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Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Chemical Engineering Journal

Thermo- and photo-oxidation reaction scheme in a treatment system using submerged plasma



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HIGHLIGHTS

- Underwater plasma technology for pure hazardous organic liquid destruction technology and performance.
- Characterization of UV spectrum coming from underwater non-transferred arc plasma.
- Activity of reactive species such as OH or H₂O₂ produced by underwater plasma.
- Kinetics of hydroxyl radical reaction with residual organics in process water.
- Thermo-oxidation and photo-oxidation scheme in an underwater plasma process.

ARTICLE INFO

Article history: Received 24 November 2016 Received in revised form 6 February 2017 Accepted 12 February 2017 Available online 1 March 2017

Keywords:
Organic liquids destruction
Submerged plasma
Plasma UV emission
Reactive species production
Photochemistry
Reaction scheme

ABSTRACT

Some of hazardous liquid organic wastes, radioactive or not, are waiting from outlet to be destroyed. The ELIPSE process is a new technology of organic liquid destruction, involving a thermal plasma working under a water column, which ensures the cooling, the filtration and the scrubbing of the gases coming from the degradation. This study deals with the ability of the ELIPSE process to destroy the pure organic liquids and then to reduce the amount of organic matter remaining in the aqueous solution by means of the thermal or radiative properties of plasma.

Preliminary test have shown how efficient the process is for the destruction of the organic liquids when they are directly fed in the plasma hearth. Extensive researches have been performed to assess the ability of the submerged plasma to destroy the remaining organic matters either by reinjecting them with the aqueous solution into the plasma or by using the UV ray coming from the plasma itself. A comparison of the experimental results obtained with various mechanisms proposed by the work carried out highlighted that this UV radiation could, by excitation of water molecules, produce radicals OH which may either dimerise to produce hydrogen peroxide H_2O_2 , or react with organic substances present. The calculation of an activation energy of $8.5 \pm 0.9 \,\mathrm{kJ}$ mol $^{-1}$ during the experiments shows that these radicals OH act directly after having been formed which explains a low H_2O_2 content stability when the solution contains organic compounds. Thus, this photo-oxidation taking place in the water column could be used to improve the destruction of residual organic matter in the solution by maintaining the plasma after processing a given amount of organic liquids.

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1. Introduction

Processing industrial organic liquid waste, whether radioactive or not, represents a major challenge because this waste comes in many different forms and is widely dispersed in the various facilities in which it is produced. Treatment currently available is often exclusive, as is the case for trichlorethylene, polychlorobiphenyl (PCB) or chlorofluorocarbon (CFC) with chlorine content greater

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than 7% mass. The latter are currently treated in a conventional burner at the base of an oven that has to treat for at least 2 s at more than $1200\,^{\circ}\mathrm{C}$ [1,2] which requires large-sized structures with metal or refractory components subjected to extremely corrosive physical-chemical conditions.

A desirable technique would be one that allows universal treatment of these various liquids, regardless of their compositions, in the same unit.

The first studies conducted in this area were mainly focused on evaluating the capability of a submerged plasma to produce HO or O radicals, or even ozone, in a solution. The idea was then to deter-

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mine the means for decontaminating aqueous solutions contaminated by organic pollutants. In the 1980s, Alekseev et al. [3,4] studied heat transfer from a plasma to the aqueous solution in which it is submerged, and estimated that the quenching rate for gases is approximately $10^7 \, \mathrm{K \cdot s^{-1}}$. Extremely high speeds such as these made it possible to fix the radicals capable of oxidizing the organic compounds present in the water.

It was based on this phenomenon that certain processes were proposed as possible decontamination solutions. Bernier et al. [5], for example, propose a concept using an arc plasma torch submerged in a solution containing cyanides to be decontaminated. This concept uses a draft tube working as an hot air lift near the plasma plume.

Although this concept can be used to treat aqueous solutions, it cannot be used for the treatment of pure organic liquids. Other processes have therefore been developed to propose suitable outlets. Uchiyama et al. [6], for example, propose a system which is quite representative of what has been proposed by others. It uses a technology which destroys organic liquids in a combustion chamber, where the output is atomized directly in an aqueous solution. A system was designed to treat flow rates of approximately 1L·h^{-1} for waste solvents (TBP-Dodecane) used in fuel treatment operations.

Studies of this type of process show that the combustion is not truly submerged, as a combustion chamber with refractors is used. The heated zone which generates the combustion reactions and gas transit is therefore quite large, and subject to the aggressive nature of the combustion gases which contain heteroatoms that may cause corrosion. The range of liquids that could be treated in this type of structure is therefore quite small.

Processes have also been developed by JAEA in Japan [7] for the treatment of TBP/dodecan. JAEA has two main processes for this application, a steam reforming process and a submerged combustion process. In the second case, the liquid mixture is supplied at a rate of $1-3~{\rm kg\cdot h^{-1}}$ to a gasification chamber where it is vaporized and pyrolyzed. The decomposition gases are then completely burned in a submerged combustion reactor to prevent soot and dioxins generation.

In this latest example, what is called "submerged combustion" concerns only the afterburner and not the whole thermal treatment of the waste. Corrosion may then dramatically occur in the hot zone.

Studies conducted on the subject at the CEA have enabled a new procedure to be proposed whose concept is based on the implementation of a submerged arc plasma in which the liquid to be treated is directly injected. Called ELIPSE [8], it means the treatment of various organic liquids can be considered by implementing chemical reactions of type (1) carried out at extreme speeds at the core of the plasma.

$$C_x H_y XM \xrightarrow{plasma/O_2} xCO_2 + \frac{y}{2} H_2 O + XH + MOz$$
 (1)

X and M represent the hetero atom generally produced in the form of a mineral acid that subsequently has to be neutralized and M a mineral charge initially present and oxidized in the oxygen plasma.

The current configuration of the ELIPSE process is described in Fig. 1. The plasma torch can be seen submerged at the bottom of a vessel filled with water which is continuously processed in a system with a heat exchanger, a filter and a neutralization system in series. The plasma torch with a power that can reach 50 kW has a nozzle specially designed to receive and destroy an organic load supplied at its base. It is the only hot point in the process, as the rest is kept at the temperature of the aqueous solution which ensures quenching, filtering and washing of the gases from the reaction (1). This set of functions essential in a single step explains

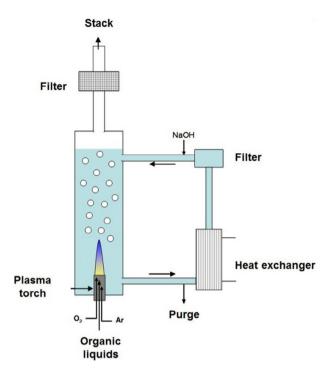


Fig. 1. The ELIPSE process diagram.

the high degree of compactness of the process. Keeping the assembly cold explains the optimal resistance to any form of corrosion which leads to considering a system of 'universal' treatment of organic liquids.

2. Material and methods

2.1. Fitted out plasma nozzle

The combustion reaction of the organic load as described by Eq. (1) can only be optimal on the condition that a suitable nozzle is set up in which the organic liquid brought to high temperature reacts with the oxygen plasma by generating combustion products containing little or no undesirable compounds such as carbon monoxide (CO) or certain derived carbonyls. Contrary to the tube drafting aqueous solution in the process proposed by Bernier [5], the plasma nozzle is design as a micro-reactor able to be fed with pure organics together with pure oxygen.

This nozzle is placed downstream of the torch anode producing a stream of gas of about 230 NL min⁻¹. In addition, the nozzle is composed of three stages as represented in Fig. 2:

- An injection stage that introduces the liquid directly into the plasma
- A dilution stage which ensures re-injection of the solution in which the plasma is immersed. This stage has a dual functionality:

To reintroduce the solution containing organic residue from incomplete destruction efficiency of around 99.7%. This reinjection will help study the ability of the system to improve overall destruction efficiency.

To cool by spraying water in order to induce the production of CO₂ by displacing the CO/CO₂ balance.

 A cooling stage which gives a sufficient stay time to establish chemical reactions including the combustion of any carbonaceous particles present.

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