# Development of a New Thermal HF Plasma Reactor for the Destruction of Radioactive Organic Halogen Liquid Wastes

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## ABSTRACT

A newly patented process employing thermal plasma for destruction of radioactive organic halogen liquid wastes is proposed. This studied safe system can destroy a great variety of wastes, even mixed together, using plasma torch as high temperature source. At the exit of the process, only non-toxic products are formed as atmospheric gases, liquid water and halogen sodium salt. The process has been built with the help of thermodynamic and kinetic simulations. A good atomic stoichiometry is necessary for avoiding the formation of solid carbon (soot) or toxic $COCl_2$. That why liquid water is added to the waste in the plasma flow. Then, an introduction of air cools and dilutes the formed gases and adds oxidant agent achieving oxidation of explosive $H_2$ and toxic CO. Due to the high concentration of hydrochloric acid, an efficient wet treatment using soda traps it. Subsequently, the exhaust gases are only composed of Ar, $O_2$, $N_2$, $CO_2$ and $H_2O$. In the first experimental step, pure organic molecules, mixed or not, without halogen have been destroyed. The experimental results show that all the compounds have been completely destroyed and only $CO_2$ and $H_2O$ have been formed without formation of any toxic compound or soot. After these encouraging results, chlorinated compounds as dichloromethane or chloroform have been destroyed by the process. In this case, the results are close to the previous one with an important formation of hydrochloric acid, as expected, which was well trapped by the soda to respect the French norm of rejection. A specific parameter study has been done with dichloromethane for optimising the operating condition to experimentally observe the influence of different parameters of the process as the stoichiometry ratio between waste and water, the air addition flow, the waste flow. The final aim of this study is to develop a clean process for treatment of radioactive organic halogen compounds. A small scale reactor is being studied to prove the capability of the process for radioactive organic halogen liquid waste.

## INTRODUCTION

Due to the industrial development in high technological societies, the quantity of generated wastes constitutes a problem that must be treated at an industrial scale. If global solutions are already operated for domestic wastes, special destruction facilities are required for special industrial wastes such as chemical products. If well-working industrial solutions for common

wastes exist, specific high stability products have no satisfactory treatment solution. Destroying them requires high energy process.

The destruction of wastes, which cannot be easily and safety recycled, can be accomplished by combustion if these wastes do not present high temperature stability and do not produce toxic off-products after burning. The environmental pollution by by-products, such as ozone-depleting-gas, greenhouse effect gases or dioxin, must be considered initially at the earlier conception of the process and by controlling continuously the off gases. That is why thermal plasma processes can be used: they present a high-energy power and a great adaptability. They have been first applied for vitrifying fly ashes from domestic waste incinerators, for example, with the EUROPLASMA process. Another application concerns also asbestos vitrifying by the same process. State of the art shows many thermal plasma processes destroying gases or vitrifying solid wastes. After solids, the second application has been to destroy gases such as ozone depleting gases. For example, the PLASCON process has been developed to remove chrolofluorocarbons (CFC) but also liquids such as dichlorophenoxyacedic (2-4 D) or oils contaminated by polychlorobiphenyl (PCB). In Japan, NIPPON STEEL CORP. has built another plant to remove CFC.] Other research papers have been proposed using different kind of plasma.[5]

These problems are more serious for radioactive wastes because of their own specificities. They require the highest level of control for not releasing radioactive elements to the environment. For these reasons, development of a new process working with thermal plasma gun is here proposed with several goals. It has to constitute a clean opportunity for destroying radioactive organic halogen wastes, pure or in mixture. It has to present a high efficient rate of destruction, a control of recombining atoms for only environment-friendly off-gases and toxic product trapping. Finally, it has to be compact and safe for working in nuclear fields. Inductive plasma torch technology presents both interests of using a wide range of gases and the opportunity of introducing compounds-to-destroy directly inside the torch, in the highest temperature zone and that, without any gun material degradation.

The paper presents the different steps of development, design and operating experiments of this facility.


**PRELIMINARY STUDIES**

For defining and building a new process, preliminary studies by numerical simulation can accelerate design and development. They can also define operating parameters by testing different conditions. So, firstly, thermodynamic studies help to define the temperatures needed to obtain the desired reactions. But they can't estimate the time life required and so the global reactor design. So, next step consists in kinetic reaction studies with dynamic flow works for estimation of time needed for both the product destruction and atom recombination. In this case, the temperature evolution in the reactor must be previously known.

To realize this preliminary study, a test compound must be first chosen to represent organic halogen liquid waste. Because it is used in many applications and presents a relatively high

stability and toxicity, dichloromethane, $CH_2Cl_2$, has been selected. Furthermore, the presence of only one carbon simplifies the reaction mechanisms.

**Thermodynamic studies**
The computation code used, ALEX, calculates the gas composition at thermodynamic equilibrium versus temperature. This code is based on fundamentals of equilibrium thermodynamic: minimisation of Gibbs energy for closed insulated system, minimisation of free enthalpy, energy conversion law and electrical neutrality. Then, the complete gas composition at different temperatures, and pressures and thermodynamic parameters as mass enthalpy can be determined.

The initial data needs for the calculation are: the atoms present in the considered system, the resulting species which could be formed with this atoms, enthalpy and entropy of all the species. Aims of the thermodynamic studies are:

- Minimising the presence of noxious CO by favouring $CO_2$ formation;
- Minimising toxic $Cl_2$ generation by encouraging the formation of hydrochloric acid;
- Favouring the water formation;
- Minimising the presence of the neuron-toxic phosgene, $COCl_2$, of other organic compounds and of solid carbon that can trap radioactive elements and be a good catalyser for the formation of new toxic compound.

The temperature calculation range is 500 to 5000 with increments of 20K. In first time, the pressure is fixed at 1 bar. 10 moles of argon and 1 mole of dichloromethane are added to variable quantity of oxygen, hydrogen or water from 0 to 10 moles each. Only argon plasma has been studied even if air plasma is cheaper. In fact, air plasma is not a good choice because of the high level of temperature that can encourage NOx formation. As inert gas, argon does not react with other injected products.

If only argon and dichloromethane are mixed at high temperature, there is formation of soot and organic compound as methane, $CH_4$, and so on. When oxygen is added, it favours the $CO_2$ and $Cl_2$ formation. So keeping oxygen quantity at 1 mole for avoiding soot, the influence of hydrogen is tested. The hydrogen addition favours the CO formation, the $CH_4$ formation at low temperature (<1000 K) and soot at low quantity of hydrogen; but it also decreases the $Cl_2$ concentration by stabilising chlorine onto hydrochloric acid form. So both oxygen and hydrogen are useful for controlled recombination. The addition of both atoms has been studied using a linked stoichiometry: water. The increase in water quantity favours $CO_2$ formation by decreasing that of CO. Cl is stabilised on HCl form for all water quantity added. There is no formation of soot when enough water is added but at low temperature (<1500 K) methane is formed if not enough water is injected. It can be avoided too by a fast gas cooling. To obtain complete reaction, an over stoichiometry of water is required. Then, the influence of the pressure, in the range of 0.1 to 10 bars, is examined and there is quite no modification of the reaction for all the pressure tested. There is just a slight increase in $COCl_2$ with the increase in pressure. So, pressure is not a significant parameter of the reaction.

So, the following operating conditions are taken out from the thermodynamic study:

- Argon must be in excess to approach inert mixed gases;
- 4 moles of water must be added for 1 mole of dichloromethane;
- Pressure should be just under atmospheric pressure for safety reasons (avoiding leak);
- Gases must be rapidly cooled after reacting.

Hydrogen increases significantly the plasma enthalpy at high temperature (>1500 K). This atom is already introduced in the mixed gas with water. So it will not change notably any reaction if more hydrogen is added to the plasma. So to increase plasma temperature (as the electrical power remains constant), $Ar/H_2$ mixture may be used.

**Temperature effect**

For kinetic works, the effect of the temperature versus time must be known: this curve is in connection with the temperature and the position time of each species moving though the first stage of the reactor. The reactor has been modelled by a C.F.D. (Computational Fluid Dynamics) code: ESTET. The plasma temperature in the reactor axis has been determined versus time with only gas flow and no charge. A correction must be taken into account when liquid products are introduced in the reactor. Both system compositions and specific enthalpies, with and without charges, are calculated versus temperature supposing LTE (Local Thermodynamic Equilibrium). After that, supposing the total specific enthalpy conservation to both systems (they have the same main enthalpy source: plasma torch energy), the two curves are connected through the specific enthalpy. Then, it can be observed that the plasma gas and the liquid product temperature increase to a maximum above 5000 K in about $2 \cdot 10^{-4}$ s. After that, the temperature slowly decreases to 2500K in about 0.56s.

**Kinetic model**

The chemical reaction kinetic has been determined with the code C3GAZ developed for combustion or pyrolysis. It can study systems at constant pressure and variable temperature versus time, in a piston flow.

The operating conditions defined by the previous thermodynamic study and the temperature evolution in the reactor have been used for the kinetic simulation. The mass flow of the mixture (product and water) is 17.5 g/min.

The kinetic results show that:

- The chemical reactivity is very important: dichloromethane drastically decreases in less than $10^{-7}$ s and totally disappears in $2 \cdot 10^{-2}$ s.
- Some chemical species containing C, H and Cl atoms appear during the reaction but disappear with the temperature decreases.
- The toxic molecules as phosgene, $COCl_2$, or $COCl$ are absent (concentration less than $10^{-6}$).
- At the end of the stage, stable species with two or three atoms as $H_2O$, $CO_2$, $H_2$ and HCl, are present but there are also some less stable and toxic species as H, O, CO and Cl present due to high temperature.

The reactor design seems to be efficient to obtain the wanted reactions. They are all initiated but not still completely achieved. The gas should be cooled with oxidant agent to limit the presence of non-stable molecule at room temperature.

**Synthesis of model studies**
The high temperature, allied with a relative long time life (less than 1 s) of the products in the hottest zone, leads to vaporization and complete break up of the molecules, even the most stabilized one, in elementary atoms. The molecular flow rates of the two liquid (products and water) are in correlation such as the carbon and halogen atoms from products and the oxygen and hydrogen atoms from water can react following the reaction:

$$C + 2O \leftrightarrow CO_2 \qquad \text{(Eq. 1)}$$
$$Cl + H \leftrightarrow HCl \qquad \text{(Eq. 2)}$$

An excess of water can saturate the previous reaction but diminishes the temperature in the hot reaction zone.

## MATERIALS AND METHODS

**Process Description**
Short description of the process is presented here due to an in-progress-patent. Inductive plasma torch, PL 50 gun from TEKNA Inc., working with argon/hydrogen mixing, transforms the electric energy into mainly thermal energy at the head of the reactor (Fig. 1). It is a double-flux gun working with argon as primary gas and argon/hydrogen as sheath gas. The gases are ionized at high temperature (more than 12 000 K) as thermal plasma and flow inside the reacting chamber. Wastes and water are introduced in the plasma plume at the head of the reaction chamber. The reacting chamber, where molecules are destructed, presents an appropriate design to avoid cold areas, with a refractory wall. At the end of the destruction zone, an air introduction accelerates and achieves the molecule oxidation. Then a recombination stage ends the chemical reaction. After complete reactions, the off-gases are cleaned in a wet treatment unit using soda to trap halogen atoms. Then, the gases are cooled by a heat exchanger before evacuation to the atmosphere by pump. The pump has another goal: regulating the inside pressure in the process by slight depression to avoid leak.

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                          ┌──────────────────┐
                          │  Waste and water │
                          │    injections    │              Plasma gas
                          └──────────────────┘

  ┌──────────────────┐    ┌══════════════════┐
  │ Electrical Power │────║  Inductive torch ║
  └──────────────────┘    ║                  ║
                          ║   Destruction    ║
  Air introduction ⇒      ║      And         ║────►  ┌──────────────┐
                          ║  Recombination   ║       │ Cooling water│
  ┌──────────────────┐    ║     Stage        ║       └──────────────┘
  │ Mass spectrometer│◄───║                  ║
  └──────────────────┘    └══════════════════┘

                          ┌──────────────────┐
           Soda ⇒         │ Halogen treatment│⇒ H₂O
                          │      unit        │⇒ NaCl
                          └──────────────────┘

  ┌──────────────┐
  │ HCl analysis │◄──
  └──────────────┘         ┌──────────────────┐
                           │  Heat exchanger  │
                           └──────────────────┘

                           ┌──────────────────┐
                           │      Pump        │
                           └──────────────────┘

                                Off gases
                           Ar, N₂, O₂, CO₂, H₂O
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Fig. 1.  Simplified set-up of the process

Short description of the process is presented here due to an in-progress-patent.  Inductive plasma torch, PL 50 gun from TEKNA Inc., working with argon/hydrogen mixing, transforms the electric energy into mainly thermal energy at the head of the reactor (Fig. 1). It is a double-flux gun working with argon as primary gas and argon/hydrogen as sheath gas. The gases are ionized at high temperature (more than 12 000 K) as thermal plasma and flow inside the reacting chamber. Wastes and water are introduced in the plasma plume at the head of the reaction chamber. The reacting chamber, where molecules are destructed, presents an appropriate design to avoid cold areas, with a refractory wall. At the end of the destruction zone, an air introduction accelerates and achieves the molecule oxidation. Then a recombination stage ends the chemical reaction. After complete reactions, the off-gases are cleaned in a wet treatment unit using soda to trap halogen atoms. Then, the gases are cooled by a heat exchanger before evacuation to the atmosphere by pump. The pump has another goal: regulating the inside pressure in the process by slight depression to avoid leak.

**Operating parameters**
The main operating parameters are collected in Table I. Argon and hydrogen, for increasing the gas enthalpy, are introduced in the torch to generate the thermal plasma. Due to the rather bad thermal efficiency of inductive gun, less than 50% of the electrical power is transferred to the gases at the torch exit. The target wastes are collected in Table II. The water/carbon ratio and oxidation ratio (real air flow/stoichiometry air flow ratio) present for all experiments are resumed in Table III with the liquid flow rate. The non-chlorinated mixed liquid contains 1,4-dioxane, ethanol, methanol and acetone by order of importance.
After starting the process and controlling the well working conditions, the injection of liquid product can begin. Before and after each product injection, water alone is introduced for cleaning the injection system and the reactor.

Table I.  Operating Parameter of the Process

| Parameters | Values and units |
|---|---|
| Argon central flow rate | 30-32 slpm |
| Argon sheath flow rate | 98-106 slpm |
| Hydrogen sheath flow rate | 7 slpm |
| Plate power | 41-45 kW |
| Pressure | $0.9 \cdot 10^5$ Pa |
| Additional air flow rate | 100-260 slpm |
| Initial soda concentration in treatment unit for chlorinated products | 10-36 g/l |

At the end of experiments, the plasma is stopped by decreasing the power after closing $H_2$ addition. Then, the different stages of the process are cooled with an important air flow during most of the time more than two hours. This time is enough long due to the cooling of the refractory which has stocked up heat during experiment.

**Analysis materials**
Several thermocouples measure the gas temperature to manage the process. For example, before and after air injection, they control the well-done oxidation reactions. The temperatures of the water for cooling the reactor are measured before and after every process elements.

Table II.  Properties of Injected Products

| Product | Formula | Structure | Molar mass (g/mol) | Density |
|---|---|---|---|---|
| 1,4-dioxane | $C_2H_8O_2$ | | 88.11 | 1.03 |
| acetone | $C_3H_6O$ | | 58.08 | 0.79 |
| chloroform | $CHCl_3$ | | 119.38 | 1.49 |
| dichloromethane | $CH_2Cl_2$ | | 84.93 | 1.32 |
| ethanol | $C_2H_6O$ | | 46.07 | 0.81 |
| methanol | $CH_4O$ | | 32.04 | 0.79 |
| methyl-iso-butyl ketone | $C_6H_{12}O$ | | 100.16 | 0.80 |
| n-butyl alcohol | $C_4H_{10}O$ | | 74.12 | 0.81 |
| n-dodecane | $C_{12}H_{26}$ | | 170.34 | 0.75 |
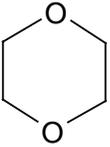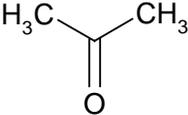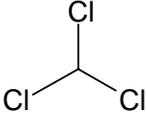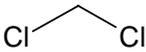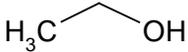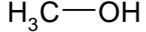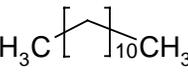
Gases are online analysed at the end of the reaction zone, after air introduction, by a mass spectrometer type MONISTAR GSD 300 C2 from PFEIFFER VACUUM. The gas composition is then explored with a quadrupole analyser using a Faraday collector. The results appear as the current intensity peaks for each atomic mass. The scale of atomic mass, between 0 to 100 or 200 of atomic mass unit, is adapted to the injected product. A post-treatment of the spectrograms compares the different curves with the experimental parameters. So estimating the gas concentration from the real flow of the non-reacting gas (argon or nitrogen for example) is possible to get mass balance but not very accurate.

Before exhausting to the atmosphere, gaseous HCl concentration measurements are realised with an analyser LASERGAS 2000 from NEO MONITORS. This analyser is based on the absorption spectroscopy of infrared laser light.

Experimental parameters are recorded every two minutes except for the HCl concentration which is automatically recorded every 30 seconds.

Table III. Injection Parameter for Experiments

| Product | Product flow (g/min) | Water flow (g/min) | $H_2O/C$ ratio | Oxidation ratio |
|---|---|---|---|---|
| 1,4-dioxane | 3.56 | 10.20 | 4.00 | 4.50 |
| acetone | 2.89 | 9.87 | 4.00 | 4.47 |
| ethanol | 4.13 | 9.64 | 3.49 | 3.21 |
| | 3.50 | 8.16 | 3.49 | 7.78 |
| | 8.90 | 20.76 | 3.49 | 4.46 |
| | 6.59 | 7.73 | 2.00 | 5.60 |
| methyl-iso-butyl ketone | 2.22 | 20.10 | 8.56 | 5.18 |
| n-butyl alcohol | 2.01 | 17.70 | 9.32 | 5.60 |
| n-dodecane | 1.83 | 22.71 | 9.79 | 5.03 |
| mixed non-chlorinated liquid | 1.10 | 10.57 | 13.24 | 6.36 |
| chloroform | 12.95 | 11.04 | 5.65 | 5.51 |
| dichloromethane | 15.81 | 17.01 | 5.08 | 4.10 |
| | 26.90 | 7.88 | 1.38 | 2.83 |
| | 18.72 | 9.78 | 2.47 | 3.67 |
| | 25.32 | 19.97 | 3.72 | 2.96 |
| | 25.32 | 19.97 | 3.72 | 2.07 |
| | 18.88 | 19.14 | 4.78 | 3.28 |
| | 18.88 | 19.14 | 4.78 | 1.82 |
| | 24.12 | 19.22 | 3.76 | 3.07 |
| | 18.17 | 18.59 | 4.83 | 3.74 |

**Non-Halogenated Organic Molecules**
In the first stage, just before air addition and without liquid injection, the gas temperature rises up to around 1200 °C (first curve of Fig. 2a), when the thermal equilibrium is steady. This temperature, measured quite far from the plasma torch, is in good agreement with simulation results.**Error! Reference source not found.**] Consequently, the high upstream temperature is efficient to destroy completely the wastes. Several injections have been carried out in the same test leading to a rather long test duration showing therefore the good process stability.

The only water introduction into the plasma induces temperature drops due to molecular decompositions at the first step of the temperature measurement. The introduction of non-halogenated organic product and water mixture in the process presents the same temperature evolution as only water one for the same global flow rate. After the injection end, the plasma has been stopped, after more than 5 hours working. Then, the gas temperature decreases rapidly first then more slowly in a second time. This effect is due to the energy stored in the refractory wall which is released gradually.
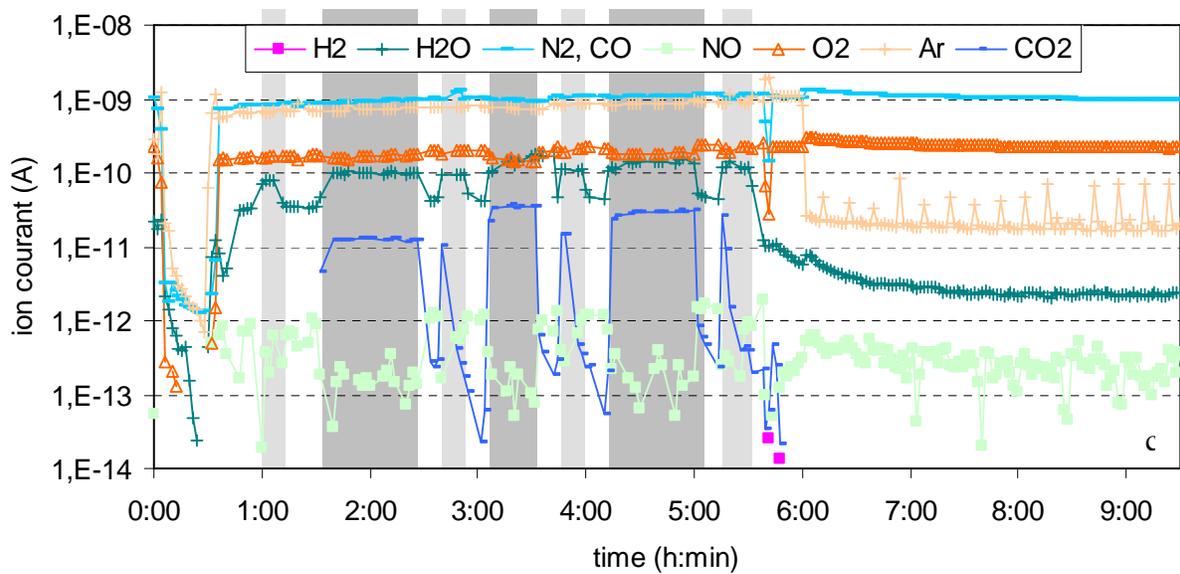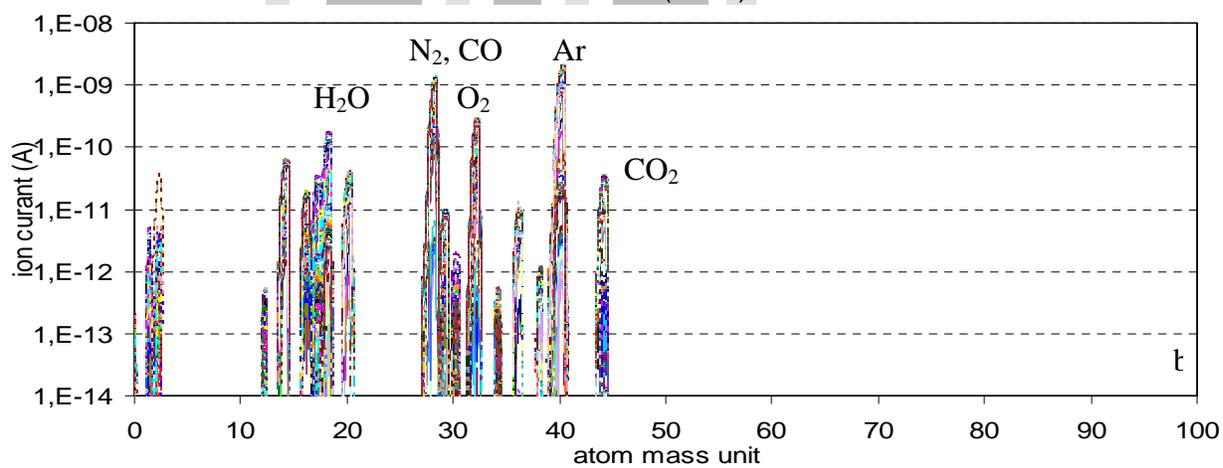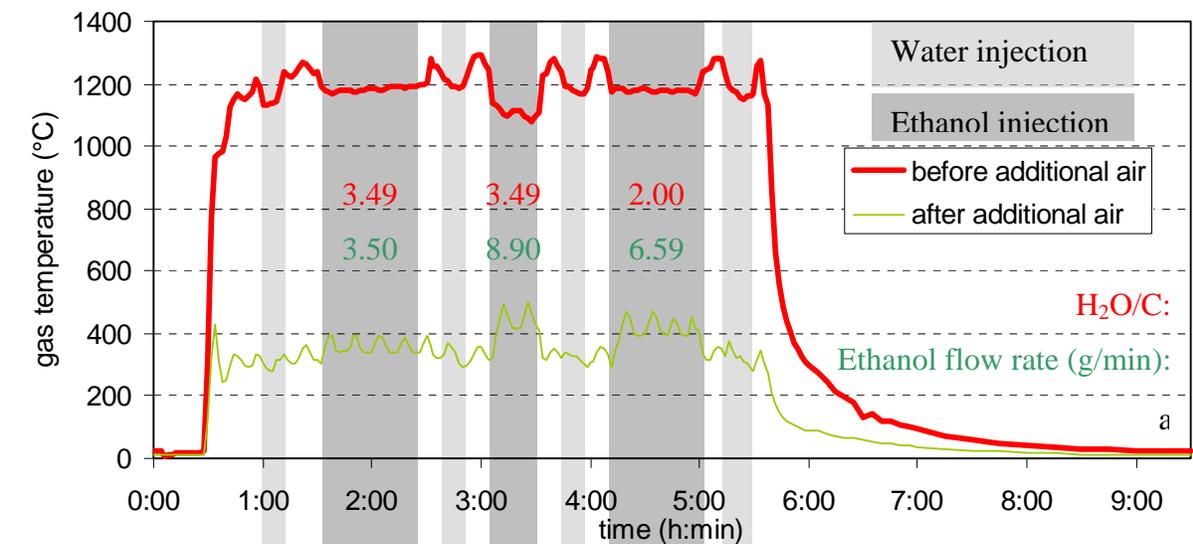
Fig. 2.  Gas temperature (a) and gas composition during ethanol injection experiment (b) and temporal evolution of gas composition (c).

After air introduction stage and still without liquid injection, the gas temperature rises up to nearly 400 °C (second curve of Fig. 2a). This curve has the same trend than the previous one with different amplitudes without or with water injection. But during organic product introduction, a significant increasing of temperature can be observed despite the temperature drop before air addition. This brings to the fore the exothermic reaction of oxidation of residual CO and $H_2$. After molecular recombination, the mass spectrometer analyses show the presence of only simple and non-toxic molecules: Ar, $N_2$, $O_2$, $CO_2$ and $H_2O$ (Fig. 2b). In all experiments, the initial organic molecules have never been detected by the spectrometer. Then, the destruction and removal efficiency must be very high (close to 100 %) but not quantifiable.

The maximum intensities of peak representing the inert gas (Ar, $N_2$) remain constant during plasma working. The other detected gases have a significant time evolution corresponding to the different phases of the experiment. Focussing on $H_2O$ curve, the quantity of steam increases notably when water, alone or not, is injected and decreases when injection stops. About $CO_2$, its quantity increases drastically during the organic compound injection and at the beginning of the following water injection due to pipe cleaning. At the other time periods, the intensity of the $CO_2$ peak is very slight. Associated to the $CO_2$ peak evolution, the $O_2$ evolution presents small decrease during organic compound injection (mostly visible in Fig. 2c for the two last ethanol injections). The $O_2$ bringing by air injection is used for the oxidation obtaining CO and $H_2O$. Furthermore, due to similar molecular mass, CO and $N_2$ are plotted together. Because of no significant evolution during organic compound injection, the carbon oxidation reaction seems to be completely achieved. If not, it stays at low level.

For ending, a small decrease of NO peak intensity can be observed during organic compound injection, as if O from NO is used for the oxidation of unstable molecules. Nitrogen oxides have left at low concentration, process working, and so, no nitrogen oxide treatment unit is needful. When air is added, the temperature is not high enough to generate nitrogen contained pollutant. $N_2$ works only as inert gas as argon.

From mass spectrometry analyses and knowing the flow rate of inert gas, a mass balance can be estimated for the carbon. For all experiments with non-halogenated organic compound, between 78 to 97 % of injected carbon is transformed in gaseous $CO_2$. These results are very good especially that there is no real calibration. Besides, no soot layer has been observed in the process after experiment. So the destruction of non-halogenated organic compound by the process has been proved.

**Halogenated Organic Molecules**
The temperature evolution without injection or with only water injection is similar to previous experiments curves. Introducing the halogenated organic compound and water mixture in the process has leaded to a severe temperature drop: the temperature is less than 1000 °C during the product injection (first curve of Fig. 3a).**Error! Reference source not found.**, 10] With the same volume flow rate of halogenated organic compound and water mixture as one of only water, the temperature drop is higher than one during only water injection, due to the endothermic reaction of the hydrochloric acid formation.
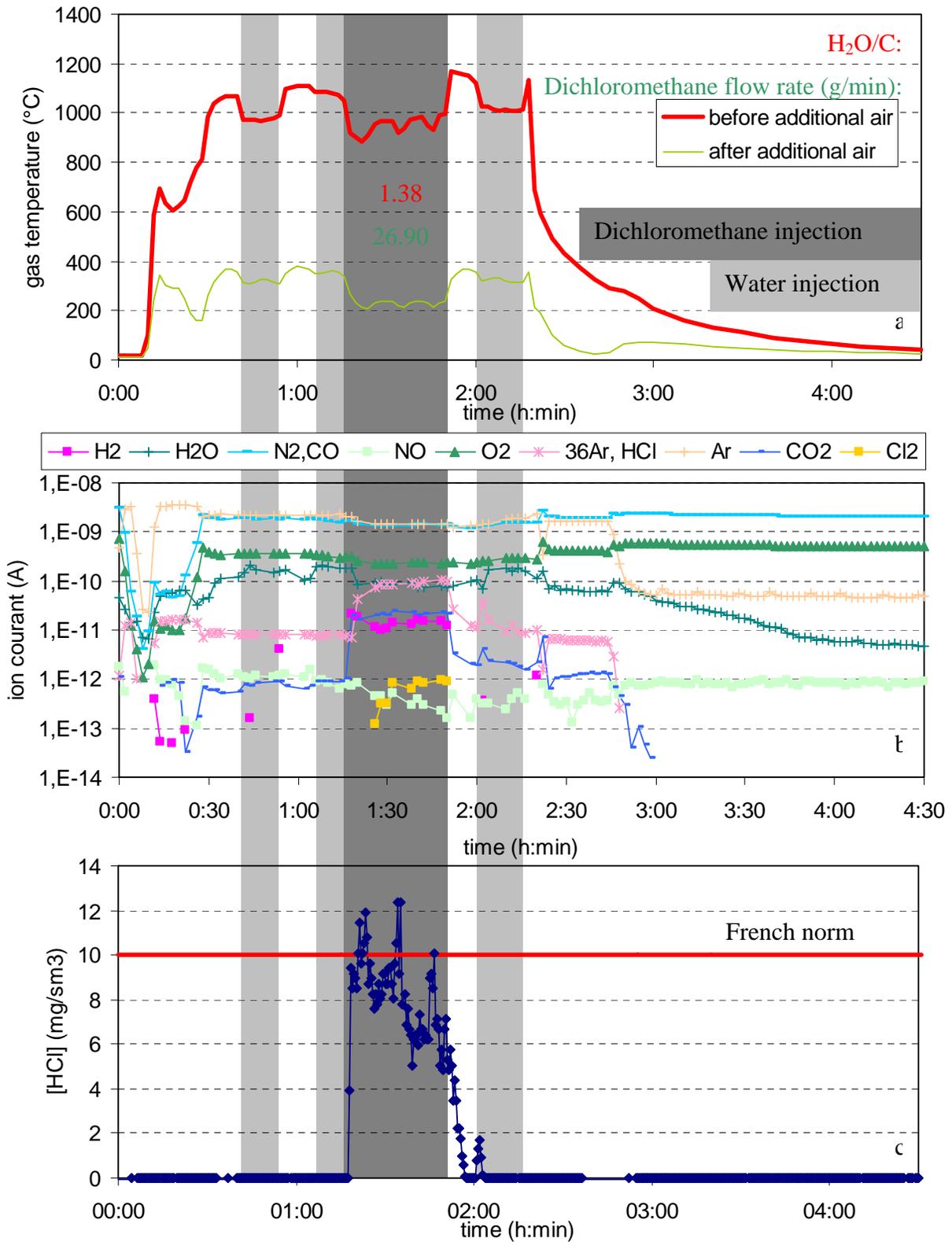
Fig. 3. Gas temperature (a), gas composition (b) and hydrochloric acid concentration ejection into atmosphere (c) during dichloromethane injection experiment.
After air addition, the curve has the same trend than the previous one with less amplitude (second curve of Fig. 3a). In this case, exothermic oxidation reactions are not visible due to the too important drop of temperature before air addition.

After molecular combination, the same elements have been detected by the spectrometer with one more element: HCl, as expected, and sometimes $Cl_2$ can be observed but this latter is always at very low level. The initial products have never been detected by the spectrometer.

The gas composition evolution versus time presents the same tendency for most gases (Ar, $N_2$, $O_2$, $CO_2$, CO and NO) than for non-halogenated organic compound. During chlorinated organic compound injection, there is an increase of HCl as expected. This is observable by the evolution differences between Ar curve and Ar-36, HCl curve which are plotted together due to their similar molecular mass. So, this implies that HCl concentration in the gas has a comparable evolution as $CO_2$. Associated to the HCl concentration increase, a few molecules of $Cl_2$ and $H_2$ have been detected. Their presence is probably due to unachieved reaction before additional air because of relative low temperature or stabilised quantity for this composition of the mixed gas. In opposition to the hydrochloric acid evolution, when it is present, the quantity of steam decreases notably. Assumptions about water deposition by condensation onto cold walls and deposit saturation could be proposed. After air addition, the gas cools down on cold wall. Consequently, there is an important condensation of steam on the reactor wall. When chlorinated organic product is introduced into the plasma, a great HCl formation appears and this gas has a great affinity with liquid water. So, a part of HCl dissolves into the condensed water. When the liquid is saturated by hydrochloric acid, equilibrium is obtained and $H_2O$ and HCl quantities remain stable. A great quantity of liquid highly concentrated in hydrochloric acid has been founded at the bottom of the reactor before halogen trap unit. Then, between 8 to 39 % of the introduced chlorine has been trap in this liquid depending on the experimental conditions. That's confirmed this hypothesis.

The analyses by mass spectrometry can estimate the mass balance of the carbon: between 33 to 96 % of the injected carbon have been transformed in gaseous $CO_2$ for experiment with chlorinated organic compound. The mass balance of carbon in the process can not be managed without any good explanation. In fact some dark particles are found in the process but X ray diffraction analyses do not detect any soot formation: it was mostly metal chlorine compound.

After that, the gas treatment unit has trapped efficiently hydrochloric acid gas and has limited its concentration in the off gases (Fig. 3c). The HCl concentration is quite always lower than 10 mg/sm$^3$ which is the French HCl off gas concentration norm defined for dangerous waste incinerator.**Error! Reference source not found.**] The average of the HCl concentration ejected into atmosphere is between 1.5 to 8.2 mg/sm$^3$ depending on experiment parameters. This low concentration indicates also the well-operating of the gas treatment which traps between 48 to 79 % of the introduced chlorine.

## PROCESS OPTIMISATION

The process has good destruction rate but it has to be optimised. Dichloromethane is used as target waste. The influence of three main input injection parameters (injection flow rate of dichloromethane, water/carbon ratio, real added air/stoichiometric air ratio) on different results has been investigated. For all this optimisation procedure, the plasma conditions are similar.
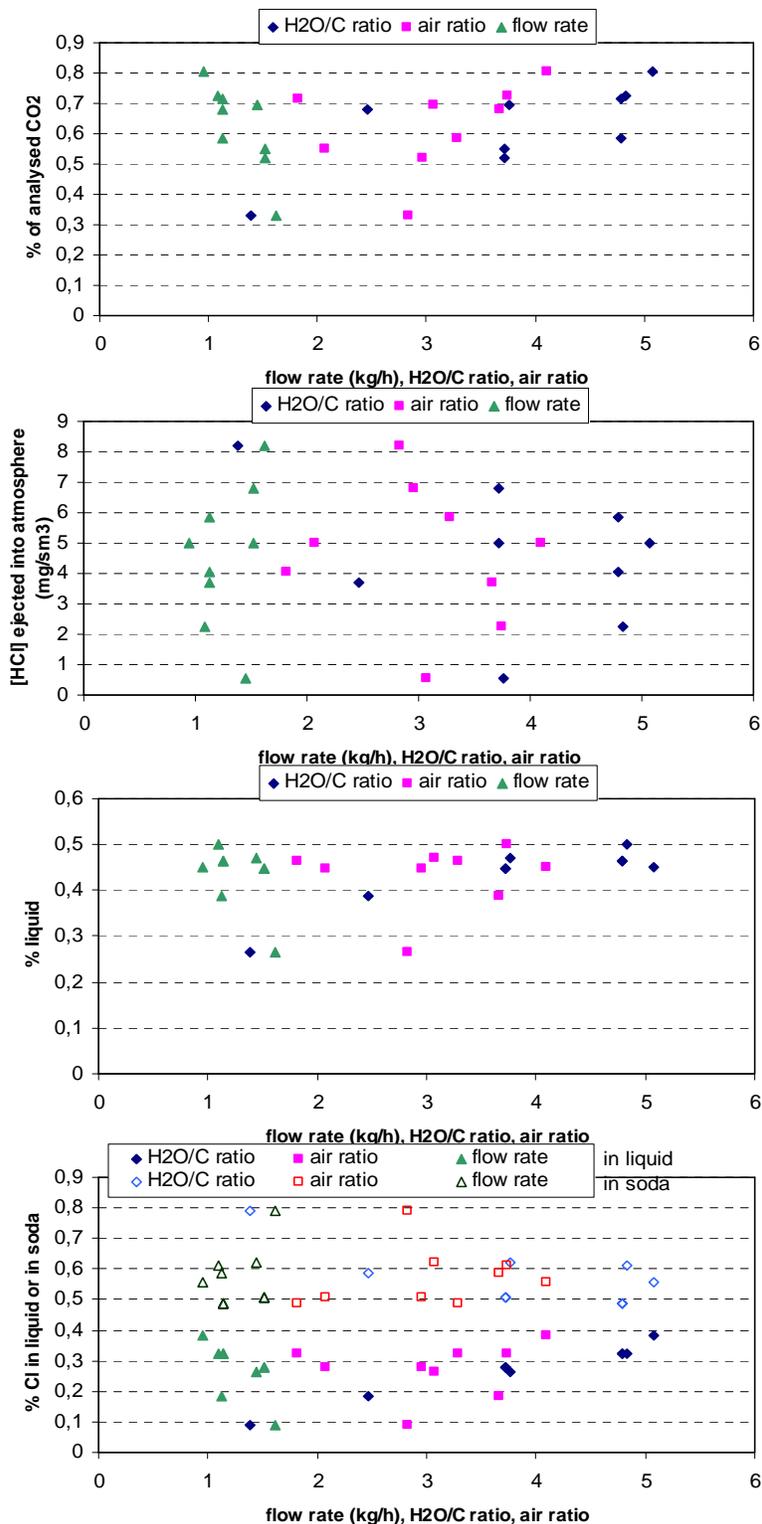
Fig. 4.  Influence of different input parameters on output parameters of the process. All the initial conditions used in the process are synthesised in Table III. The global reaction in the process is set on equation 3 with variable x and y parameters.

$$CH_2Cl_2 + xH_2O + yO_2 \leftrightarrow CO_2 + 2HCl + xH_2O + (y-1)O_2 \quad \text{With } y>1 \tag{Eq. 3}$$
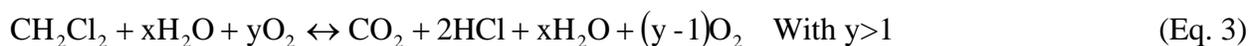
The quantity of $CO_2$ analysed by the mass spectrometer appears not to be dependant on air ratio but links with the injection flow rate and $H_2O/C$ ratio (Fig. 4a). The lower the dichloromethane flow rate is, the higher the gaseous $CO_2$ concentration is. On the other side, the higher the $H_2O/C$ ratio is, the higher the quantity of gaseous $CO_2$ analysed is.

None of the three input parameters are in connexion with the HCl concentration in off gases (Fig. 4b).

On one side, the greater the $H_2O/C$ ratio is, the greater the water condensation (Fig. 4c) and the greater the HCl trapped into water quantity are (Fig. 4d). On the other side, less chlorine is trapped by the gas treatment. The air ratio and the dichloromethane flow rate seem not having a significant importance on the chlorine mass balance.

To conclude, the most important parameter seems to be the $H_2O/C$ ratio to control the mass balance of chlorine. About $CO_2$ analysed by the spectrometer, is seems to be only controlled by the dichloromethane flow rate. The over-stoichiometry air ratio does not seem to have any importance on each output process parameters. Then, it could be reduced close to the stoichiometry without a great incidence on the process. In fact, for the same experimental condition, two air ratios were studied twice. When the air ratio decreases, it can be observable that the gaseous HCl concentration ejected into atmosphere slightly reduces. The gas treatment seems to be more efficiency because of a greater time life of the gas in contact with soda due to the global decrease of gas flow rate. However, all these parameters are linked. A statistical approach should give better tendency specially that there are only few experiments with a large parameters number. This study will be ended afterwards.

**NEW INQUIRY**

The final aim of this study is to develop a clean process for treatment of radioactive organic halogen compounds. A small scale reactor is in study to prove the well-done of the process for radioactive organic halogen liquid waste. These wastes are contaminated by C-14 and H-3. In the first time, the small scale process will be tested with non-radioactive chlorine organic products to validate the scale change. Then, the process will be introduced in a nuclear safe compartment. After that, some nuclear test products will be injected into the process before the destruction of real nuclear wastes.

**CONCLUSION**

As many industrial stable chemical wastes present risks for environment and human being do not have destruction ways, a new process working with thermal plasma gun for destroying organic halogen liquid wastes has been proposed.

With thermodynamic and chemical kinetic reaction studies, and numerical simulation, the different concepts of development have led to a compact, safe and efficient facility which can accept organic halogen liquid wastes, pure or in mixture. The by-products are only innocuous gases, with low $CO_2$ concentrations, and mineral salts, such as NaCl, trapped in a specific treatment unit.

Next step consists to introduce radioactive wastes but implies the development of the facility with the nuclear specific security requirements.

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