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The use of an Induction Plasma Reactor for the decomposition of Aqueous Solution

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Abstract

A study of the treatment of liquid wastes in a radio frequency (rf) induction plasma reactor is reported. Ethylene glycol was used as a surrogate for the waste owing to safety considerations. Thermodynamic analyses demonstrated complete and safe decomposition in the conditions studied. The solution was injected axially into the centre of an argon/oxygen plasma operated at 50 kW to study blast atomization and operating conditions. A factorial analysis revealed, at a confidence level of 0.99, that both reduction of pressure and liquid flow rate increase the destruction and removal efficiency (DRE) and that a higher plate power increases DRE. The study also revealed that poor atomization was responsible for the reduction of the DRE by 10 to 15% (to 80-85%), that 94% of the exothermic energy of the reaction was available for further uses, but that only 5% of the plate power was useful for the treatment resulting in a specific energy consumption of 8.33 kWh kg^{-1}solute.

Keywords :

Thermal Plasmas, induction plasma reactor, toxic wastes, energy distribution, mass balance, energy balance

Introduction

The rf plasma technology for the treatment of toxic liquid wastes has already been studied for various plasma gas and wastes. A brief review of these studies is discussed here. The PERC^{TM} process (Plasma Energy Recycle and Conversion) [7] demonstrated the feasibility of a plasma process for converting hazardous military wastes to potentially useful materials, such as «syngas», a mixture of CO and H_2. The process is based on an induction-coupled plasma reactor operated at 15 kW with argon plasma in presence of water. Ethylene-diamine and Malathion were used as a surrogate for the liquid rocket fuel and conversion of more than 99% was achieved. Toluene reforming was also investigated in a h.f. plasma reactor at atmospheric pressure [9]. Argon was used as the central plasma gas while the sheath gas was composed of argon and hydrogen. Experiments performed at 40 kW showed that it is possible to obtain DRE greater than 99.99% with low production of solid carbon, PAH's and benzene. Carbonization of hexane and toluene was also investigated in an inductively coupled rf plasma [10]. Argon was used as plasma and sheath gas. Power level of 2.1, 2.9 kW and feed rates of 0.3, 0.6 g min^{-1} showed that the main product formed is carbon black (soot), though the formation of some polycyclic aromatic hydrocarbons and insoluble hydrocarbons was also detected. Takeuchi, Mizuno and their cowokers, [6] and [11], studied the decomposition of ozone depleting substances (ODS) by a steam plasma. The results showed a conversion to CO_2 and hydrogen halides, which are quenched and neutralized to yield calcium halides. The conversion achieved, with a feed rate of 50 kg/h of CFC-12 and halon-1301 injected in a steam plasma operated at a plate power of 180 kW, was up to 99.99%. The electric power consumption was 4 kWh kg^{-1}.

Far less attention have been given to rf plasma applications for treatment of toxic liquid wastes compare to dc (not reported here). However, all the work done demonstrated the potential of this technology. This paper focused on the rf plasma which is a high energy source involving rapid transfer by radiation and allow design of smaller unit. Compare to incineration and DC plasma, rf plasmas also offer a broader control of the chemistry and increase the residence time compared to dc plasma systems. Since many toxic wastes are in aqueous phase the work done in this research focused on the energetic and chemical aspects of the treatment of an aqueous waste.

The objective of this project was to study the phenomenon involved in the exothermic decomposition of a waste instead of usual endothermic reaction. Such study involved risk associated with manipulation and treatment of toxic wastes. Owing to safety considerations, ethylene glycol was used as a surrogate. The choice was based on the low toxicity of ethylene glycol, its complete solubility in water, low viscosity, low partial pressure and its well known chemistry.

More specifically, the study focused on a factorial analysis of the influence of pressure, plate power and feeding rate on the DRE in conditions of incomplete decomposition. Based on the same experiments, analysis of the availability of the exothermic energy of reaction was studied. Then special attention was given to the effect of the design of the liquid atomization nozzle on the limit of decomposition (DRE) and finally, characterization of the limit of utilization of the plasma energy was done.

Theoretical Background

Thermodynamic study

The chemistry of oxydation of ethylene glycol is known to follow the following reaction

$$C_2H_6O_{2(g)} + \tfrac{5}{2}O_2 \qquad 2CO_2 + 3H_2O$$

The enthalpy of reaction is $H_R^0 =$ -1257 kJ/mol and the Gibb's free energy of reaction is $G_R^0 =$ -1170 kJ/mol.

From the thermodynamic properties of the reactants and products, it was possible to predict the composition of the system at equilibrium by a minimization of the Gibb's free energy as a function of temperature for a fixed pressure of 1 atm. The software EQUILIBRIUM , developped by LANTAGNE, MARCOS and CAYROL [5] at the Université de Sherbrooke was used to perform these calculations. The solution is based on the Modified Newton Method applied to the following relation :

$$\frac{G}{RT} = \sum_{i=1}^{n} n_i \left[\frac{G_i^0}{RT} + ln\frac{n_i}{n_t} + ln\frac{P}{1atm} \right] + \sum_{s=1}^{m} n_s \frac{G_s^0}{RT}$$

The thermodynamic data were taken from JANAF Tables [3], TRC Tables [1], DUFF and BAUER correlations [4] and from the data bank DETHERM. In order to apply these calculations to the system, in the conditions identified in table 1, the following hypothesis have been defined :

- ideal gas mixing ;
  negligible kinetic influence ;
- negligible kinetic influence ;
- all possible products have been considered ;
- variations between thermodynamic data sources do not cause error ;
- composition at 2500K is the most representative [2].

Table 1 Conditions of Thermodynamic equilibrium calculations

	condition # 1	condition # 2
solute	$C_2H_6O_2$	
mass fraction of solute	1	0.4
pressure	1 atm	
MOLAR COMPOSITION		
solute	0.133	0.0787
H_2O	0.000	0.409
O_2	0.333	0.197
Ar	0.534	0.315

Computation carried out over the temperature range from 500 to 4000 K showed that in both cases the equilibrium composition demonstrated the complete decomposition of ethylene glycol and that no hydrocarbon are formed nor toxic compounds over the entire temperature range studied. The major difference in conditions was the presence of water in the original reaction mixture.

From the results of thermodynamic equilibrium of ethylene glycol, the presence of water has no effect on the Ar-C-H-O system. Injecting water then allowed the study of energetic aspect of water presence without affecting the reacting system.

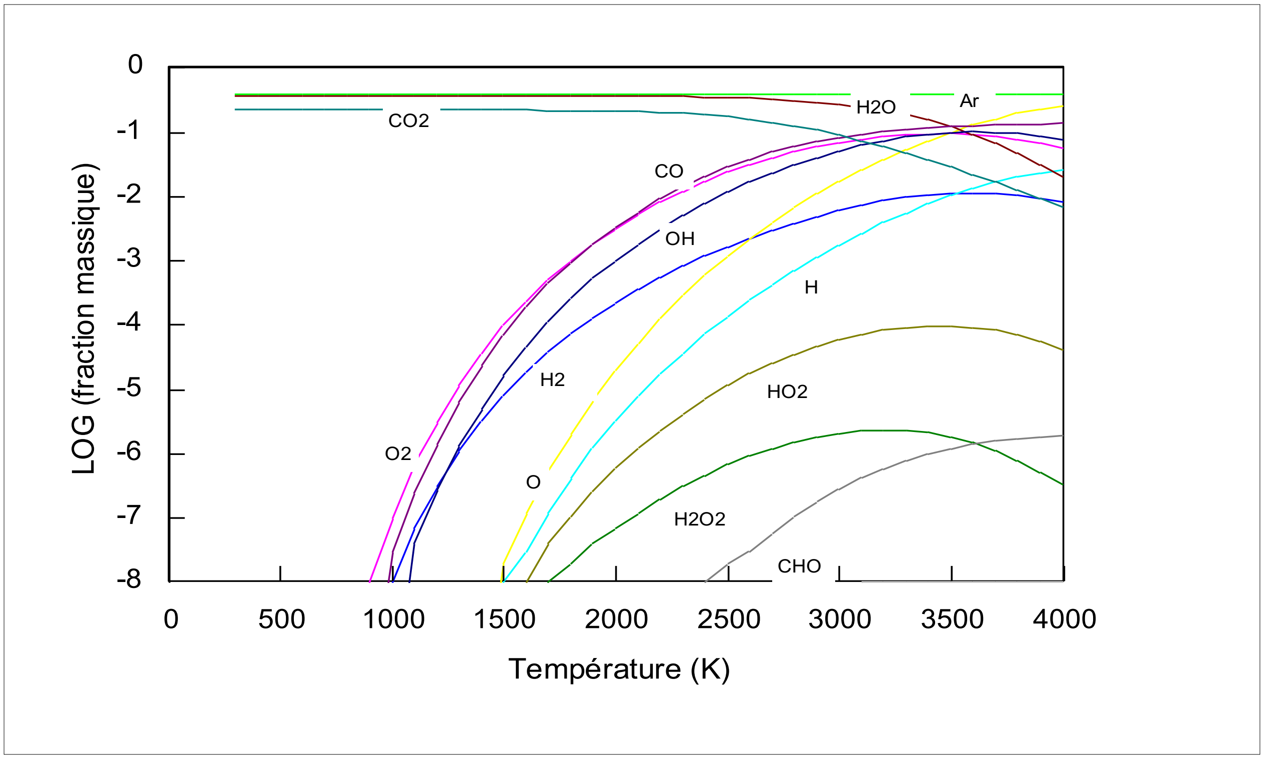

Figure 1 Thermodynamic results at 1 atm , $C_2H_6O_2$ in presence of O_2, without water

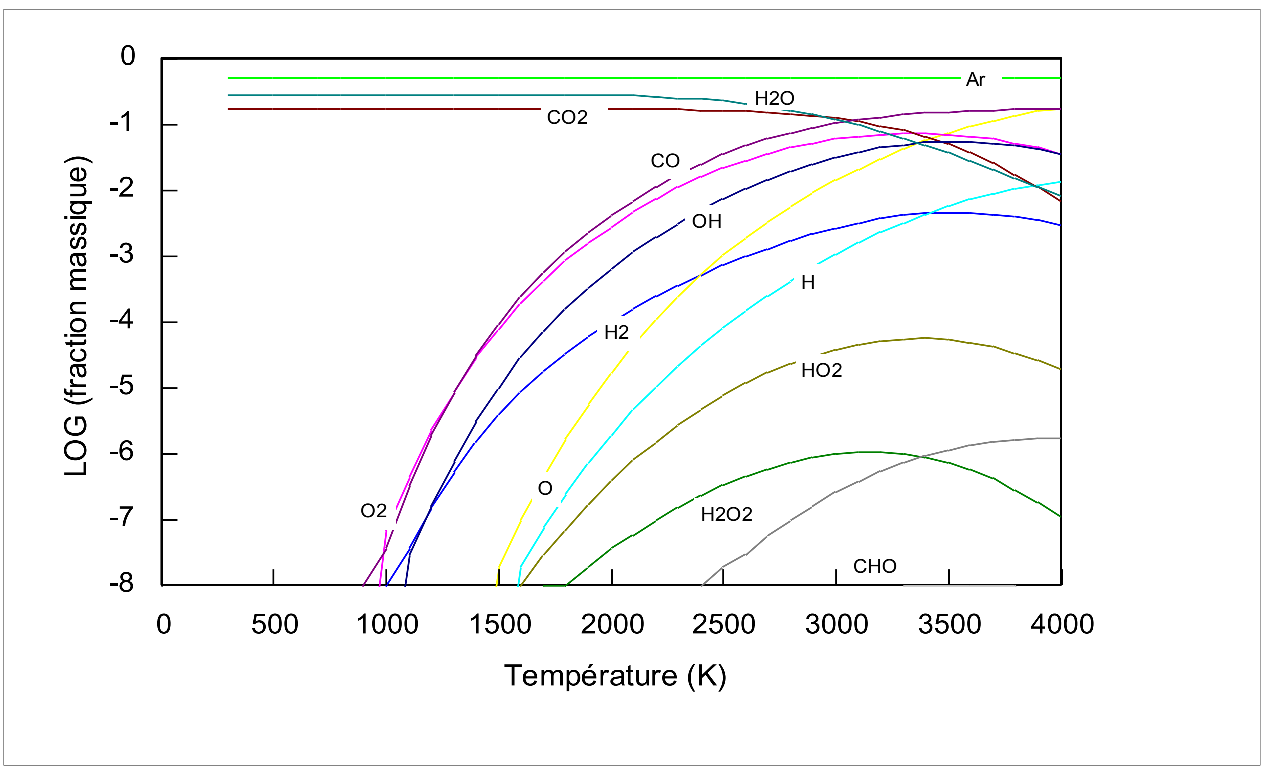

Figure 2 Thermodynamic results at 1 atm , $C_2H_6O_2$ in presence of O_2, with water (0.6 wt)

Heat and Mass Balance

Heat and Mass Balance

The results of the analysis were used to prepare mass balances in order to calculate the DRE obtained in each set of operating conditions. The mass balance was performed on water and is based on the hypothesis of formation of a water saturated off gas. The following equation show the relation used to calculate each DRE .

DRE (1)

(1)

The results of the previous experiments were also used to study the energetic aspect of the treatment. Energy balances were performed on the results obtained during the operation of the plasma system alone and during the feeding. The energy balance is defined as the ratio between the energy dissipated in the system and the plate power. Those results were also used to determine the energy distribution in the system and to evaluate the amount of exothermic energy available.

All calculations of enthalpy were based on the sensible heat of each gas and the temperature of the stream. The enthalpy of the stream was then determined by the sum of the enthalpy of each gas calculated as

(2)

(2)

The mean sensible heat for each gas was calculated at the specific arithmetic mean temperature, determined on the specific temperature range for each gas, by the Cp equation and coefficients found in [8], except for $C_2H_6O_2$ taken from [1] and are shown in the following table.

Table 2 Mean sensible heat of stream gas

gas	temperature range (K)	C_p mean (J/mol K)
$C_2H_6O_2$	[298-470]	175.60
Ar	[298-1500]	20.77
O_2	[298-1500]	33.80

$H_2O(l)$	[298-373]	75.75
$H_2O(g)$	[373-1500]	40.25
CO_2	[298-1500]	51.99

The energy balance also considered the energy used to vaporize ethylene glycol and water which are from [1]:

Table 3 Latent heat of vaporization

liquid	(kJ/mol) (kJ/mol)
$C_2H_6O_2$	49.6
H_2O_2	40.7

Finally, the effect of the pressure, power and feeding rate on the torch and global efficiencies was also investigated. Those efficiencies are defined by the following equations.

torch efficiency (3)

(3)

global efficiency (4)

(4)

where

$H_{cooling\ water}$: enthalpy of cooling water
$H_{gas,\ liq}$: enthalpy of effluent gas and liquid
a : atomizer
r : reactor
h : heat exchanger
t : torch
I_p : plate current
V_p : plate voltage

Experimental Set-up

The experimental set-up used in the study of decomposition of ethylene glycol was an induction plasma reactor as shown in figure 1. Liquid ethylene glycol and water were atomized axially through a water-cooled plain-jet gas-blast atomizer. The atomization gas, argon or oxygen, was fed at a rate of 12 slpm. The plasma gas flow rates were : central gas 30 slpm Ar, sheath gas 90 slpm O_2. The diameter of the torch was 50 mm i.d. with a coil of 4 turns. The induction generator was a Lepel 50 kW having an oscillation frequency of 3-5 MHz.

The exothermic reaction took place in a reactor divided in two parts. The first section (15 cm i.d., 50 cm length) was lined, in some identified tests, with a tube of quartz (3 mm thick) to maintain a high temperature. The other part (13 cm i.d., 52 cm length) had water cooled walls to quench the off gas and to initiate condensation of water.

The gases were further cooled through the heat exchanger (61 cm length, 14 tubes of 9.5 mm o.d., 0.8 mm thick) and were analysed by an on-line mass spectrometer (VG Instrument, Micromass PC). The liquid was collected at the bottom of the reactor and heat exchanger by the U shape connector (10 cm i.d., 33 cm centre to centre) to be analysed by gas chromatography (Hewlett Packard 5890A, column Poraplot Q). Two types of atomizer have been used in this investigation. Figure 2 shows the geometry of both designs. The main difference between those configurations is the cylindrical zone, in type B, that creates a pressure drop and allows formation of a smaller mean droplet diameter.

Figure 1 Experimental set-up

Type A **Type B**

Figure 4 Configurations of atomizers used

Experimental techniques

Experimental techniques

To study the influence of pressure, power and feeding rate on DRE, a factorial analysis 2^3 with 2 replicates was done. The operating conditions of each test are summarized in Table 4. All data necessary to elaborate the mass and energy balance were noted after a period of stabilization of 10 minutes of the plasma and then during the feeding of the solution after the same period allowed to reach steady-state.

Table 4 Operating conditions of the factorial analysis

Fixed Parameters	
atomization gas flow rate , Ar (slpm)	12
central gas flow rate, Ar (slpm)	30
sheath gas flow rate, O_2 (slpm)	90
initial solute mass ratio	0.4
atomizer type	A

Variable Parameters			
Test #	pressure (kPa)	plate power (kW)	solution feed rate (g/min)
1	33.3	50	50
2	66.7	50	100
3	33.3	30	50
4	66.7	30	100
5	33.3	50	100
6	33.3	30	100
7	66.7	50	50
8	66.7	30	50

To analyse the off streams generated during the tests, mass spectrometry and chromatography was used. The off gas of the process were analysed on-line by a mass spectrometer which was calibrated with external standards. The concentrations of O_2, CO_2 and Ar were obtained with a relative error on volumetric composition of 4%. However, it was not possible to evaluate the amount of water entrained with the off gas. The hypothesis of saturated gas was made to complete the characterization of the off gas. To complete mass balances, a sample of the collected liquid was analysed by gas chromatography. Normalized calibration with external standards was used at four levels and relative error of 8% is obtained.

Another important aspect of the treatment of toxic wastes is the specific energy requirement of the system. To evaluate this property, experiments were done at a power level that allows to reach a maximum flow rate of complete destruction. To evaluate the minimum energy required the atomization quality was improved by the utilization of the type B atomizer, optimum conditions identified from the factorial analysis were used, quartz lining was placed in the first part of the reactor and oxygen was used as atomizing gas.

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Table 5 Operating conditions of the parametric study

parameter	value
pressure (Torr)	150
power (kW)	13.8
quartz lining	in the first section
atomizer type	B
atomization gas flow rate, O_2 (slpm)	12
initial solute mass ratio	0.6

Results and Discussion

The factorial analysis was performed using the type A atomizer. A reproductibily analysis of the results, summarized in table 6, determined that the variation of DRE is ± 4.8%. The variance analysis on the DRE was based on the IBM software TECH-ED STATPAC version 2.23. It showed, with at a confidence level of 99%, that both increase of pressure and feeding rate reduces DRE and that plate power favours higher DRE.

Table 6 Results of the water mass balance and DRE of the factorial analysis

Test #	deviation from 100%		DRE %	
	test	replicate	test	replicate
1	-12.7	11.7	95.2	94.2
2	0.1	-10.4	77.7	75.8
3	-3.7	33.6	78.4	88.3
4	-3.4	-2.2	71.7	60.3
5	-4.3	-5.9	89.9	94.7
6	-9.8	-4.5	80.4	76.7
7	0.1	-10.5	87.9	86.4
8	-7.6	-16.4	80.1	77.1

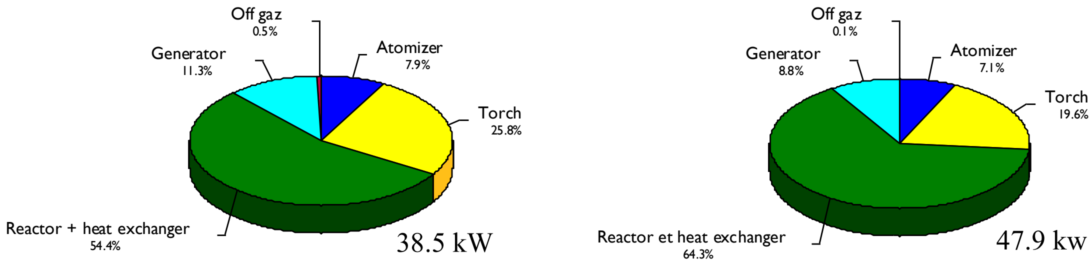
mean deviation	*2.87*
standard deviation	*11.3*

Energy balances (summarized in table 7) and the evaluation of the efficiencies in each operating condition studied was also done. The torch efficiency was on average 72% and global efficiency was 49%. A reproductibily analysis determine that variation of the torch and global efficiency are 2.2 and 3.7 % respectively. A variance analysis of the efficiency, using the same software, determined that only pressure reduces both efficiencies.

Table 7 Results of the energy balance of the tests of the factorial analysis

Test #	Electrical Input	Reaction Energy	Energy recovered	Energy balance
	$A = I_pV_p$ (kW)		C (kW)	(C+B)/A*100
1	50	-5.71	43.83	76.2
2	50	-10.19	50.08	79.8
3	30	-4.77	27.96	77.3
4	30	-9.61	33.15	78.5
5	50	-11.40	49.70	76.6
6	30	-10.13	31.63	71.7
7	50	-5.66	43.56	75.8
8	30	-5.24	28.39	77.2
			mean balance	76.6
			standard deviation	2.22

The deviation of the energy balance from 100% might be partially explained by the hypothesis there was no energy lost to the environment during the treatment. The energy balances were also used to study the energy distribution in the system. Calculation of the energy recuperated in the cooling water of the different parts of the system was performed. It can be seen from the following figure that the energy of the exothermic reaction (10 kW, in this example) was almost completly recovery and mainly in the reactor and heat exchanger.



a) b)

Figure 5 Distribution of the energy in the system a) before feeding and b) during feeding of a plasma system operated at 50 kW and 100 g/min of 0.4 wt solution.

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From a comparison of the energy recovered in the cooling water during the treatment with that recovered without the feeding, it was possible to account for 94% of the exothermic energy of the decomposition reaction over all the tests. An example of calculation is presented in the following table.

Table 8 Energy recovered in cooling water before and during feeding for test #4

	cooling water kW		supplementary
	before feeding	during feeding	kW
atomizer	2.34	2.66	0.32
torch	7.40	6.78	-0.62
generator	2.75	2.86	0.11
reactor, heat exchanger	11.52	20.85	9.33
		sum	9.14
		theoritical reaction energy	9.61
		recuperation %	94

The DRE obtained during the experiments of the factorial study were in the range 80-85%. To increase the efficiency of destruction, the atomization quality was improved by the use of the type B atomizer. The reproduction of few tests, test #1 and #5, presented in table 5, demonstrated that it was possible to reach complete destruction with good atomization. The rest of the experiments was carried out using the type B atomizer.

Table 9 Analysis to compare the atomizer

Test #	DRE %
1	96.7
5	100

Complete destruction was then known to be possible and it was essential to determine what was the energy required by this process. Experiments performed with the type B atomizer, at plate power of 14 kW, showed that at this level, the limit of the system was reached, as shown on the figure 6. An increasse of plate power level to 50 kW, demonstrated that at this plate power, it was not possible to reach a feeding rate, limited by stochiometric oxygen, at which the DRE is not 100%.

Figure 6 Influence of feeding rate on DRE for different plate power

Based on the hypothesis of a linear relation between feeding rate and DRE, it was possible to determine that the limit of complete destruction at 14 kW was 46 g of solution min^{-1}. It was possible to determine from this feeding rate that only 4.6% of the plate power was useful to the treatment. In fact, as shown by figure 7, 0.21 kW was used to heat ethylene glycol to the vaporization temperature (1.6%) and 0.42 kW was used to vaporize it (3.0%). Then, only 0.63 kW was used out of the 13.8 kW coming from the generator. Heating and vaporizing of water, for example, also used energy 4.9 kW (35.5%) but it was not necessary to the treatment. Considering that the real electric consumption of the system is about twice the plate power, the useful energy drop from 4.6% to 3%, which is quite low. Finally, the specific energy of consumption was, from those results, 8.33 kWh kg^{-1} of ethylene glycol, in compararison to the theoritical energy requirement of 0.38 kWh kg^{-1} for the decomposition of pure ethylene glycol and 3.35 kWh kg^{-1} when the mass fraction is 0.6.

Figure 7 Energy utilization during the treatment

Summary and Conclusion

The potential of rf plasma for the treatment of toxic waste was demonstrated by the present study. Ethylene glycol, used as a surrogate, was successfully decomposed when fine atomization and optimal conditions were used. Poor atomization may reduces DRE to 80-85%. The factorial analysis performed in conditions of incomplete decomposition (gross atomization) indicated that both pressure and feeding rate reduce the DRE and that plate power favours higher DRE. A variance analysis on the torch and global efficiencies showed that only pressure reduces efficiencies. No interaction was detected between the three parameters studied for influence on DRE and efficiencies.

The results from these experiments also demonstrated that the energy liberated by the exothermic reaction was available to the treatment. In fact, 94% of the energy of reaction was dissipated in the cooling water. Using a low plate power fo 14 kw, it was also possible to demonstrate that only 4.6% of the plate power was efficiently utilized and that the specific energy consumption of the system was 8.33 kWh kg^{-1}, compared to 0.38 kWh kg^{-1} for the theoritical energy requirement of pure ethylene glycol and 3.35 kWh kg^{-1} when the mass fraction is 0.6. Those results demonstrates that the presence of water influence the energetic efficiency of the system and that the energy consumption of the system was higher than the value of 4 kWh kg^{-1} obtained by [6] and [11]. Concentrated wastes could then be treated more efficiently in consequences of the reduction of the energy used to heat and vaporized water.

Further works consider the use of an optical technique to characterize the atomization and to determine le lower limit of spray size that produces good results. In this manner, no more energy than needed will be put on optimizing atomization. It would also be essential to improve the energy transfer efficiency of the rf plasma torch to increase the specific energy consumption.

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