SUPERCRITICAL FLUID TECHNOLOGIES WITHIN CHEMATUR ENGINEERING AB

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Abstract

The Chematur Engineering group of companies is presented, briefly describing the business areas within the group. Activities in the field of supercritical fluids are given. The range of equipment as well as applications for supercritical carbon dioxide and supercritical water oxidation are presented. The Chematur Engineering demonstration plant for SCWO is described in detail and results from some performed treatability studies are given, including de-inking sludge and sewage sludge. The results clearly show that SCWO is a very effective method for treatment of sludge.

Introduction

The Chematur Engineering Group is a group of companies delivering process plants to the chemical industry based on proprietary as well as licensed technologies. The group is headquartered in Karlskoga, Sweden with subsidiaries in Finland (Chematur Ecoplanning), Sweden (Electrocell & Supercritical Fluid Technology Sweden) and USA (Weatherly).

Production plants for the following technologies are offered by the group:

- Explosives & Propellants
- Nitric Acid
- Fertilizers
- Isocyanates (TDI, MDI)
- Nitroaromatics
- Ethanol and its derivatives
- Hydrogen peroxide
- Acid concentration and recovery systems
- Evaporation & Crystallisation
- Electrochemistry
- Supercritical Fluids

The Supercritical Fluids business area is rapidly expanding and the area where most of the development resources are used. There are two key thrust technologies in this area. The first is the use of supercritical fluids to enhance reactions and separations. The current emphasis is on using supercritical carbon dioxide (scCO2).

With respect to scCO2 there is a range of units, from the pilot unit with a flow capacity of 50 kg/h up to large units with a CO_2 flow of 10 ton/h. All units are as standard designed for a max. pressure of 500 bar. Applications include environmentally friendly degreasing of metal parts, the Rotowasher™, extraction of nutraceutical extract from e.g. herbs, the Xtractor™ series, and the use of scCO2 as solvent for carrying out chemical reactions, the Swan SCF™ unit (1). The Swan SCF multi purpose unit is the first of its kind that has been built and it offers true continuous production of fine and speciality chemicals on a large scale. The client, Thomas Swan & Co., is targeting areas like hydrogenation, acid catalysed reactions and hydroformylation. The engineering was very challenging with design pressure and temperature at 500 bar and 200 °C.

Figure 1 scCO2 Pilot plant, Xtractor™ 500/50

Figure 2 Swan SCF™ chemical reaction system

Figure 3 Xtractor™ 500/1000, 1000 kg/h, 500 bar scCO2 extraction plant

Figure 1 shows the multipurpose pilot unit, figure 2 shows the novel continuous reaction plant installed at Thomas Swan & Co, UK and figure 3 a production plant for aromas extraction.

The Rotowasher unit, similar in appearance to the Xtractor 500/50 unit, features a revolutionary rotating cleaning basket to enhance mass transport and cleaning performance. It has been in successful operation at Viking Sewing Machines, Huskvarna, Sweden since 1999, cleaning small sintered metal parts (2,3).

The second thrust area and currently where the largest effort is being expended is in Supercritical Water Oxidation (SCWO). A state of the art demonstration plant has been built in Karlskoga, Sweden. Chematur Engineering has made every attempt to construct the demonstration plant in the same way as a commercial scale plant would be constructed. This enables Chematur to gain experience regarding the best engineering solutions, taking into consideration all the key aspects such as corrosion, fouling, strength of construction material, manufacturing and permitting.

Supercritical water oxidation

To achieve a sustainable society, future pollution control must include the concept of complete destruction of toxic substances and sludges. Two options exist for the complete destruction of toxic or persistent substances in wastewaters and organic sludges. These two options are incineration and supercritical water oxidation.

SCWO has proven to be a very promising method for many different wastewaters and sludges. SCWO utilises the unique features of water in its supercritical state (SCW), above 221 bar and 374 °C. SCW is, contrary to normal water, totally miscible with organic substances and gases. This feature eliminates all mass transport limitations and together with the relatively high temperature of the process, 400-600 °C, it ensures rapid and complete reactions. A destruction efficiency of 99.9 % or better is typically achieved in about one minute reaction time. All substances are destroyed irrespectively of their structure and in fact it has been reported (4) that SCWO destroys dioxins found in fly ashes from conventional incineration. Furthermore, no NO_x or SO_x is formed so there is no effluent gas cleaning requirements. As a matter of fact there is not even a chimney as effluent gas is released at close to ambient conditions. Finally, the process is normally autothermal and heat of oxidation can be recovered in an effective way even in quite diluted systems, containing as much as 90 to 95 % water.

Chematur Engineering expanded its activities in the field of environmental protection in 1995 with a license agreement for SCWO, signed with Eco Waste Technologies (EWT). In 1999 Chematur acquired the EWT technology on a world-wide basis. Chematur is now a world leader in this field and the Chematur SCWO process is marketed under the trade names Aqua Critox®, Aqua Reci™ and AquaCat®.

In early 1998 Chematur inaugurated its 250 kg/h SCWO demonstration facility and since then several successful treatability tests have been performed. The Chematur demonstration unit is built as a tool for commercialising the technology, by showing potential users that this method is applicable for their wastes. During these demonstration runs several successful and extensive treatability tests with actual wastes have been performed.

The demonstration plant

A simplified flow sheet of the plant is shown in figure 4. The bottom outlet from the feed tank is connected to a grinder pump. This eliminates the risk of big particles entering the high-pressure pump. It also provides mixing of the wastewater by means of a recirculation loop. The plant is equipped with two different high pressure feed pumps, one for clear liquids and one for dispersions and sludges. The high pressure feed pumps raise the feed pressure to about 250 bar and pumps the feed through the SCWO system.

The feed enters the tube side of a double-pipe economiser where it is preheated by the reactor effluent. After leaving the economiser, the feed enters the heater.

From the heater outlet, the hot feed enters the reactor. In the reactor, oxygen is injected to start the oxidation reaction. The oxidation reaction generates heat and, as a result, the reactor temperature increases. In some cases, the inlet feed concentration may be too high for complete oxidation of the organic material to occur in one step without exceeding the reactor's design temperature, 600 ºC. In these cases the waste may be oxidised in two stages, using a proprietary and patented method. At the beginning of the second stage, quench water is added with the oxygen. The water cools the effluent from the previous stage enough to allow the additional oxygen to continue the oxidation reaction without exceeding the temperature limit.

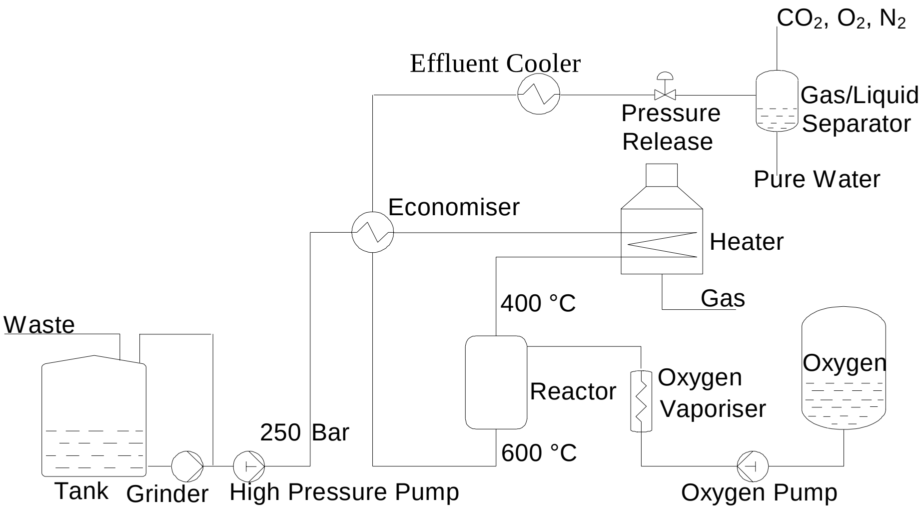

Figure 4 Simplified flow schema of the pilot plant

After passing through the reactor, the effluent flows through the economiser, outer tube, where it preheats the incoming feed. The effluent is cooled to its final exit temperature in the effluent cooler prior to passing through the pressure release system. The pressure release is done in a proprietary and patented system using a series of capillary coils and choke water addition upstream of the coils to control system pressure. The effluent then enters a gas/liquid separator where the carbon dioxide generated in the process is separated from the effluent.

Treatability tests

De-inking Sludge

When recycling paper, de-inking sludge is formed as a by-product. This sludge contains about 3% organic material, mainly fibres, and 3% inorganic material, mainly paper filler. The ability of SCWO to completely destroy the organics in this sludge has been proven elsewhere (5,6). In addition to destruction of the organic matter, the industry has an interest in recycling the paper filler after the SCWO treatment.

A lot of experiments has been performed in cooperation with Stora Enso research and Stora Hylte (7,8). After fine-tuning the reaction conditions, very bright paper filler was recovered from the process. The brightness of this paper filler was close to the value of virgin material, figure 5. According to representatives from the paper industry it can easily be recycled to the paper mill. Several long-term tests have been performed and the recycling of recovered paper-filler has been successfully tested in a full scale paper machine at the Hylte mill.

Figure 5 Feed de-inking sludge and effluent after SCWO treatment

Sewage sludge

A detailed description of the use of the Aqua Critox® process for destruction of sewage sludge and results achieved have been described elsewhere (9,10). This paper is giving a brief summary of achievements to date with focus on the Aqua Reci™ process, a joint development with Feralco AB. The Aqua Reci process is treating sewage sludge by SCWO but offers in addition the recovery and recycling of valuable inorganic components from the effluent stream. This concept was verified in a 100 h test conducted for the major Sewage Treatment Works operators in the Greater Stockholm area, Stockholm Vatten, Käppalaförbundet and SYVAB. The result of this work has been reported (in Swedish), spring 2003, Aqua Reci, Etapp 1, R nr 12 – 2003.

A simplified flow scheme of the Aqua Reci process is shown in figure 6.

The Aqua Reci process offers complete oxidation of organic material in sewage sludge, without formation of hazardous by-products such as NO_x and dioxins, hence, no need for expensive effluent gas cleaning equipment. The process works auto-thermally at low dry solids (DS) content in the sludge, eliminating the need for expensive dewatering and

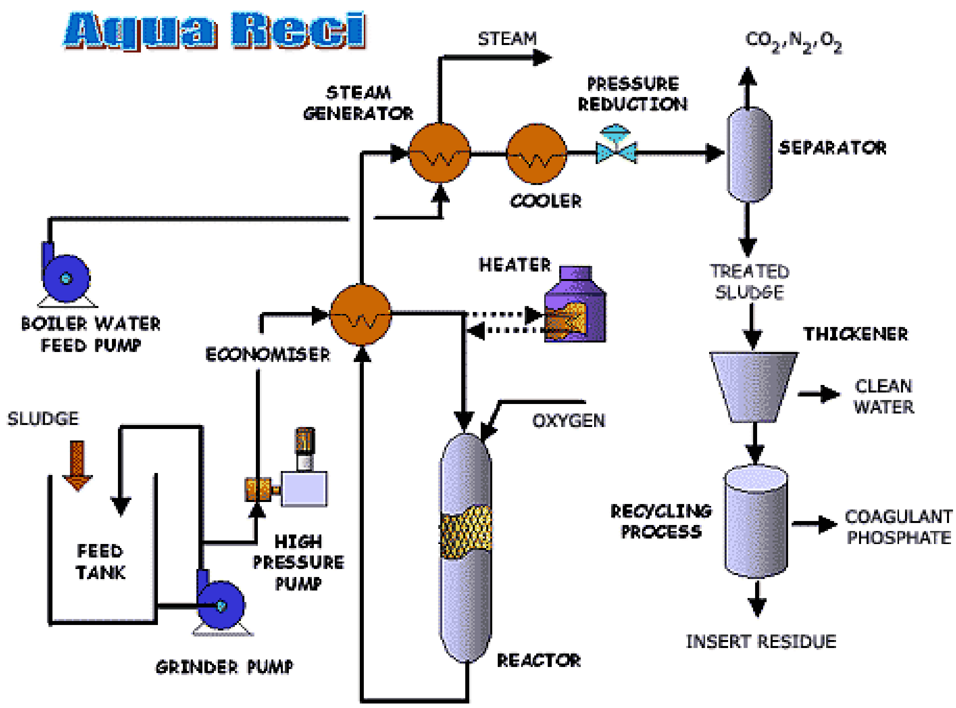

Figure 6 Simplified flow scheme of the Aqua Reci™ process

drying equipment. Optimum DS content of feed sludge is about 15-20 %. The heat of oxidation can easily be recovered and made into useful energy, e.g. district heating.

Because of the high efficiency and the relatively low process temperature, the inert solid residue after treatment is very pure and reactive. By dissolution it in acid followed by careful pH adjustments, the valuables (Fe, P and Al) can be recovered in pure fractions. Finally the heavy metals can be precipitated, leaving only a minute amount of solid residue consisting mainly of inert silica. Figure 7 shows the appearance of feed sludge and effluent from the SCWO process before and after filtration.

Figure 7 Feed sewage sludge, effluent from SCWO process and decanted water phase

Spent Precious Metal Catalysts

In cooperation with Johnson Matthey, Chematur has developed a special application of the SCWO technology, the AquaCat® process (11). Using this process, spent catalysts containing valuable metals, such as palladium and platinum, can be treated to destroy the combustible material, leaving the precious metals as an oxide precipitate in the clean effluent water. Figure 8 shows a simplified flow scheme of the process.

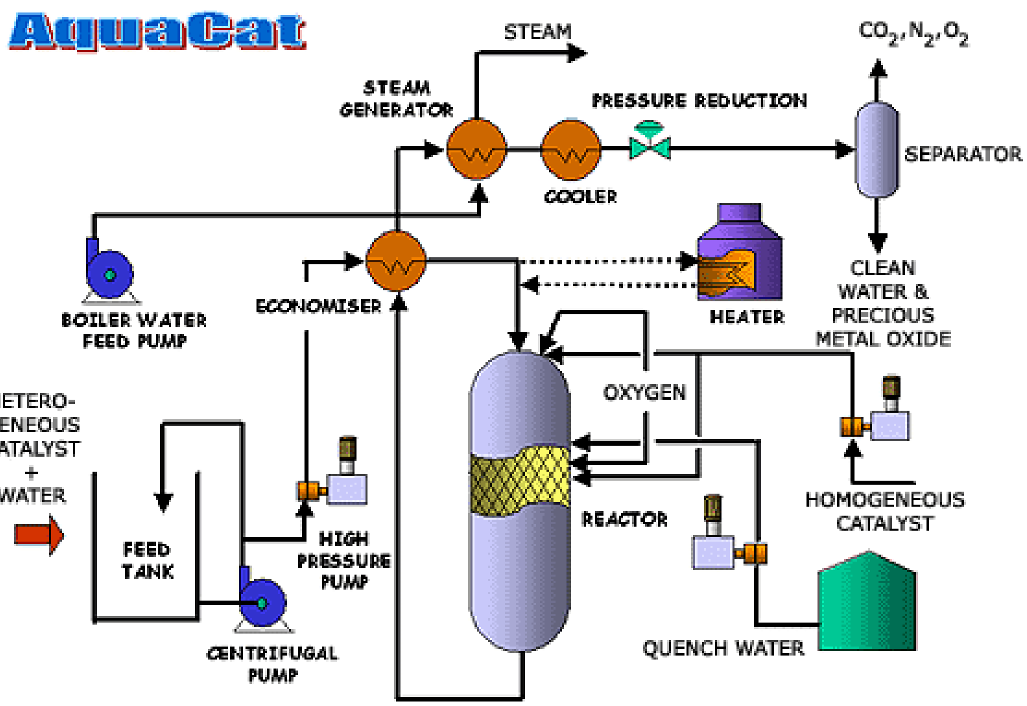

Figure 8 Flow scheme of the AquaCat® process

The process can handle both heterogeneous and homogeneous spent catalysts. The first type is slurried in water and introduced into the system like sludge, with the main feed pump. For homogeneous catalysts a novel direct injection route has been developed. Concentrated spent catalyst is injected into supercritical water pre-charged with oxygen through a nozzle.

A commercial scale plant has been constructed at Johnson Matthey's Brimsdown site, just north of London. This plant is the first commercial SCWO application in Europe and the capacity, 3 m^3/h, makes it the largest SCWO plant in the world. The plant is now in successful operation.

Conclusions

The presented studies of waste treatment with SCWO, performed on a state of the art demonstration plant, show that the SCWO technology is ready for a commercialisation, not only for clear organic wastes but also for treatment of organic sludges. For waste such as de-inking sludge, SCWO treatment offers, besides an extremely clean effluent, the possibility to recover valuable inorganic compounds that can be recycled to the manufacturing process.

The use of scCO2 technology offers environmentally friendly solutions in many cases and, in the case of a chemical reaction system, also the ability to perform chemical reactions with higher yield and selectivity than can be achieved in conventional processes.

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