Glycerin degradation by submerged plasma

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Abstract: A plasma-chemical reactor with submerged plasma jet for treatment of liquid residues are presented. High local temperature of plasma and low temperature of treated liquid promotes high quenching rate that preserves radical concentration and promotes advanced oxidation of aqueous effluents in highly turbulence flow. The principal working characteristics and result of glycerin degradation by thermal air plasma are presented.

Keywords: Thermal in-liquid plasma jet, environmental pollutant treatment.

1. Introduction

Thermal plasma is widely applied for incineration of solid, liquid and gaseous hazardous waste [1]. In the last decades, the environmental pollution become a worldwide problem due to the significant increase of municipal, industrial (including radioactive materials) and hospital waste. Among these, liquid wastes with a high content of harmful organic pollutant call for greater attention due to the possibly contamination of the environment (by releasing wastewater effluents) to affect the health of humans besides unbalance the bio systems.

Organic contaminants (for example in wastewater effluents) cause serious problems due to their high chemical oxygen demand (COD), low biodegradability, and toxicity. A vast number of contaminants cannot be adequately eliminated by conventional treatment. Advanced oxidation processes, based on the generation of extremely reactive radicals, is an alternative that come with high efficiency for the oxidation of the bulk of organic compounds.

Organic liquid waste is commonly incinerated in cement plants (in the capacity of an inexpensive fuel) or in a conventional burner in a furnace [2]. Many efforts have been made to find low cost and effective methods for treating various types of liquids, with efficient removal of contaminants and without forming greenhouse effect gases (dioxins or ozone depleting gases) that harm the environment. For this purpose, non-equilibrium and thermal plasmas were actively studied [3] and numerous reactor geometries were developed to induce chemical reactions in treated liquids. The principal operating principles can be applied by three approaches [4]:

(i) Direct discharges in liquids

(ii) Discharges in the gas phase over a liquid, including when a conductive liquid work as an electrode, and

(iii) Discharges in multi-phase environments (discharges in bubbles, or foams, sprayed liquid).

The type of discharge, the energy liberation and the composition of plasma determine the kind of chemical reaction initiated. Formation of active species (OH, H_2O_2, O_3, etc) occurs in a thin layer near to the free surface that separate liquid and gaseous states. Primary and secondary species can penetrate (dissolve) into the liquid. Penetration depth of reactive particles into solution is very small and attain some dozens microns [5]. So, an active mixing is necessary to cover all volume of liquid.

Recently, the submerged in-liquid plasma has been applied for the treatment of liquid wastes with elevated content of organic material, as well as for the remediation and treatment of water, [6]. Remediation of chemical residues, in addition to water treatment, requires the study of the interaction processes between plasma and liquid environment.

An equilibrium composition (in molar parts) of the water vapor plasma at atmospheric pressure is shown in Fig. 1. It is clear that above 4000K the plasma consist principally of H, O with formation of hydroxyl radical OH in limited quantity. Variation of the hydroxyl radical concentration is shown in the insert of the Fig.1. The temperature 3500K is the optimal for OH forming.

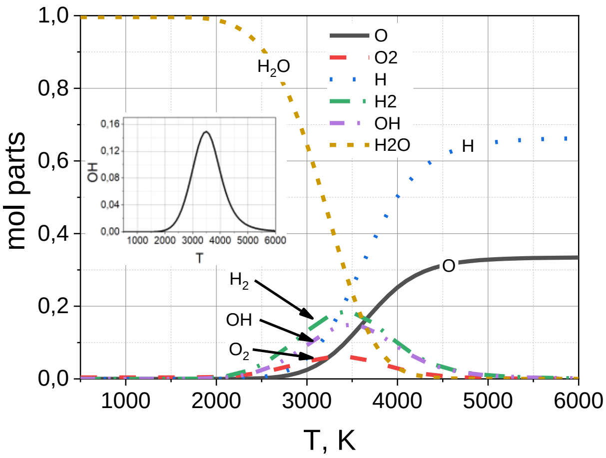

Fig. 1. Equilibrium composition of water vapor plasma.

2. Experimental setup

This work will present the results of glycerin degradation in a plasma-chemical reactor designed for the liquid waste treatment. The reactor was equipped with a conventional air/oxygen linear plasma torch, but a water vapor plasma torches can be used as well. The outlined benefit of the reactor are:

- high temperature of plasma jet and low temperature of treated liquid, which diminishes corrosion of the reactor wall;
- elevated quenching rates (10^6-10^7 K/s) preserves high concentration of radicals produced in discharge (O, OH, H, O_3, H_2O_2, O_3) to promote advanced oxidation processes for decontamination of aqueous effluents and suppress its recombination;
- high turbulence, induced by plasma jet, contribute to intense mass transfer from plasma to liquid;
- UV radiation from electric arc;
- off-gas treatment system (cooling, filtration, and neutralization) embedded to the reactor.

The plasma chemical reactor with direct contact between plasma and liquid is shown in Fig.2. The reactor principal parts are: bottom (1) and top (3) vessels, mist eliminator (9) and entrance to heat exchanger (10) to diminish the produced gas temperature. The reactor is equipped with thermocouples (8). The liquid waste injected to the top of reactor (7) and drained from the reactor bottom (not shown), and pass through additional heat exchanger designed to maintain the temperature of treated liquid. The plasma torch is attached to the bottom flange (4) with plasma jet, oriented to the top of the reactor, injected directly to the solution, axially to the draft tube (6). The last is placed above the torch, for many purposes: maximize the liquid recirculation inside the reactor, increase agitation and mixture between plasma gas and treated liquid and increase the active particles residence time. The reactions occur nearly liquid-gas boundary, while the bulk temperature of solution remains relatively low.

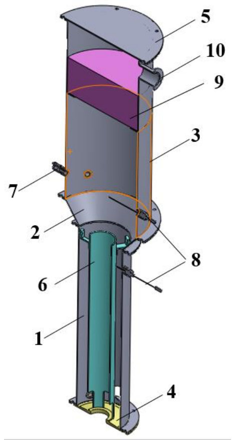

Fig. 2. Plasma chemical reactor.

3. Cold test and numerical modelling

Primary, the dynamic behavior of the gas jet submersed in water was investigated by using the high-speed camera. The results obtained for a cold air jet at Reynolds number (Re~10^4) similar to the plasma jet are presented in Fig. 3. Large bubble (~ 5 cm in diameter and ~15 cm in length) is formed periodically with frequency some hundreds Hz. The size of the bubble and the appearance frequency dependent on the jet velocity and surface tension, which are function of the physical properties of fluids and plasma torch nozzle diameter.

Detaching from nozzle, the main bubble is fragmented to small bubbles (~3-5 mm diameter). Due to viscosity, the gas (bubble) velocity decreases rapidly and in the upper part of the reactor the velocity of the bubbles no longer depends on the initial velocity of gas injection. The hydrostatic (surface tension) and buoyancy forces determine the terminal velocity.

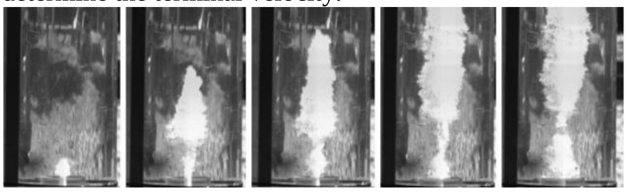

Fig. 3. Cold test of the reactor. Periodic structure of gas jet observation.

The reactor's cold model was simulated. In the numerical model the two phases (gas and liquid) were treated as an interpenetrating means and accompanying an average concentration of the phases. Each phase was associated with own velocity field. To describe the dynamics of each of the phases were applied the continuity equation and the momentum balance equation. The model was simplified by supposing the following hypotheses:

• The gas density is negligible compared to the liquid;

• The movement of the gas bubbles in relation to the liquid is determined exclusively by the balance between the viscous and pressure drag forces;

• The two phases share the same pressure field.

The interaction between liquid and gaseous phases is shown in Fig. 4. On the left side of Fig the distribution of liquid phase velocity inside the reactor is shown, while on the right side is shown the distribution of the volumetric fraction of the gas phase.

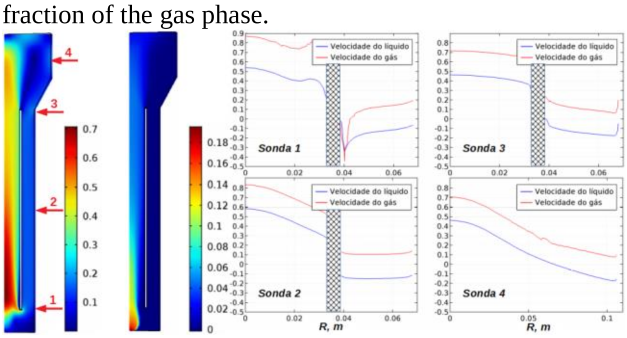

Fig. 4. Numerical modelling of plasma chemical reactor: a) – liquid phase velocity, m/s; b – gas phase volumetric fraction; c) – velocity distribution for marked points

In order to obtain the profile of the parameters inside the reactor, 4 probes were "installed" at the positions marked 1 to 4 in Fig 4. The profiles of the liquid phase velocity and the gas phase at the position of the probes are presented on the left of the Fig. 4. It can be seen that in a movement from bottom to top the velocity profile tends to become uniform inside the central tube (probes # 1-3). The gas velocity is always greater than the liquid one. Outside of the central tube (39mm<R<70mm) the liquid velocity is negative that indicate a recirculation of the liquid. However, the gas flow always has a positive direction, i.e. the upward movement prevails. Just near the entrance to the central tube (probe # 1) there is a negative flow of gas phase induced by the movement of the more denser liquid phase.

4. Glycerin degradation by submerged thermal plasma: Results and discussion

For this reactor an ability of submerged thermal air plasma to destruct organic contaminants was investigated. A crude glycerin (by-product of diesel production) was used as contaminant. The glycerin, at elevated amounts, intensely produces foam in contact with water. Thus in the experiments we use small amounts of contaminant so the foam appearance does not disturb the dynamics of the experiment.

An elemental analysis of the glycerin sample is presented in Table 1. The heat of combustion is 12,32 MJ/kg (LHV) and 13,96 (HHV). The experiments were carried out at the plasma torch arc current 80-150 A, arc voltage 110-150V with plasma forming gas (air) flow rate of 200 l/min. Spectroscopic measurements shown the plasma jet temperature nearly 5000K. The reactor working volume was 13 l. Thermal efficiency of the system was 40-50% for the liquid recirculation flow-rate of 0,35 l/s. For that conditions the nominal temperature of the treated liquid was 45°C.

Table 1. Elemental analysis of glycerol, %m/m

Water	15,50
Carbon	25,80
Hydrogen	7,73
Nitrogen	0,20
Oxygen	52,00
Sulfur	1,89

To characterize the glycerol degradation a specific input energy (SIE), *E*,

$$E(t) = \frac{1}{V}\int_0^t \phi I(t)U(t)dt$$

and a degradation efficiency, η,

$$\eta = \left(1 - \frac{c_t}{c_0}\right) \times 100$$

were defined. Here, *V* is the treated liquid volume; ϕ is the reactor thermal efficiency; $I(t)$ and $U(t)$ are temporal variation of the arc current and voltage, respectively; c_t and c_0 are the Chemical Oxygen Demand (COD) at treated and initial conditions, respectively.

Fig. 6 shows the effect of SIE on principal characteristics of treated liquid. For our working conditions, the acidity and quantity of dissolved oxygen diminishes exponentially and after SIE=800 kJ/l attain its limiting values. However, the electrical conductivity of liquid keep grooving. A generation of the arc plasma jet is unaffected by the liquid's properties.

Fig. 5. Experimental installation

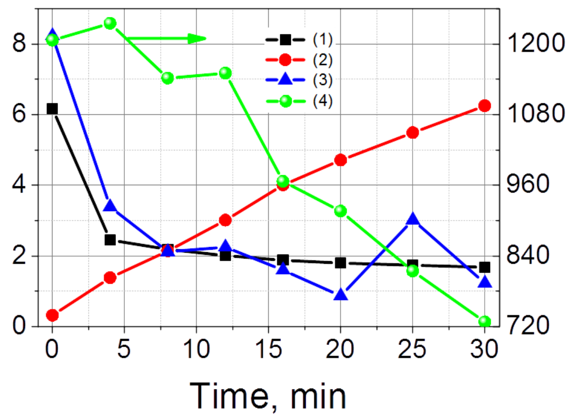

Fig. 5. Temporal variation of normalized values: (1) – pH; (2) – Electrical conductivity of liquid, mS/cm; (3) – Dissolved O2 in liquid, mg/L; (4) – COD (Chemical Oxygen Demand), mg/L

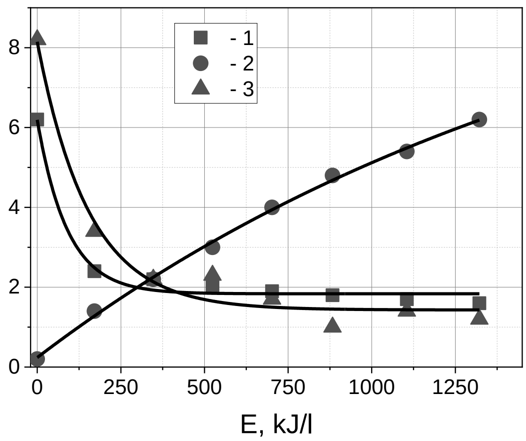

Fig. 6. Effect of SIE on acidity (1); electrical conductivity of liquid, mS/cm, (2); dissolved O2, mg/L (3).

Submerged thermal plasma provides direct thermal and oxidizing contact between plasma, oxidizing gas, and organic materials in solution. The Fig. 7 shows that after 30 min treatment (1322 kJ/l) the concentration of organic materials decreases up to 15% (η = 85%). All organic are decomposed significantly in the plasma reactor. Therefore, submerged thermal plasma has significant ability for organic removal from solutions.

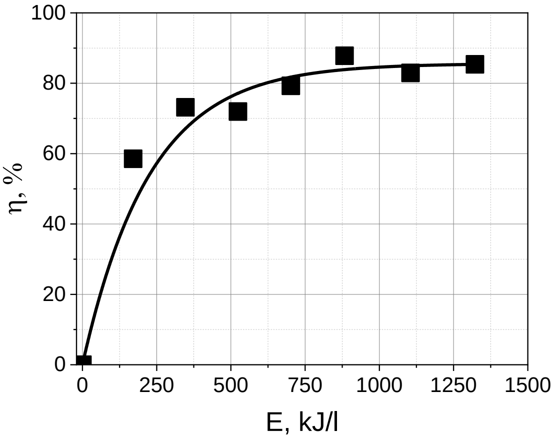

Fig. 7. Effect of SIE on glycerol degradation efficiency

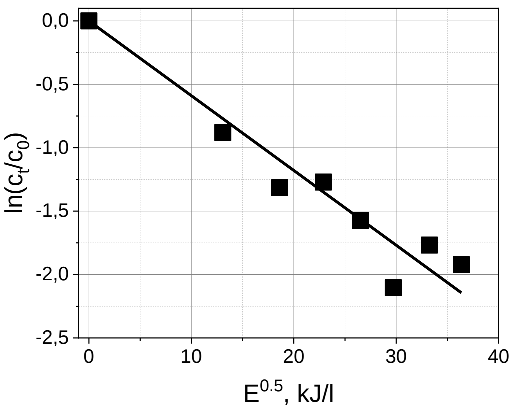

Fig. 7. Kinetic plots of glycerol degradation.

An overall reaction constant, *k*, and reaction order, *n*, of the glycerol degradation were estimated. Taking into account that the reactive species production rate is linearly depends on enthalpy of plasma discharge the degradation can be presented in the form

$$\ln\frac{c_t}{c_0} = kE^n$$

Plotting the degradation relation logarithm versus specific input energy (see Fig. 7) and making fitting it can be possible to obtain the values of k and n. For this particular case the reaction order is n=0.5 and overall reaction constant k=0.059.

5. Conclusion

The plasma chemical reactor for liquid waste treatment was developed and successfully tested at the process of the treatment of water contaminated with crude glycerin. The experimental results shown positive influence of the submerged injection of plasma by turbulization and induced recirculation of the treated liquid, beside an increase in interaction area due to bubbles fragmentation. Utilization of the plasma torch and electrical discharge outside of the reactor assure a plasma generation independently of properties of the treated media.

It was found that the energy input 1000 kJ/l permits to decay 80% of contaminant by effectively utilizes the low pH and high-temperature environment.

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