Wet air oxidation for the treatment of solid wastes generated on autarkic sites

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Keywords: wet air oxidation, waste, subcritical water, autarkic.
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Abstract

Waste management on autarkic sites (islands, oil rig, boats, isolated communities) does not hold any simple solutions because of specific limitations: space availability, restricted recycling opportunities, impacts on environment… Wastewater treatment processes are usually physico-chemical or biological processes, and solid wastes (plastics, cardboard, glass, ...) are stored and transported to treatment units. Wet air oxidation process consists to oxidize the organic fraction of wastes containing organic matter little or no biodegradable by contacting an oxidizer (air, pure oxygen, hydrogen peroxide) in aqueous medium. Wet air oxidation process occurs in water sub-critical conditions: pressure from 0.5 to 20MPa and temperature from 100 to 320°C. This study on wet air oxidation ability to destroy solid organic wastes (paperboard, plastics, food residues) was performed in batch reactor. Effect of parameters such as reaction temperature and residence time was investigated. The experimental results showed that wet air oxidation can effectively remove organic solid matter with a sufficient reaction temperature as main factor of the total organic carbon removal efficiency. For plastic (polypropylene and polystyrene) wastes, for temperature of 300°C and initial total organic carbon of 3428mg.L^{-1}, a residence time of 15min is enough to obtain 90% of total organic carbon removal. This removal increases with the rise of reaction temperature and residence time for each solid waste tested.

Introduction

Industrial effluents have variable compositions depending on the industry: refineries, pharmaceuticals, distilleries, food processing, paper mill…The most widespread treatment of effluents containing organic pollutants is the biological way, but microorganisms are unsuitable in the case of low biodegradable compounds or toxic products. Legislations regulate more and more severely the management of these wastes and favour the development of alternative processes allowing to treat effectively particular pollutions, as in pre-treatment before a biological process or for a complete degradation of organic matters in carbon dioxide and in water. Other technologies are under research and development to be applied to this drawback, as for instance wet air oxidation (WAO), especially for wastewaters that contains high chemical oxygen demand.

WAO or hydrothermal sub-critical oxidation was developed at first by the company ZIMPRO [1] in the United States. The first WAO process allowed the synthesis of vanillin from liquid residues of paper mill industry. In the years 1960-1970, Sterling (which detained ZIMPRO patents) developed low temperature processes to treat various types of waste (urban, agricultural, regeneration of active carbon, etc.). It is in the 80s that WAO knows a renewed interest as treatment method for residual liquids, because of new regulations at the world level for environmental protection.

WAO aims at oxidizing the organic fraction of an aqueous effluent by contacting organic pollutants with an oxidizing agent. WAO processes work mostly in conditions of temperature ranging from 100 to 320°C and a total pressure (of air or pure oxygen, according to the choice of the oxidizer) of 0.5 to 20MPa [2-4]. The oxidation yield is about 70 to 95 % with a residence time of 30min to several hours. 5 to 30 % of organic matter are usually not totally transformed into the liquid phase. It is mainly acetic acid, formic acid and other volatile fatty acids. That is why most of WAO units are followed by a biological treatment to degrade these acids. In these conditions pf pressure and temperature, the solubility of oxygen in water is more important than in the ambient conditions. That favours the degradation of the organic fraction in carbon dioxide and water. Andreozzi et al. [5] suggest that this technology is the most adapted for the aqueous effluents having a chemical oxygen demand between 20 and 200g.L^{-1} what corresponds approximately to 1 to 10 % of organic matter. From 20g.L^{-1}, the heat necessary for the functioning of the process is roughly supplied by the exothermicity of the oxidation reaction. Beyond 200g.L^{-1}, the amount of oxidizer becomes too important and generates higher operating costs (compression of the oxidizer, etc.) that makes incineration more attractive. The choice of the reactive gas is generally on air or pure oxygen. The difference between the two is economic: the cost of air compression is higher, but the cost of production is lower. Pure oxygen also presents higher explosive risks. A study of oxidation in supercritical water, operating at pressures and temperatures above the critical point of water, provides some basis for comparison [6].

Autarkic sites (oil rig, single communities, hotel on a Polynesian atoll…) generate liquid waste streams (black/gray water, cooking greases, oils, infirmary discharges) and solid (catering waste, paper, cardboard, plastics) containing organic matter, that are often stored for longer or shorter periods, then transported and incinerated by specialized companies. The recent scientific literature is dense about the experimental studies in laboratory on WAO of simple organic compounds or more complex effluents. WAO can be catalysed or not. In homogeneous catalysis, Cu $(NO_3)_3$, Ni $(NO_3)_2$ or Fe $(NO_3)_2$ transition metal salts are used [7]. Solids are used in heterogeneous catalysis: metal oxides (copper, zinc, ...), noble metals supported on oxides (alumina) or activated carbon (platinum, ruthenium, iridium) [8]. Multiphase gas-liquid-solid contactors are often used in chemical engineering process. For instance, the gas phase can be dispersed into the liquid or suspension in the form of bubbles in using a gas sparger generally placed at the bottom of the column. This kind of reactors, like bubble column reactors, are generally used in chemical, biochemical, petroleum and metallurgical industries (oxidation, polymerisation, hydrogenation, gas conversion to produce fuels, fermentation, biological wastewater treatment ….) [9;10].

However, all these studies do not supply enough information to design this process to industrial scale. On the reaction aspects, this work consists to run experiments with oxygen concentrations suitable for designing an industrial treatment unit and on real wastes. For that purpose, studies are conducted with an initial total organic carbon (TOC) concentration about 3000mg.L^{-1} of solid wastes. The different solid wastes are chosen for these experiments to be representative of what is found in real wastes (canteen food wastes, can film packaging, corn flakes package, water bottle). The oxygen excess chosen for the experiments (70% excess of oxygen) is realistic from an industrial point of view, contrary to 1000–2000% of excess usually found in literature [11;12].

Materials and methods

Experimental setup

WAO reactor (stainless steel, supplied by Top Industrie, France) is a vertical cylinder with a volume of 200 cm^3. A gas sampling system is installed at the head of the reactor and a sintered cane equipped with a sintered liquid can be withdrawn at the bottom of the reactor. It is equipped with a magnetic drive stirrer whose maximum speed is 2,000 rpm to ensure the homogenization of the medium. The stirring device is a Rushton propeller with 8 blades. Temperature is measured by a type-K thermocouple in the cell. Temperature in the cell is kept stable thanks to a hot/cold control system. A 1 kW heating collar is used to heat the cell up to a maximum operating temperature of 350°C. For cooling, the control valve opens, and air circulates in the reactor body to evacuate heat. Compressed air is cooled by a vortex tube: air enters the rotating chamber tangentially, allowing the air column inside the tube to rotate at a very high speed. To measure the pressure, the cell is equipped with a 0-50MPa manometer. A rupture disc, at 40 MPa (± 10%), is connected to avoid exceeding the maximum working pressure set by the manufacturer at 38 MPa. All pipes and fittings used on the experimental set-up are 1/8" high pressure. The upper flange is equipped with a 3/8" tapping through which the waste (liquids, or suspensions, the diameter of the orifice being 6mm) can be injected at the beginning of experiments, using a syringe. The general layout of the installation is shown in Figure 1 .

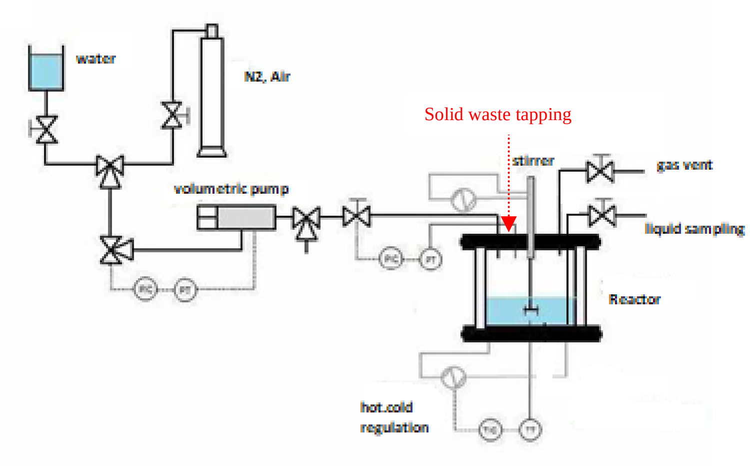

Figure 1. Simplified diagram of the pilot used for WAO experiments

The reactor is supplied with gas (nitrogen, air) via 20MPa pressurized gas cylinders supplied by AIR LIQUID (purity> 99%). The positive displacement pump (Top Industrie,France) has a volume of 50 cm^3. The liquid circuit is connected to the capillary and the gas circuit is directly connected to the reactor. Supervision is carried out via a control box allowing to set temperature of the heating system and the speed of the stirrer.

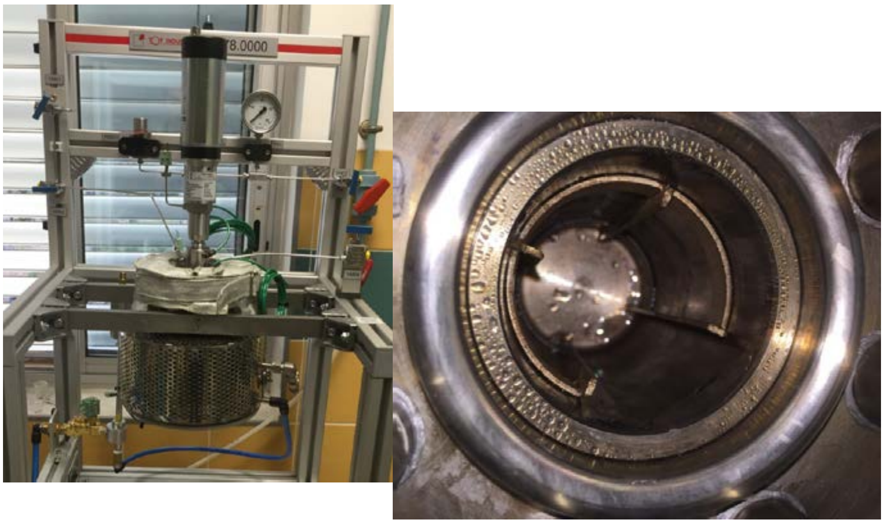

Figure 2. WAO experimental apparatus

Experimental protocol

Experiments are performed according to the protocol described below. 50mL of wastewater (water and solid waste) are introduced into the reactor by the tapping before pressurizing the system with about 0.5 to 2MPa of nitrogen. This pressurization allows to have an inert atmosphere. Then the heating system is settled and stirring speed of 800rpm is fixed during all experiments. When the set temperature is reached, the reactor is pressurized to set pressure (12 or 15MPa). The opening of the reactor feed valve marks the beginning of the reaction. Air is injected into the reactor until the desired total pressure is reached, and then the reaction zone is isolated. Liquid samples are taken during tests by the valve connected to plunging tube in the liquid phase, at the bottom of the reactor. Air ratios (amount of air introduced into the reactor on amount of stoichiometric air) were calculated using an Excel® macro developed during a previous work [13]. These calculations are determined considering the temperature, the nitrogen pressure initially applied in the reactor, the total pressure after the air injection and the volume expansion of the liquid phase in the reactor.

The reaction evolution is monitored by analysing samples by TOC measurement (analyser Shimadzu VCPH). The calibration of total carbon and inorganic carbon is made from mother solutions at 1000ppm. Two experiments were carried out for each operating condition, to verify the reproducibility and to have for each waste TOC reduction curves as a function of time with sampling every 15 minutes. The operating conditions are in the range of 200 to 300°C and 12 to 15 MPa. The different wastes are the following: food wastes, grey&black water simulant, paper & cardboard, plastic packagings.

TOC reduction calculated after measuring liquid and solid TOC on every WAO samples, according to the formula below (equation 1).

$$TOC\ reduction = \left(1 - \left(\frac{TOC(sample)}{TOC°}\right)\right) \times 100 \qquad (1)$$

with TOC° the initial TOC of the waste.

Food sludge is reconstituted from waste collected at the restaurant of the Europôle de l'Arbois site (next to M2P2 laboratory). The waste listed below was recovered from trays sent to the crockery area for the duration of the service: remains of plates (meat, fish, chicken, salad, vegetables, quiche, pie, pasta, ...), fruit leftovers (pineapple, melon, watermelon, lemon, orange, ...), pieces of pain and cakes (pies, shortbread …), remains of yogurts and cheese, content of glasses or bottles (beer, soda, water, ...). Wastes were ground in a blender to obtain a homogeneous slurry with TOC of 3385mg.L^{-1}.

Plastic wastes are made of polypropylene (PP) and polystyrene (PS). These are commonly used in food packaging: yoghurt pots, food trays (cooked dishes, etc ...), biscuits trays. The plastics waste was cleaned (no food remains to study the behaviour of the plastic alone, without interaction with another deposit), cut into chips and placed in WAO reactor before impoundment. Plastic cutting (< 5mm pieces) is not necessarily representative of the future industrial grinding but mainly addresses a problem of introduction into the WAO autoclave. Initial TOC of plastics waste (diluted in demineralized water) is 3428mg.L^{-1}. Two other kinds of plastic wastes were tested during the experiments: polyethylene (PE) food packaging films that are commonly used food packaging films (water bottles and soda cans, food trays) and water bottles in polyethylene terephthalate (PET), respectively with initial TOC of 3100 and 2887mg.L^{-1}.

Paper and cardboard waste consists of commonly used products - handkerchiefs, paper towels and food packaging board (biscuits, cereals) - cleaned (no food residue), cut into chips and mixed with demineralized water. Wastes were ground in a blender to obtain a homogeneous slurry with TOC of 3205mg.L^{-1}.

Results and discussion

Two experiments were done for every type of waste and set temperature (200, 250 and 300°C), for reproducibility and to avoid doing too much sampling (of a few millilitres) which decreases the volume of the liquid phase during the 2 h experiments. The samples are taken every 30 min by shifting 15 min between the two tests. The melting temperature of PET being 245°C, only four tests were conducted on this waste at 250 and 300°C, to ensure that the polymer is melted before air injection to avoid clogging of the small diameter piping.

Food wastes

Figure 3 shows that TOC reduction is temperature dependent, as it is generally observed in oxidation reaction. Studies have established kinetic models for "simple" waste with temperature dependence according to Arrhenius’s law [15;15] which are adapted to real effluents: dyes, petrochemical effluents, paper industry, agro-food, or even urban effluents.

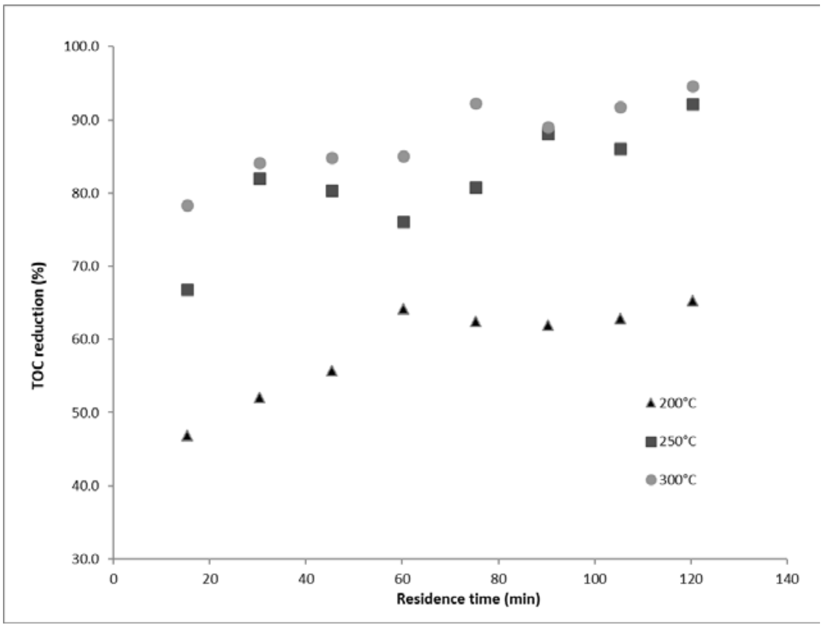

Figure 3. TOC reduction as a function of residence time during WAO experiments on food sludge

After a residence time of 30min at 200°C, no more suspended matter is visible. All suspended matter is converted to CO_2 or carboxylic acids and water. These fatty volatile acids, such as acetic acid, are known to be refractory to oxidation under these "soft" conditions, which explains the residual TOC. Higher TOC removal requires more severe temperature conditions of the order of 330-340°C [14]. Nevertheless after 1 h of treatment at 300°C, TOC reduction observed is higher than 90%. Figure 4 shows the change in visual appearance of the samples as WAO treatment progresses. The initial solution (left) shows a suspension of crushed and diluted food residues and every 30 min sampling, the colour disappears as the coloured intermediates are progressively degraded into colourless by-products to the refractory fatty acids.

Figure 4. Visual appearance of food waste before and during OVH treatment – initial t° (left) until t°+120 min sample from left to right

The difference in performance between 200°C and 250°C is significant (respectively 65% and 92% of TOC reduction after 120 min of residence time). It can be explained by the effect of temperature on reaction mechanisms, favouring CO_2 production at 250°C and refractory intermediates at 200°C. Debellefontaine et al. [17] studied the degradability of various chemical substances by WAO (1 h at 260 ° C and a P_{O2} oxygen partial pressure = 2 MPa) and shows the two-way abatement rates in the form of a "degradability" scale for chemical substances. Under air, despite a treatment temperature of 260°C, the abatement rates obtained on short carboxylic acids (acetic, formic, propionic) are very low. These compounds accumulate in the treated effluent and explain the residual TOC measured during the analysis. When the reaction mechanisms promote the formation of these intermediates, the overall yield of the reaction is then impacted.

Plastic wastes

TOC measurements reveal a low abatement rate about 50% under the 200°C/12 MPa conditions after 2 h of treatment (Figure 5). The sample taken after 15 min, although faintly coloured (yellow), strongly smelt the molten plastic. It is probable that PP/PS polymers decompose thermally (depolymerization) during the heating phase under an inert atmosphere, but no sample of the reaction medium before the injection of air have been done, because the risk of clogging of the sampling rod (1/8" tube) is important. There is moreover for this waste a significant effect of increasing temperature, which can be explained by a greater decomposition during the heating phase or a reaction mechanism favouring the formation of intermediates refractory to oxidation (at 200°C) and a direct mechanism of carbon dioxide formation (at 250 and 300°C).

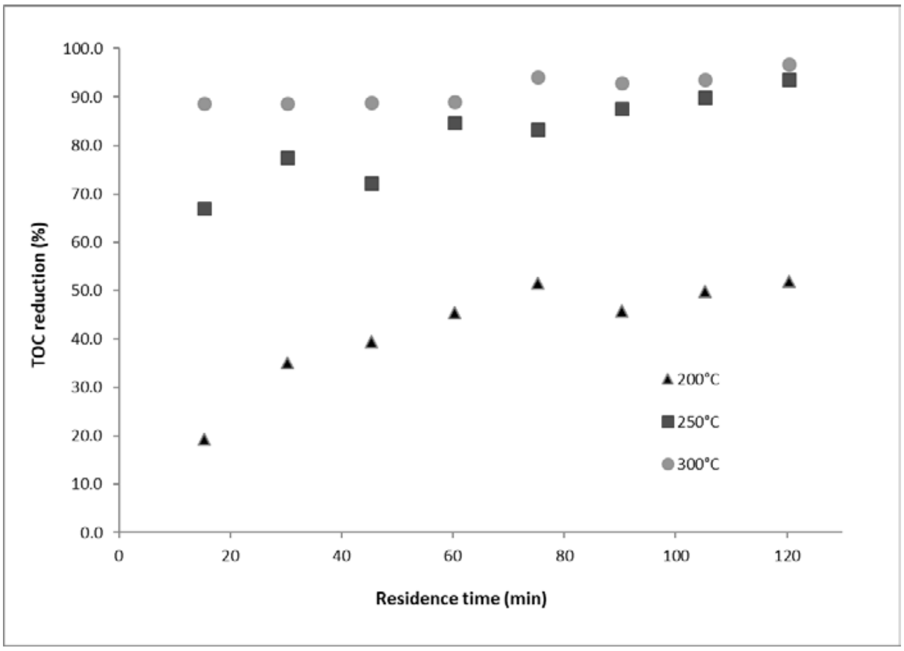

Figure 5. TOC reduction as a function of reaction time during WAO experiments on plastic PP/PS wastes

TOC reductions are very significant with over 90% reduction after 105 min of treatment at 250°C, which can be achieved after about 30 minutes at 300°C. A gap of degradation performance is still observed between 200 and 250°C, with about 50% at 200°C and 120 min against more than 90% at 250°C.

On PE films, TOC measurements show a reduction rate of the order of 80% under 200°C and 12MPa conditions after 90 min. This yield, under the mildest conditions, is higher than that observed on the PPS/PS chips. This could be explained by the shape of the chips (soft film for PE, hard plastic chips for PP/PS blend) and a lower melting point for PE (85°C, compared to 160°C for PP). Depolymerization would thus be more advanced during the heating phase. Residual TOC observed between 60 and 120 min are then equivalent to those observed for PP/PS since the oxidation phase produces its effect. The final yields (> 90%) are close. The treatment at 300°C makes it possible to reach the "residual TOC level" in a much shorter time, one can thus observe a reduction of TOC of 93% after 15 min at 300°C against only 70% at 250°C.

Figure 6 shows that at 300°C, a yield of about 80% is observed after 15 min of treatment (against about 50% at 200°C), and even higher than 90% after 30 min. As for other wastes, there is a "plateau" of TOC reduction, whatever the reaction temperature, the difference between these operating conditions being in the value of the bearing and in the time necessary to reach it.

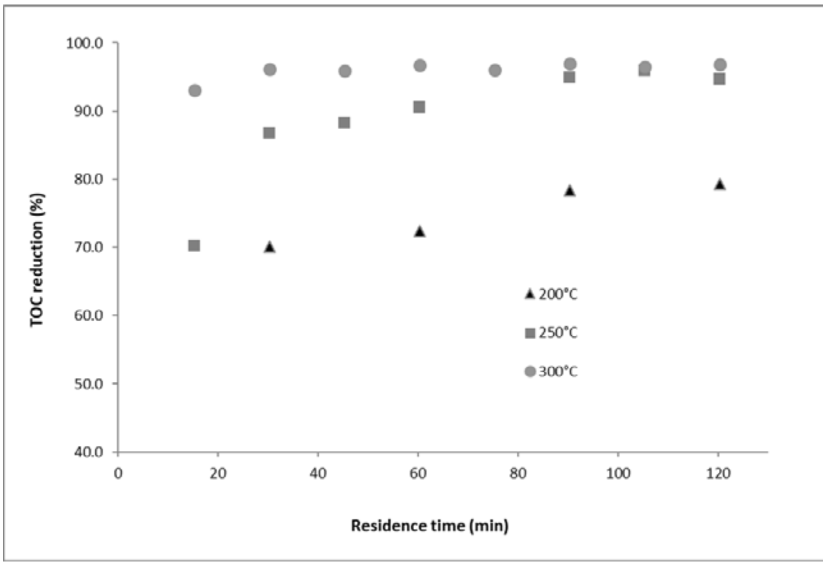

Figure 6. TOC reduction as a function of reaction time during WAO experiments on plastic PE wastes

The TOC measurements on PET degradation samples reveal a significant reduction rate of the order of 80% under 250°C and 12MPa after only 15 min of treatment and more than 95% at the end of the test. It can also be noted that this yield is reached in less than 30 min at 300°C (Figure 7).

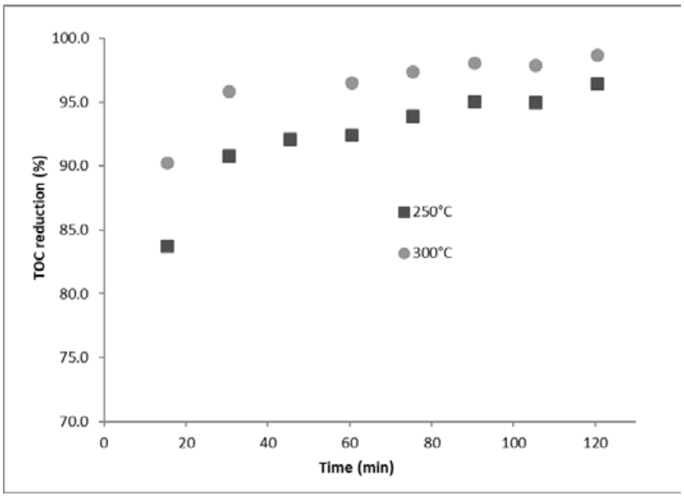

Figure 7. TOC reduction as a function of reaction time during WAO experiments on plastic PET wastes

During a test at 300°C, a sample was taken at the end of the heating phase, just before the injection of air. The mixture contains a solubilized white substance which settles at the bottom of the sample bottle (after standing). It can be assumed that during the depolymerization phase, PET was broken down into different smaller intermediates as the monomer, terephthalic acid (leading to the colour of the mixture) [17].

Paperboard & Paper wastes

TOC measurements reveal a significant reduction rate of 85% under the conditions of 200°C and 12MPa and more than 95% under the most severe conditions (after 2 h of treatment). Temperature effect is still present, particularly in the first 15 min of reaction, with almost 80% of TOC reduction at 300°C against 50% at 200°C. The sample taken after 15 min at 200°C is yellow without solid content which suggests that the reactions lead to organic matter composed of shorter organic molecules, soluble in water.

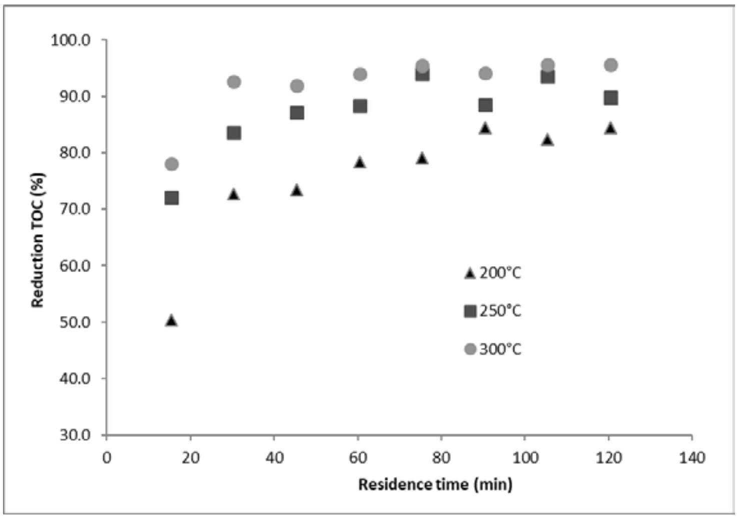

Figure 8. TOC reduction as a function of reaction time during WAO experiments on paper/paperboard wastes

For paper/cardboard waste, after 30 min of residence time, the performance gap between 200 and 250°C is much less significant than for other solid wastes. The compounds present in this type of waste (mainly cellulose fibers) must degrade according to mechanisms favouring the formation of CO_2 instead of refractory fatty acids.

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Conclusions

The results obtained show that WAO is a high-performance alternative (TOC reduction > 90% at 300°C) for the destruction of organic solid wastes generated on autarkic sites. The experimental data obtained (operating conditions, TOC reduction) will be used to carry out a techno-economic feasibility analysis for the implantation of WAO unit on this kind of site, with an environmental comparison (done by life cycle analysis methodology) with the conventional solution. One of the main challenges of this industrial scale-up will also be to ensure the preparation of solid waste so that it is pumped by the high-pressure system and does not cause clogging in the pipes or heat exchangers. These experiments give also very important information for the sizing of treatment units. Thus, depending on the performance to be achieved and the specific limitations of implantation, it may be preferred a milder temperature with a longer processing time (larger capacity reactor) or fast treatment at 300°C or more, with a more compact system.

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