Supercritical Water Oxidation (SCWO) for Poly(ethylene terephthalate) (PET) Industry Effluents

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Supercritical water oxidation (SCWO) provides high destruction efficiencies for a wide variety of hazardous wastes at low reactor residence times. This paper studies the feasibility of the SCWO process for the treatment of the esterification wastewater from the poly(ethylene terephthalate) (PET) industry, for which the major contaminant product is ethylene glycol. Both the feed and the liquid-phase product were analyzed in terms of total organic carbon (TOC) to determine the efficiency of the process. Effluent from the PET industry contained 16000 mg/L TOC, equivalent to 4 wt % ethylene glycol. Experiments were carried out in a pilot plant equipped with a pressure shell and a cooled-wall reactor. The effects of temperature and oxidant concentration on removal efficiency were investigated. Tests were performed in the range of 550−750 °C at a pressure of 23×10^6 Pa. Results showed elimination efficiencies of up to 99.9% at 630 °C and residence times of less than 50 s. The scale-up of this plant has been simulated using the software Aspen Plus.

Introduction

Complete biochemical or chemical oxidation to carbon dioxide and water is the most common alternative for removal of organic compounds from wastewater. Biotreatment of industrial and hazardous wastes is limited to nontoxic and biodegradable compounds. Chemical oxidation of wastewater can be employed to oxidize pollutants to terminal end products or to intermediate products that are more readily biodegradable or removable by physical processes. Common oxidants are chlorine, ozone, hydrogen peroxide, and potassium permanganate. Conventional oxidation processes for aqueous mixtures and/or solutions are carried out at slightly high pressure and temperature with the purpose of keeping the oxidant in the liquid phase. This process, known as wet oxidation, does not achieve sufficient efficiency to allow direct emission of the effluent, and a subsequent treatment process is generally required.

Because of the unique physical-chemical properties of water above its critical point (374.2 °C and 22.1×10^6 Pa), supercritical water (SCW) is an effective reaction medium for oxidation of organic compounds. In the region near the critical point, water properties change rapidly with both temperature and pressure. Gases are miscible in SCW, and the main limiting factor of wet oxidation disappears. Moreover, nonpolar organic compounds that are barely soluble in water at STP conditions are completely miscible with SCW. Therefore, oxygen and waste can come into intimate contact in a homogeneous phase without interface transport constraints and with reasonably fast kinetics, and the oxidation can proceed rapidly to completion.[1,2]

High destruction efficiencies can be achieved at low reactor residence times working at $T > 374$ °C and $P > 22.1 \times 10^6$ Pa, so that the reaction products are basically carbon dioxide, water, and nitrogen. In addition, the reactions that take place are exothermic, and depending on the nature and concentration of the hazardous chemicals and the design of the process, excess heat might be used for process heating or for cogeneration of electricity.[3] Therefore, the SCWO process can be considered as an attractive technology for the treatment of a wide range of wastes containing oxidizable components.

Poly(ethylene terephthalate) (PET) has an increasing commercial importance. In addition to the more traditional polyester fiber production, PET is taking the place of poly(vinyl chloride) (PVC) in many applications, mainly in bottles for spring water. The process using direct esterification of terephthalic acid (TPA) with ethylene glycol has gained acceptance because of the greater availability of highly purified TPA.[4]

Esterification wastewater will mainly be composed of unreacted raw materials, mainly ethylene glycol, and products of secondary or degradation reactions, with terephthalic acid esters, methanol, acetaldehyde, and crotonaldehyde being the most significant.[5,6]

Because of the high TOC concentration, anaerobic treatment seems to be the best available technology for the biological treatment of PET wastewater. The excellent review of Macarie[7] (1999) shows that at least nine PET producers use anaerobic technology, mainly Up-flow Anaerobic Sludge Bed (UASB), Expanded Granular Sludge Bed (EGSB), or hybrid reactors. The applied organic loading rate ranges from 1 to 18 kg COD/(m^3 d), with an average value of 8 kg COD/(m^3 d).

According to PET manufacturers, the typical wastewater is a clear liquid with average values of COD = 27000 mg/L; TOC = 8400 mg/L; BOD_5 = 19700 mg/L; and TSS, N-TKN, $N-NH_4^+$, and $P-PO_4^{-3}$ < 1 mg/L. The ratio BOD_5/COD clearly indicates the biodegradability of the wastewater, thus allowing for biological treatment. The deficiency of macronutrients (N and P) is obvious.[8] Nevertheless, a significant portion is not easily biodegradable, and a subsequent treatment is

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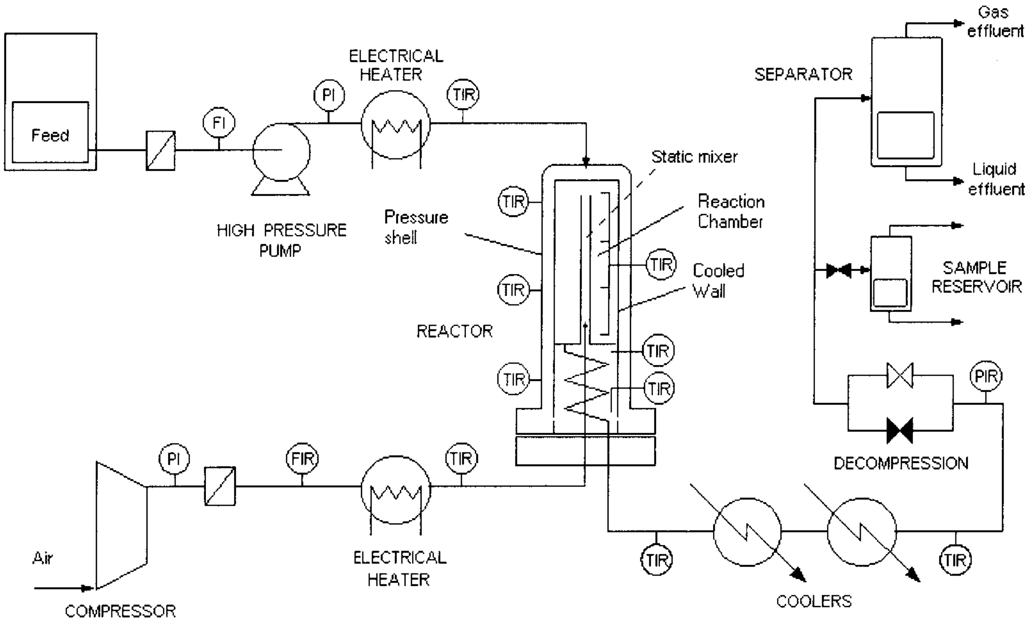

Figure 1. SCWO pilot plant flowsheet. FI = flow indicator, PI = pressure indicator, FIR = flow indicator register, PIR = pressure indicator register, and TIR = temperature indicator register.

necessary. In that sense, SCWO provides the possibility of achieving nearly total contaminant destruction.

The aim of this paper is to study (i) the viability of the SCWO process for treating wastewater from PET manufacturing processes; (ii) the main operating conditions *T*, *P*, and the oxidant ratio; (iii) scale-up to an industrial treatment plant with SCWO technology; and (iv) mass and energy balances.

Experimental Section

Plant Description. The SCWO pilot plant was developed in the Chemical Engineering Department of the University of Valladolid, Spain.[9] It is a continuous-flow plant with a treatment capacity up to 45 kg/h of water, and it uses air as the oxidant. In these experiments, the operating conditions were pressure 25×10^6 Pa, temperatures of 550−750 °C, and residence times ranging from 40 to 100 seconds.

The basic flowsheet is shown in Figure 1. The major components of the plant comprise a feed tank, a high-pressure feed pump, a high-pressure air compressor, preheaters, a reactor, a cooling system, a back-pressure regulator, a gas−liquid separator, and the sampling ports.

The reactor design was developed in the Chemical Engineering Department at the University of Valladolid (Spain).[10] The aim of this reactor was to reduce the cost of such equipment by reducing the amount of high-cost materials that are necessary to withstand the high-pressure oxidant atmosphere during the reaction. Two concentric tubes compose the reactor; the inner one is made of Inconel 625, and the outer shell is made of SS 316. The oxidation reaction takes place inside the inner tube (reaction chamber). In the gap between the tubes, the pressurized feedstream moves downward, cooling the reaction medium and heating itself at the same time. In such way, the inner tube does not withstand any pressure at all, having the same pressure on one side as on the other, and the thickness of the inner tube (Inconel 625) can be reduced. The reaction chamber has a volume of 14.3 L, and because it is filled with alumina spheres of 4-mm diameter, the effective volume of reaction is 5.4 L. (The void volume was estimated by adding a known volume of water to a known volume of dry packed material. By measuring the volume taken up by the water, a void fraction of 0. 38 was obtained.)

A piston metering pump (Dosapro, model Milton Royal C) is used to pressurize the feed solution.

The air, which is used as the oxidant in the oxidation reaction, is compressed to the operation pressure by a four-stage compressor (Ingersoll-Rand H15T4), inter-cooled by air. Both streams are mixed in a static mixer inside the reaction chamber, as shown in Figure 1. During the start-up periods, two electrical heaters (3.9 kW each of them) can be used to preheat the feedstream and the air to the target operating conditions and then switched off when the desired temperature is reached. In the steady state, the feed stream is preheated while it falls down along the wall of the reaction chamber.

The effluent reactor is cooled in two heat exchangers, where a tap water stream is used as the cooling medium.

The cooled effluent is then passed through the back-pressure regulating valve, where the pressure is reduced to almost atmospheric pressure. This effluent is finally flowed to the gas−liquid separator, where the gas phase is sampled or directly vented. Liquid samples are collected from a sample port located in the effluent line from the gas−liquid separator.

Temperature is measured in the feedstream, and air and effluent streams. In the reaction chamber, there are four thermocouples (type K Inconel 625) at different heights in order to identify the temperature profile, and three more are located in the outer wall of the reactor. The time progress of these data, together with the pressure, is recorded by a PC computer for their later study.

Plant Operation. The real wastewater from Catalana de Polimers (Spain) used in the experiments had a concentration of 16000 mg TOC/L, equivalent to 4 wt % ethylene glycol. A flow rate of 30−35 kg/h was brought to operating pressure (about 23×10^6 Pa) by means of the piston pump. Air flow rates in the range of 30−34 kg/h were used in order to study the effect of

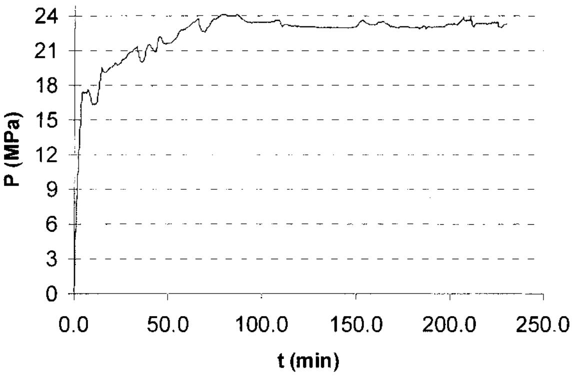

Figure 2. Typical pressure evolution during pilot plant operation.

the amount of oxygen. Experiments were carried out within the supercritical zone, at a nearly constant pressure of 23 × 10^6 Pa. The typical pressure evolution during pilot plant operation is shown in Figure 2.

Analytical Techniques. The total organic carbon (TOC) contents of the liquid product and the feed streams were determined in order to evaluate the destruction efficiency (TOC Analyser 5050, Shimadzu). The oxidation efficiency is evaluated as a percentage of total organic carbon removal.

In addition, liquid samples were analyzed by GC with a Hewlett-Packard 5890 chromatograph in order to determine the existence of intermediate oxidation products, using an INNOWax capillary (for ethylene glycol) and using Supelco 10% SP1000 + 1% H3PO4 (for organic acids) by FID.

The gas phase was analyzed for CO and CH_4 by GC with a Hewlett-Packard 6890 chromatograph using a Porapak N 80/100 sorbent sample tube and molecular sieve 13 × 45/60 adsorbent by TCD.

Results and Discussion

This section includes a discussion of the selection of the main operating conditions, as well as an explanation about the carbon balance to support TOC elimination. A scaled-up plant simulated by Aspen Plus is also described in the present section.

Operating Conditions. The effects of pressure, temperature, oxidant amount, and residence time on the SCWO process were studied in the plant.

Pressure. The effect of pressure has been deeply studied at the pilot plant for several compounds: isopropyl alcohol, ethylene glycol, phenol, acetonitrile, ammonia, pyridine, aniline, etc. Experiments were developed in two different pressure ranges, 25−27 × 10^6 Pa and 23−25 × 10^6 Pa, with TOC destruction over 99.9% obtained in all cases. These results confirm that the effect of pressure on TOC removal efficiency is almost negligible, in agreement with Gloyna and Li.[11] Consequently, a pressure of 23 × 10^6 Pa was selected for test performance.

Temperature and Residence Time. The main feature of this pilot plant is the autothermal operation, using the oxidation energy released in the reaction to heat the feedstream from room temperature to reaction temperature. Therefore, reaction temperature is strongly dependent on the organic matter feedstream concentration. The original wastewater from the PET industry contained 16000 mg TOC/L. With this concentration, the reaction temperature reached in the plant was 450 °C, but this temperature was not high enough to provide nearly total TOC destruction. To achieve higher values of reaction temperature, the enthalpic content of the feed was increased by addition of ethylene glycol. The effect of temperature was studied in the range of 550−750 °C using stoichiometric amounts of air. Under these conditions, the effluent leaves the reactor at a temperature above 300 °C in every case. (Figure 4). In the steady-state operation of the plant, this effluent can be used to preheat the feed up to a temperature that guarantees a high reaction temperature, whereas ethylene glycol would only be added to the feed during the start-up period. Preheating the feed stream at a specific temperature allows us to reach high reaction efficiencies without adding organic matter to the feed.

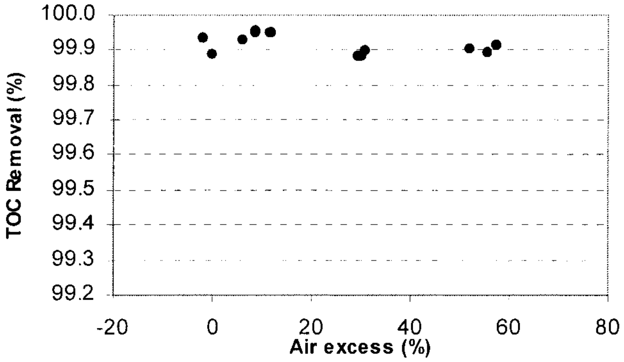

Figure 3. Effect of air excess on TOC removal. Reaction temperature = 635 °C.

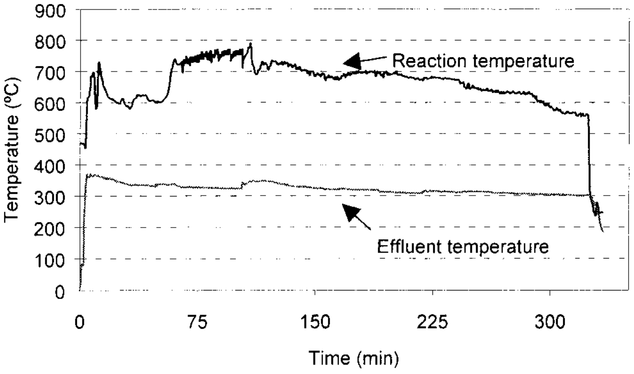

Figure 4. Time evolution of reaction temperature and effluent temperature during one experiment.

Experiments were performed at residence times below 1 min, which is typical for this kind of oxidation because of the speed of the reaction. Experiments employed 30−35 kg/h of liquid feed with a TOC content of 55000−62000 mg/L [15−17% (wt) ethylene glycol] and 30−34 kg/h of air, leading to a residence time of 50 s.

Residual organic compounds were analyzed by GC. Results showed that the remaining TOC was due to unreacted ethylene glycol. No acetic acid was found in the effluent.

Figure 5 shows the dependence of TOC removal on reaction temperature. TOC removal was nearly constant at around 99.9% for temperatures exceeding 630 °C.

Oxidant Amount. Assuming that only oxidation takes place, the minimum amount of oxygen necessary for complete oxidation of the organic matter can be calculated with regard to the COD of the feed.

Nevertheless, experiments were performed with different air flow rates and constant reaction temperature, to study the effect of oxidant concentration.

Air excess was varied from stoichiometric concentration (5.8 kg/h of oxygen for a flow of wastewater of about

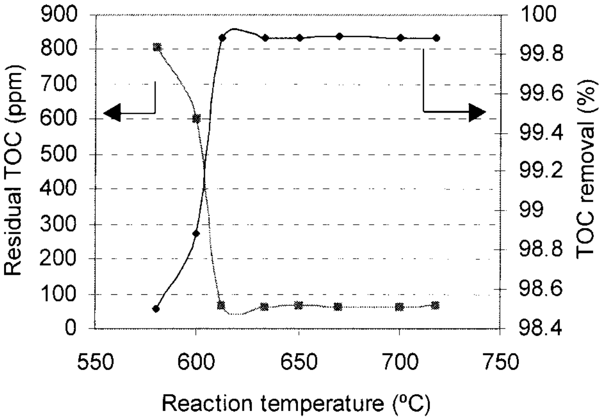

Figure 5. Effect of temperature on removal efficiency. Residence time of 50 s, Co = 54000 ppm TOC.

30 kg/h containing 55000 ppm of ethylene glycol) to 60% excess, and no dependence on the amount of oxidant was detected. As shown in Figure 3, TOC removal was always more than 99.9%, even at low air excess. Similar results for air excess were found in the elimination of a large number of compounds.[12,13]

From all of these experiments, it can be established that the stoichiometric amount of oxygen is enough to reach the highest efficiency level for the PET wastewater.

Carbon Mass Balance. The wastewater feed containing about 55000 mg/L of TOC (15 wt % ethylene glycol) is oxidized at the pilot plant, reaching a destruction of over 99.9% (residual TOC = 54 mg/L). Both liquid and gaseous effluents were analyzed to determine their composition. Only ethylene glycol was present in the liquid effluent; neither acetic acid nor propionic acid were found. The gaseous effluent composition varies depending on whether the plant is operating with a deficit of oxidant or at the stoichiometric rate. With a deficit of oxygen, CO and CH_4 were detected in the effluent. However, CO_2 and H_2O were the only compounds detected when operating at stoichiometric and greater oxygen amounts. Carbon mass balance is complete with an error of under 0.1%.

Flowsheet Simulation. Once the technology has been validated for this type of wastewater, the scale-up to an industrial SCWO plant has been done by a flowsheet simulation using the software Aspen Plus (Figure 6).

There are three sections in the plant, as follows:

Pretreatment. A representative feedstream of 5000 kg/h containing 4 wt % ethylene glycol was used in the simulation. This stream is pressurized to the operating pressure in a piston pump, and it then crosses a preheater to reach supercritical temperature. The air, which is used as the oxidant agent in the oxidation reaction, is compressed to the operating pressure in a four-stage compressor with intercoolers between two consecutive stages.

Mixing and Reaction. Both streams are mixed in a static mixer inside the reaction chamber, as shown in Figure 1. Reaction takes place in the reaction chamber of the cooled-wall reactor, reaching temperatures of about 650 °C for total conversion of reactants.

Separation and Conditioning of Effluents. The effluent that leaves the reactor splits in two fractions at a ratio of $^{5}/_{6}$ to $^{1}/_{6}$. The major fraction, stream (3) in the flow diagram, enters the preheater as a hot fluid, heating the feed aqueous stream. Gases undergo a partial condensation because the temperature drops to 44 °C, so that a gas stream (10) and a stream of condensate (14) are obtained. The gas stream (10) enters a gas–liquid separator (Flash), where a gas stream (15) and a liquid stream (17) are obtained. The latter joins the stream of condensate (14), generating a new stream (19) that expands through a series of reducing pressure valves, and then enters another gas–liquid separator (Flash). Two streams leave this unit: a liquid effluent

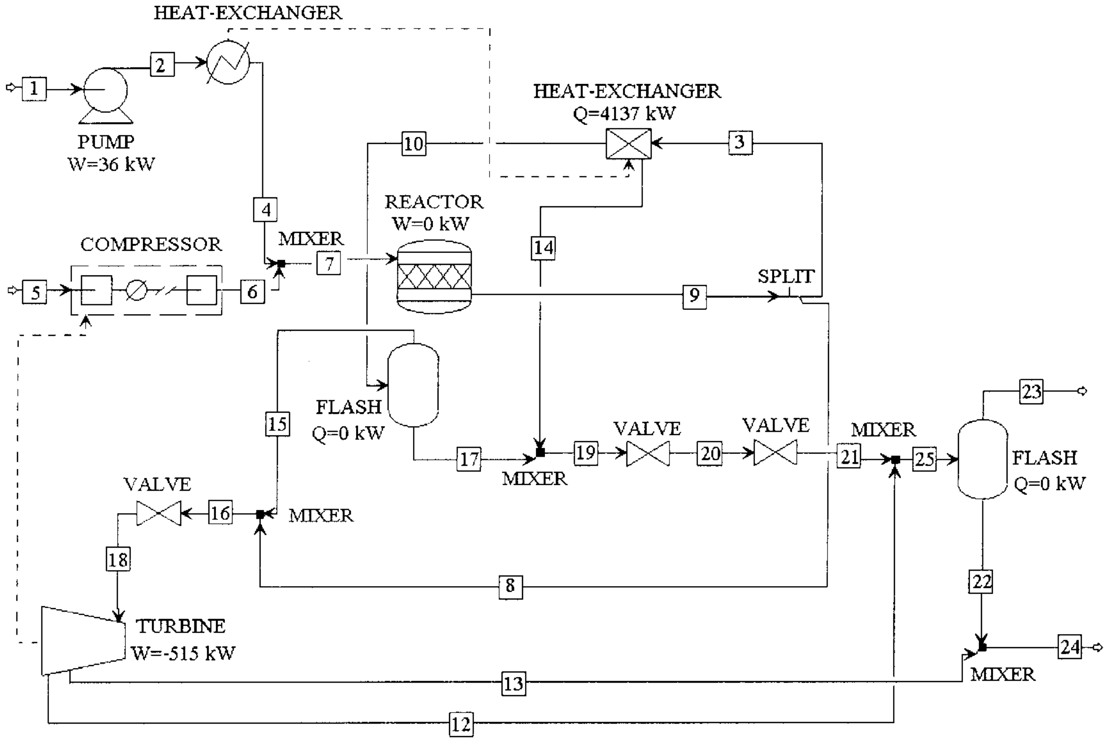

Figure 6. Flowsheet simulation for SCWO full plant.

Table 1. Detailed Mass Flow and Conditions of the Main Streams of the Simulation

stream number	1	4	5	6	7	9	16	18
temperature (°C)	25.0	470.0	25.0	213.2	433.3	653.2	448.8	442.7
pressure (MPa)	0.101	23.305	0.101	23.305	23.305	23.305	23.305	20.265
mass flow (kg/h)	5020.0	5020.0	1182.9	1182.9	6202.9	6202.9	2083.0	2083.0
mass flow (kg/h)								
H_2O	4825.0	4825.0	–	–	4825.0	4994.8	875.0	875.0
ethyl-glycol	195.0	195.0	–	–	195.0	–	–	–
O_2	–	–	275.5	275.5	275.5	24.2	24.2	24.2
CO_2	–	–	–	–	–	276.5	276.5	276.5
N_2	–	–	907.4	907.4	907.4	907.4	907.4	907.4

(22) and a gaseous effluent (23), both at 0.1 MPa and 83 °C.

The minor fraction, stream (8), joins the gaseous stream (15) to expand in a gas turbine in order to produce the amount of energy demanded by the compressor. A stream of condensates (13) leaves the turbine, joining the liquid stream from the flash (22). The gaseous stream from the turbine (12) enters the last flash in order to separate gas and liquid.

Two streams leave the process: a liquid stream (24), mainly formed of water, and a gaseous stream (23), which contains N_2, H_2O, CO_2, and O_2.

Assumptions made in the simulation were as follows: (i) total conversion of ethylene glycol in the reactor ocurred; (ii) total efficiency in the feed pump = 0.9; (iii) the air compressor consisted of four stages, with a refrigeration temperature between stages of 35 °C, a politropic efficiency per stage of 0.8, and a mechanical efficiency per stage of 0.9; (iv) the gas turbine had a mechanical efficiency of 0.6, an isotropic efficiency of 0.9, and a vapor quality of 0.9; and (v) thermodynamic properties were estimated on the basis of the equation of state of Peng and Robinson, which is consistent in both the sub- and supercritical regions.

Figure 6 shows the flowsheet of the simulated plant, including values for the work and heat exchanged in most of the equipment. Table 1 summarizes the operating conditions as well as the total and component flow rates of the main streams of this flowsheet.

This simulation shows the possibility for scale-up of the SCWO plant with a new design that incorporates heat integration. Making a good development of streams with high enthalpy reduces the use of utilities, a fact that implies lower operating and environmental costs.

The energy required for compression is generated in the process itself, and a substream provides the heat needed to preheat the wastewater feed stream. Hence, SCWO is an attractive alternative to other wastewater treatments because of its high destruction, nearly complete, at very short residence time and with the possibility of a good energetic integration of the process.

Conclusions

Validation of SCWO as a suitable technology for the treatment of wastewater from the poly(ethylene terephthalate) (PET) industry has been achieved with these experiments in the pilot plant of the Chemical Engineering Department at the University of Valladolid (Spain). The results showed TOC removal efficiencies of up to 99.9% for reaction temperatures around 630 °C and for residence times of less than 1 min (50 s). The main operating conditions were optimized to $P = 23 \times 10^6$ Pa, $T = 630$ °C, and the stoichiometric rate of oxidant.

The proposal of an SCWO plant for wastewater treatment is not an ordinary alternative. In addition to almost total waste elimination, simulation of a full-scale plant has shown the possibility of treating the wastewater without any external energy supply. A representative feedstream of 5000 kg/h containing 4 wt % ethylene glycol was used in the simulation with Aspen Plus. Energetic integration of the plant showed that the energy required for compression and heating can be produced by the process itself.

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