Barton
et al., the addition of a second oxidation stage after
a subcritical, wet oxidation reactor is taught.

5   Unoxidized volatile combustibles which accumulate in
the vapor phase of the first stage wet oxidation
reactor are sent to complete their oxidation in the
second stage, which is operated at temperatures both
above and below the critical temperature of water of

10   about 374°C and above and below the critical pressure
of water. U.S. Pat. No. 4,292,953, issued Oct. 6, 1981
to Dickinson, discloses a modified wet oxidation
process for power generation from coal and other fuels
in which, as heat is liberated by combustion, the

15   entire reaction mixture exceeds the critical
temperature of water, with operating pressures of about
69 bar (1000 psi) to about 690 bar (10,000 psi)
spanning both the sub- and supercritical water pressure
ranges.

20   U.S. Pat. No. 4,338,199, issued July 6, 1982 to
Modell, discloses a wet oxidation process which has
come to be known as supercritical water oxidation
(SCWO) because in some implementations oxidation occurs
essentially entirely at conditions supercritical in

25   temperature (>374°C) and pressure (> about 3200 psi or
220 bar). SCWO has been shown to give rapid and
complete oxidation of virtually any organic compound in
a matter of seconds at 500-600°C and 250 bar. Carbon
and hydrogen form the conventional combustion products

30   CO_2 and H_2O. Chlorinated hydrocarbons (CHC's) also give
rise to HCl, which will react with available cations to
form chloride salts. Alkali may be intentionally added

to the reactor to avoid high, corrosive concentrations
of hydrochloric acid in the reactor and especially in
the cooldown equipment following the reactor. In
contrast to normal combustion, which forms SO_2, the
final product of sulfur oxidation in SCWO is sulfate
anion. As in the case of chloride, alkali may be
intentionally added to avoid high concentrations of
sulfuric acid. Similarly, the product of phosphorus
oxidation is phosphate anion.

At typical SCWO reactor conditions densities are in
the range of 0.1 g/cc, so that water molecules are
considerably farther apart than in normal liquid water.
Hydrogen bonding, a short-range phenomenon, has been
almost entirely disrupted, and the water molecules lose
the ordering responsible for many of liquid water's
characteristic properties. In particular, solubility
behavior is closer to that of high pressure steam than
to liquid water. Smaller polar and nonpolar organic
compounds, with relatively high volatility, will exist
as vapors at typical SCWO conditions, and hence be
completely miscible with supercritical water. Gases
such as N_2, O_2, and CO_2 show similar complete
miscibility. Larger organic compounds and polymers
will hydrolyze to smaller molecules at typical SCWO
conditions, resulting in solubilization via chemical
reaction. The loss of bulk polarity by the water phase
has striking effects on normally water-soluble salts,
as well. No longer readily solvated by water
molecules, they frequently precipitate out as solids
which can deposit on process surfaces and can cause
fouling of heat transfer surfaces or blockage of the
process flow.

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A process related to SCWO known as supercritical
temperature water oxidation (STWO) can provide similar
oxidation effectiveness for certain feedstocks but at
lower pressure. This process has been described in
5   U.S. Pat. No. 5,106,513 issued April 21, 1992 to Hong,
and utilizes temperatures in the range of 600°C and
pressures between 25 and 220 bar. For the treatment of
some feedstocks, the combination of temperatures in the
range of 400 to 500°C and pressures of up to 1000 bar
10   (15,000 psi) have proven useful to keep certain
inorganic materials from precipitating out of solution
(Buelow, S., "Reduction of Nitrate Salts under
Hydrothermal Conditions", Proceedings of the 12th
International Conference on the Properties of Water and
15   Steam, ASME, Orlando, FL, September, 1994). The
various processes for oxidation in an aqueous matrix
will hereinafter be referred to collectively as
hydrothermal oxidation (HTO) if carried out at
temperatures between about 374 and 500°C and pressures
20   between about 25 and 1000 bar.

A key aspect of the various HTO processes is the
means by which the supercritical temperature, which
corresponds roughly to the temperature at which rapid
reaction commences, is achieved. Table 1 lists
25   relevant prior art in the HTO field, and the means each
invention utilizes to achieve reaction temperatures in
excess of 374°C.

30   Table 1. Methods used to attain oxidation at
supercritical temperature. A semicolon indicates that
the patent describes more than one initiation method.

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Author	U.S. Pat. No.	Year	Initiation Method
Dickinson	4,292,953	1981	Heat of reaction at subcritical conditions
Modell	4,338,199	1982	Recycle of hot reactor effluent using external device
Dickinson	4,377,066	1983	Fluidized bed solids
Dickinson	4,380,960	1983	Recycle of hot reactor effluent using internal venturi
Modell	4,543,190	1985	Injection of supercritical water
Burleson	4,564,458	1986	Heat exchange and subcritical reaction
Titmas	4,594,164	1986	Heat exchange, subcritical reaction and combustion of clean fuel
Dickinson	4,714,032	1987	Recycle of hot solids
Kaufmann	4,774,006	1988	Heat exchange and subcritical reaction
Titmas	4,792,408	1988	Recycle of hot reactor fluid using internal venturi
Hong et al.	4,822,497	1989	Jet induced recirculation in a large vessel
Welch et al.	4,861,497	1989	Heat exchange and subcritical reaction
Dickinson	4,898,107	1990	Recycle of hot reactor effluent using internal or external device; Heat exchange; Heat exchange to vaporized feed followed by injection of vaporized feed
Hossain et al.	5,075,017	1991	External heating and subcritical reaction

Hong	5,106,513	1992	Jet induced recirculation in a large vessel; Heat exchange; Recycle of hot reactor effluent using external device
Rofer et al.	5,133,877	1992	External heating
Fassbender	5,167,930	1992	Heat exchange
Swallow et al.	5,232,604	1993	Jet induced recirculation in a large vessel; Heat exchange; Injection of supercritical water
Copa et al.	5,240,619	1993	Heat exchange and subcritical reaction
Modell et al.	5,252,224	1993	External heating and subcritical reaction; Heat exchange and subcritical reaction
Gloyna, et al.	5,358,646	1994	Heat exchange
McGinness	5,384,051	1995	External heating or heat exchange, with injection of supercritical water

The preceding patents suffer from various disadvantages in attaining rapid reaction rates. These disadvantages are now described, with discussion limited to those patents which introduce unique initiation concepts. Patents which are not discussed rely on initiation methods covered by those which are discussed.

U.S. Pat. No. 4,292,953 of Dickinson relies on heat release from subcritical temperature oxidation, a slow reaction which may require tens of minutes. Although the process fluid density is higher at subcritical temperatures, the slow reaction rate nevertheless results

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in inefficient use of reactor volume.

U.S. Pat. No. 4,338,199 of Modell shows recycle of reactor effluent to the incoming feed stream to provide rapid heatup and reaction initiation. A disadvantage of this design is that only fully reacted fluid is recycled. It is well known that chemical reactions are frequently propagated by highly reactive intermediate species, so that recycle of incompletely reacted fluid is likely to be beneficial. Furthermore, eductor devices as shown in this patent have limited capacity for control or adjustment, and can tie the flowrate of critical streams to the recycle rate. For example, Fig. 1A of this patent shows a recycle eductor driven by a warm feed stream. The feed stream is essentially incompressible, and makes a poor motive fluid for the low density recycle fluid; the mass ratios shown are very likely impossible to attain. The eductor could potentially be driven by an air stream, but the ability to adjust oxidant level to meet changing feed oxygen requirements would then be severely constrained by the required recycle rate. Use of pure oxygen or highly oxygen-enriched air as a motive fluid, because of the reduced volumetric flow as compared to air, is likely to be impractical.

U.S. Pat. No. 4,377,066 of Dickinson relies on contact with the hot solids of a fluidized bed to achieve rapid heatup and reaction of incoming feedstock. This method may be complicated due to solids handling and fluid distribution, and requires a relatively large reactor to contain the bed of solids.

U.S. Pat. No. 4,380,960 of Dickinson teaches the recycle of fluid from the downstream end of an elongated reactor, i.e., fully reacted fluid, back to the head of

the reactor.   Thus, as with U.S. Pat. No. 4,338,199 of
Modell mentioned above, recycle of reaction intermediates
is not brought about.   In addition, because the elongated
reactor inherently possesses a significant pressure drop,

5   for example tens or perhaps even hundreds of psi, the
recycle pump must overcome significant pressure.   The
examples shown in this patent employ a venturi nozzle,
which is unlikely to generate sufficient pressure
increase for reactors hundreds of feet in length.   Such

10   reactor lengths have commonly been specified and utilized
in HTO work.   Furthermore, should solid deposits cause
constrictions in the reactor pipe, the pressure drop can
be greatly exacerbated.

U.S. Pat. No. 4,543,190 of Modell shows the injection

15   of a clean stream of supercritical water as a means of
achieving rapid heatup and reaction of incoming
feedstock.   This method requires a means of continually
heating the clean water to supercritical conditions, and
increases plant cost by increasing the process volume

20   requirement.

U.S. Pat. No. 4,564,458 of Burleson utilizes a
combination of heat exchange and reaction at subcritical
conditions to attain rapid, supercritical oxidation.   As
mentioned above, subcritical reaction is an inefficient

25   method of achieving supercritical temperatures.   The use
of heat exchange will help speed heatup of the feed, but
has the drawback of requiring additional expensive
process equipment.   The possibility of organic char
formation and corrosivity can make the operation of such

30   a heat exchanger very difficult.   Use of heat exchange
has the further effect of increasing the specific energy
of the feedstock, so that feeds must be processed at more

dilute levels. This is appropriate for feeds dilute in organic, but a disadvantage for concentrated organic feeds. For example, a cold feed with a heating value of 1800 Btu/lb will reach an adiabatic oxidation temperature
5   of about 600°C when air is used as the oxidant. If, however, this same feed has been preheated to about 375°C, it may only possess a heating value of 900 Btu/lb to reach 600°C. Thus, the organic content of the preheated feed can only be about half that of the
10   unpreheated feed.

U.S. Pat. No. 4,594,164 of Titmas uses oxidation of clean fuel, in addition to some of the methods described above, to achieve rapid heatup. Processing of clean fuel has the disadvantage of occupying unit capacity in a
15   nonproductive function. Clean fuel represents an additional expense, as does the oxidant which must be correspondingly supplied.

U.S. Pat. No. 4,822,497 of Hong et al. uses jet induced recirculation to recycle heat and reaction
20   intermediates while separating solids, including "sticky" solids such as sodium chloride and sodium sulfate, from the bulk of the process fluid. This scheme for recirculation will be referred to as "immediate back-mixing", as the recirculated fluids are taken from the
25   immediate vicinity of the feed jet, as opposed to some point far downstream. The process is carried out in a back-mixed vessel, which has a low length to diameter ratio as compared to the elongated reactor called for in some of the previously described patents. The back-mixed
30   vessel design allows for process fluid recirculation with a minimal pressure drop, but has a broader residence time distribution than an elongated reactor. Achievement of

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a given extent of reaction in a back-mixed vessel may therefore require a larger reactor volume than for an elongated reactor. In this patent, the feed stream is injected via a downwardly directed jet, which entrains

5   hot, partially reacted fluid already present in the reactor, initiating rapid reaction. Solids form as the reaction proceeds, and are projected and fall onto a cooler brine zone maintained at the bottom of the reactor. The sticky solids redissolve in the brine and

10   may be continually drawn off from the reactor. (Withdrawal of undissolved sticky solids from a high pressure vessel would be exceedingly difficult.) The solids separation is achieved because only the fraction of the process stream necessary for solids dissolution

15   and transport is withdrawn as brine. The balance of the process stream, which is frequently the largest portion, is caused to reverse flow to an upward direction within the reactor, and is withdrawn from the reactor top section. By this means, it becomes possible to recover

20   a hot, nearly solids free stream from the process. To minimize entrainment of solid particles in the upward flow within the reactor, the velocity is kept to a low value by using a large cross section reactor vessel.

25   Summary of the Invention

     The present invention describes a continuous hydrothermal oxidation process, with temperatures between about 375 and 750°C and pressures between about 25 and

30   1000 bar, which utilizes a small volume back-mixed reaction chamber to achieve at least partial oxidation. The invention is particularly suited to feed streams

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which do not create substantial amounts of solids which
accumulate in the reactor(s). The back-mixed chamber
provides for internal recycling of hot, partially reacted
process fluid with a low pressure drop, which is less
5   than 100 psi, and preferably less than 10 psi. Various
methods may be used to bring about vigorous back mixing,
including fluid jets, impingement on solid surfaces, and
internal devices such as venturis or impellers. The
chamber is designed to be of minimal process volume while
10   providing a sufficient thermal mass to cause rapid
reaction initiation of relatively cold incoming feed
streams. Once reaction has been initiated, high extents
of reaction may be attained within the back-mixed
chamber, or optionally by a second stage reactor.
15

Brief Description of the Drawings

Figure 1 is a schematic of a two-stage reactor useful
for carrying out the process of this invention; and
20   Figure 2 is an apparatus used to practice this
invention.

Description of the Preferred Embodiment of this Invention

25   Fig. 1 shows a continuous flow two-stage reactor
design which can be used for carrying out the process of
this invention. Pressurized feed material mixed with
oxidant, which mixture may be cold or preheated to some
intermediate temperature, is injected tangentially into
30   back-mixed reaction chamber 2 through pipe 1. The
incoming feed mixes with the hot, partially reacted fluid
in the chamber and begins to oxidize, liberating

sufficient heat to propagate the process as new feed continues to enter the chamber. The optimal chamber temperature depends on the particular feed material, but may for example be in the range of 375-750°C. The partially reacted process stream exits the chamber through pipe 3 and proceeds to the second stage, plug flow reactor 4, where reaction is brought to the desired level of completion, for example 99.99% destruction of the feed organic carbon. The second stage reactor will frequently operate in the range of 550-650°C, and may attain 750°C. The reacted process stream proceeds to cooldown and depressurization through pipe 5.

The "back mixing" chamber 2 of Fig. 1 may have many designs. For example, the feed and oxidant may have separate injection points, and be introduced coannularly or as opposing jets. Mixing may be stimulated by using a swirling nozzle, a spray nozzle or internal baffles identified as 2a in Fig. 1, jet entrainment, static or fluidized solids, an internal venturi, or directing the incoming flows at chamber walls. The position of the exit port may be altered as well. Likewise, reactor 4 of Fig. 1 may be other than a plug flow type. For example, some feeds contain or generate corrosive compounds such as hydrochloric or sulfuric acid, so that system components may require a corrosion resistant lining. A plug flow pipe reactor will have a relatively small inside diameter, and may be hundreds of feet in length. Installing a corrosion resistant liner in such a reactor, which would typically have numerous bends and connecting flanges, can be extremely expensive. For such wastes, a vessel reactor may be favored because of simpler liner design and, due to a much lower surface to volume ratio,

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considerably less liner material. The low surface to volume ratio of a vessel reactor has the further advantage of reducing heat loss to the environment. This feature can be of key importance in the second stage reactor, where only a minor fraction of the reaction and heat release occurs. A vessel reactor with internal baffles to guarantee sufficient residence time may prove useful in this regard, as it combines desirable features of both compact (vessel) and elongated (plug flow) reactor designs.

Fig. 2 shows the HTO apparatus which was used to demonstrate the present invention. The material to be oxidized is typically the feed material, but during system startup would be a clean fuel. It is supplied through line 10 to pump 12, which increases the fluid pressure to the system operating pressure of about 3000 psi. The high pressure fluid leaves the pump through line 14 and proceeds to line 26. Certain feeds, for example pure organic liquids, must typically be diluted with water in order to avoid excessive reactor temperatures. For this purpose, water is supplied through line 20 to pump 22, which increases its pressure to the system operating pressure. The high pressure water leaves the pump through line 24 and proceeds to line 26 to mix with the organic feed. The mixed stream is conducted through insulated tube 28 and injected in an axial direction through nozzle tip 52 into a back-mixed reactor chamber 54. To facilitate usage of preexisting equipment, chamber 54 is located within pressure vessel 50 and is thus pressure-balanced. The portion of the vessel 50 below chamber 54 is essentially isolated by the bottom plate 54a of the cylindrical chamber 54, and thus

is unused.   In actual commercial practice of this invention, use of a pressure-balanced chamber may prove useful for certain applications.   In other cases, however, chamber 54 would itself be the pressure vessel and an outer vessel 50 would not be necessary.

However, in all configurations or arrangements of mixing chambers, the entering fluid and oxygen are subjected to turbulent backmixing. For example, as shown in Fig. 2, the diameter and length of the back mixed reactor chamber 54 is designed such that the entering feed material is impacted off of the walls suchas 54a of the reactor and back-flow into the incoming feed and air to provide for turbulent mixing.

For startup purposes, water is supplied through line 30 to pump 32, which increases the fluid pressure to the system operating pressure.   Likewise, room air is supplied to compressor 42 through intake duct 40, and exits the compressor at system operating pressure through line 44.   The high pressure air mixes with the high pressure water from line 34, and proceeds to electrical heater 46.   The heater raises the temperature of the mixed stream to a suitable level, for example about 600°C.   The heated stream proceeds to nozzle tip 52 through internally or centrally mounted tube 48, the latter being disposed in an annular fashion around the insulated core tube 28.   Within the nozzle tip, the annular fluids mix with the feed from core tube 28 and are then injected into reaction chamber 54.   The residence time of the mixed fluids in the nozzle tip is on the order of 0.01 seconds, but this time may vary within the scope of this invention.   The use of the hot annular stream of air and water aids in sustaining

reaction until the system achieves full operating temperature. Once full operating temperature is achieved, pump 32 is typically shut off and the annulus fluid is comprised of the oxidant alone. Optionally, heater 46 may also be shut off, so that both the feed and oxidant are cold as they enter the reaction chamber 54. Finally, the supply to pump 12 is switched from startup fuel to the actual feed material.

Partially reacted fluid leaves chamber 54 through exit 56 and emanates into the annular head space 58 above the chamber, where temperature rapidly declines to about 300°C. Thus, reaction is quenched soon after the process stream leaves the chamber 54.

The single-phase fluid stream which exits head space 58 via line 60 passes through heat exchanger 62 to be cooled to near ambient temperature by exchange with cooling water. The cold cooling water enters the heat exchanger through line 64, while the warm cooling water leaves the heat exchanger through line 66. By virtue of the cooling, the process effluent which leaves the heat exchanger through line 70 is now comprised of separate gas and liquid phases. It has its pressure dropped from 3000 psi to about 1500 psi through control valve 72. The partially depressurized stream flows through line 74 to the medium pressure separator 80 which segregates the gas and liquid phases. The gas phase is comprised primarily of nitrogen, residual oxygen which was not consumed during the reaction, and some of the carbon dioxide which was produced by the reaction. It leaves the separator near the top through line 81, and has its pressure reduced to near ambient through back pressure regulator 82. The depressurized gas flows through lines 83 and 94,

at which point it is vented or sampled for analysis. The liquid leaves the medium pressure separator 80 from the bottom, passing through line 84 to the control valve 85 which drops the pressure to about 100 psi. This pressure reduction leads to the effervescence of most of the remaining carbon dioxide reaction product from the liquid phase. The low pressure gas/liquid stream flows through line 86 to the low pressure separator 90. The gas, primarily CO_2, leaves from the top of the separator through line 91, and has its pressure reduced to near ambient through back pressure regulator 92. The depressurized gas flows through lines 93 and 94, at which point it is vented or sampled for analysis. The liquid leaves the low pressure separator 90 from the bottom, passing through line 95 to the control valve 96 which drops the pressure to near ambient. The liquid, typically near-potable quality water, then flows through line 97 to be sampled or disposed of.

The system of Figure 2 was used in the experiments described in the following examples.

Example 1

In this test, the backmix chamber 54 was sized to provide a residence time of about 10 seconds at 600°C. The operating pressure was chosen as 3000 psig. Reaction chamber operation was monitored by 4 thermocouples which were placed either within the chamber or the exit port 56. Table 2 summarizes the feed materials treated, the operating conditions, and the results obtained. Various feed materials were treated in succession. The "Feed" column shows the feed flowrates, which were chosen to

give approximately equal rates of heat release for the
various feeds. The "Water" column shows the cold water
flowrate, chosen to dilute the feeds to give a final
reaction temperature of about 600°C. The "Air" column
shows the air flow to the reactor, approximately a 30%
stoichiometric excess. The "SCW" column shows that
supercritical water (SCW, pump 32 in Fig. 2) was turned
off for all cases shown. Heater 46 of Fig. 2 was kept
on, however, so that annular air temperatures were in the
range of 500-600°C. The "T,°C" column shows the primary
indicator of successful operation - the continued high
temperature within the chamber. Had reaction ceased,
this temperature would have dropped sharply within
seconds rather than remaining steady. For each feed, a
steady state operation was maintained for a period of at
least about 30 minutes. The "τ,sec" column shows actual
residence time τ calculated at the flowrates and reactor
operating temperatures shown in the table. The "CO,ppm"
column shows the carbon monoxide (CO) level in parts per
million volume as measured in the gaseous effluent (line
94 in Fig. 2). The CO levels compare favorably with
those obtained from common combustion processes such as
incineration or car engines (hundreds of ppm typically).
Many implementations of hydrothermal oxidation can
readily attain effluent CO levels of single ppms,
however. This could be achieved for the current
invention by using a second stage reactor after the back-
mixed chamber.

The "TOC,ppm" column shows the Total Organic Carbon
(TOC) analysis of the liquid effluent (line 97 in Fig.
2). The TOC Analyzer used in these studies utilizes the
potassium persulfate oxidation procedure, and has a

detection limit of 1 ppm (milligrams per liter). TOC was undetectable for the alcohol feeds, yielding a TOC-based destruction efficiency in excess of 99.99%. For the kerosene data point the TOC value also indicates

5   excellent destruction efficiency, however the system effluent contained a small amount of unreacted char. The TOC analysis was only carried out on the supernatant, after the char had settled out of solution. It is believed that the char formed in the nozzle tip, where

10 hot air contacted droplets of pure kerosene entrained in a cool water stream. While not shown in the table, it was found that addition of about 30 g/min of SCW via the annular flow eliminated the formation of char and gave essentially complete oxidation of kerosene. Long chain

15 alkanes such as kerosene may thus represent an instance where annular flow of SCW is desirable. It is also likely, however, that alternative feed introduction strategies could eliminate char formation in a more economical fashion. This might be done, for example, by

20 the use of cold rather than hot air in the annulus, a nozzle design which does not mix the annular and core flows before they enter the reaction chamber, or one which entrains some of the hot chamber fluid into the annular stream.

25   Despite the formation of char, the kerosene reaction was robust. At one point during this portion of the run, an erroneous control signal caused an automatic shutdown of the kerosene and cold water flows (pumps 12 and 22 in Fig. 2). Heater 46 was on to provide hot air, but SCW

30 (pump 32) was not being used, and reaction chamber temperatures rapidly declined to just above 500°C.

Kerosene and cold water were restarted, and reaction immediately resumed.

Table 2.   Backmix chamber with nominal 10 seconds residence time.

Feed	Flowrates, grams/min				T, °C	τ, sec	CO, ppm	TOC, ppm
	Feed	Water	Air	SCW				
Ethanol	8.3	50	94	0	588	9.1	54	<1
Isopropanol	7.9	52	94	0	602	8.6	38	<1
Methanol	15.0	51	94	0	599	8.9	33	<1
Kerosene	5.3	52	94	0	580	9.2	7	<1

Example 2

In this test, the backmix chamber 54 was sized to provide a residence time of about 3 seconds at 600°C. The operating pressure was chosen as 3400 psig. The apparatus and operation were otherwise the same as in the preceding example.

In the first portion of the test, the minimum SCW flow needed to avoid char formation with kerosene feed was investigated. With the annulus fluid (air plus SCW) temperature about 600°C, SCW was ramped down while feeding kerosene and cold water through the core tube 28. Table 3 shows a data point when the SCW flow was still relatively high and kerosene conversion was essentially complete. It was found that char formation began when SCW flow was reduced to somewhere between 10 to 20 g/min.

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The alcohols again showed high destruction efficiencies in excess of 99.99%, although in the case of isopropanol there was a detectable level of residual TOC. CO levels were significantly higher than for the 10 second residence time tests, but this data is not used in the destruction efficiency calculation. Acetic acid was also tested in this run, as it is one of the more refractory organics commonly encountered. While reaction was robust and self sustaining for the data point shown in the table, a significant TOC residual limited the destruction efficiency to 99.96%. Reduction of the effluent CO levels or TOC might be effected by a number of methods, including increased residence time or improved mixing in the reaction chamber or a second stage reactor such as 4 in Fig. 1 to obtain 99.99% destruction.

This run also tested the operability of the system with reduced annular air temperatures. For the second ethanol data point in Table 3, and for the isopropanol, methanol, and acetic acid, heater 46 had been shut off and the air temperature entering annulus 48 was below 100°C. The lowest annular temperature reached was 65°C during the acetic acid portion of the test, as this was the last segment to be run and heater 46 had cooled the most. Given the low heat capacity of air, this data point is believed to sufficiently demonstrate that the system can be operated satisfactorily on ambient temperature oxidant.

Table 3. Backmix chamber with nominal 3 seconds residence time.

Feed	Flowrates, grams/min				T, °C	τ, sec	CO, ppm	TOC, ppm
	Feed	Water	Air	SCW				
Kerosene	4.9	51	88	82	604	1.9	5	<1
Ethanol	7.9	50	94	0	614	3.0	190	<1
Ethanol	8.7	55	94	0	581	3.0	220	<1
Isopropanol	9.4	55	94	0	581	3.1	220	4
Methanol	12.7	50	94	0	576	2.7	210	<1
Acetic Acid	16.8	45	94	0	604	3.3	60	44

Discussion of the Invention

The present invention is similar to U.S. Pat. No. 4,822,497 in that immediate backmixing of hot, partially reacted fluid is used to propagate the oxidation reaction. That patent is directed towards handling feed streams which contain or generate substantial amounts of sticky solids, and seeks to minimize impingement of the process stream on reactor walls or internal parts. As stated within the patent, "any significant constriction" in the path of the fluid flow within the reactor must be avoided. In practicing the patent, it has been found that the residence time for the hot fluid must typically be at least 30 to 60 seconds, with additional reactor volume required for the brine zone. Furthermore, injection of feeds into the reactor at high velocities, for example more than about 15 feet per second, yields

high mixing rates within the vessel and the undesirable side effect of high levels of solids accumulation on the reactor walls.

The present invention, by contrast, can accomodate only minor amounts of sticky solids, but since the feeds which are part of this invention do not cause substantial amounts of "sticky" solids (which are, by definition, solids which precipitate and adhere to the wall of the reactor), there is no longer need to minimize process fluid impingement on the reactor wall or other surfaces. Non-sticky feeds are feeds which do not generate substantial amounts of sticky solids during oxidation, or only non-sticky solids, such as oxide solids. Also, feeds which generate a combination of salts and non-sticky solids may be utilized but those particular feeds must be tested. Limiting this invention to non-sticky feeds makes possible the vigorous mixing of newly introduced feed with the existing reactor contents by various means, and utilizes much smaller reactors than the reactors disclosed in U.S. Patent No. 4,822,497. As shown by the preceding examples, residence times of less than 10 seconds should be sufficient for many types of feed. The required residence time may vary with different feeds or operating temperatures, however. Residence time of up to about 30 seconds is expected to be useful. A particular advantage of the invention is that it does not require the use of a heat exchanger, and thus can treat relatively concentrated feeds.

Example 3

Table 4 shows representative reactor sizes useful in practicing the present invention at different scales of

operation. The reactor is assumed to operate at 600°C
with a 10 second residence time. The waste being
processed has sufficient fuel value to raise its own
temperature from ambient to 600°C, i.e., it is autogenic.
5   The oxidant is assumed to be air, and oxidation kinetics
are assumed to be unaffected by operating pressure.
Reactor sizing is carried out to obtain a sufficient
combination of residence time and operating temperature
to attain the desired degree of oxidation. For example,
10   operating temperatures below 600°C may require larger
reactor volumes (longer residence times), while use of
pure oxygen as the oxidant will allow a reduction in
reactor size. Feeds which are subautogenic may be
preheated to facilitate usage of the present invention.
15   In this case, the oxidant requirement is lower and the
reactor may be smaller in size.

Table 4. Representative Reactor Sizes in Gallons

Residence time = 10 seconds, autogenic waste, air oxidant
20   Operating temperature = 600°C

Waste	Operating Pressure				
Throughput, gpd	1000 psi	2000 psi	3000 psi	4000 psi	5000 psi
5,000	68	34	23	17	14
20,000	270	135	90	68	54
100,000	1350	675	450	338	270

While the illustrative examples of the invention have
been described with particularity, it will be understood
30   that various other modifications will be apparent to and
can readily be made by those skilled in the art without

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departing from the scope and spirit of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein.

For example, this invention may be used in conjunction with U.S. Pat. No. 5,232,604, which teaches chemical methods for facilitating reaction initiation.

PCT/US96/12228

IPEA/US 18 JUN 1997

What is claimed is:

1.   A process for continuous oxidation in a reactor, the process

3   comprising the steps of:

(a)   providing a feedstock of oxidizable material to the

reactor;

6   (b)   providing an oxidant simultaneously with the feedstock to

the reactor; and

(c)   turbulently mixing the feedstock and oxidant with the

9   contents of the reactor by directly and deliberately impinging the

feedstock and oxidant upon at least one solid surface within the

reactor, at temperatures between about 375°C and 750°C and

12   pressures between about 25 and 1000 bar, to accomplish substantial

oxidation of the feedstock within the reactor in a period of less than

about ten seconds.

2.   The process of claim 1 wherein the step of turbulently mixing is

sufficiently vigorous so that the feedstock in the reactor is substantially

3   oxidized in a period of less than about five seconds.

3.   The process of claim 1 comprising the step of transferring a

fluid stream from the reactor to a second stage reactor to obtain additional

3   oxidation.

4.   The process of claim 1, further comprising the step of

transferring a fluid stream from the reactor to a second stage reactor for

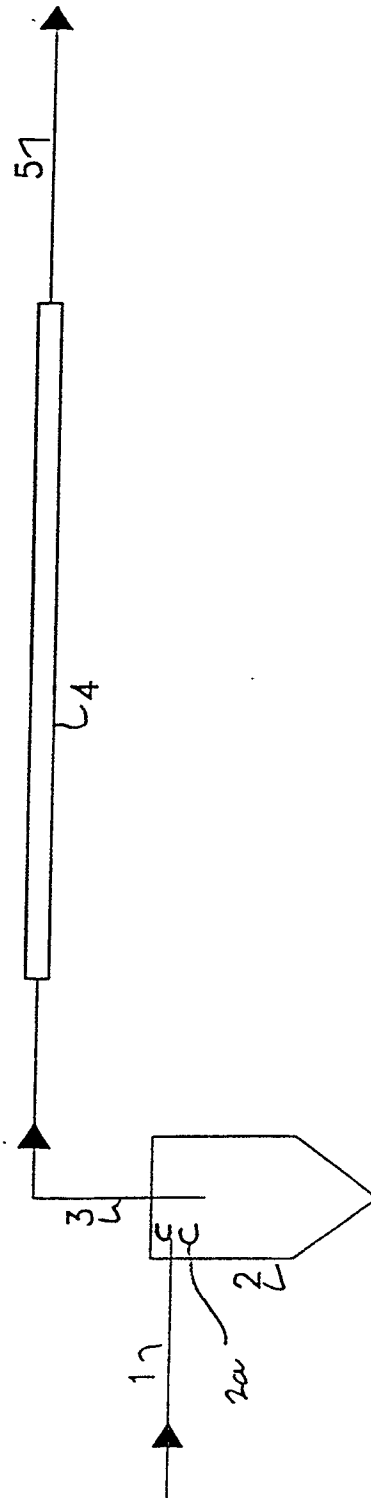3   additional oxidation at temperatures above 375°C.

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AMENDED SHEET

FIGURE 1

FIGURE 2