The Elipse Process An underwater plasma technology for hazardous organic liquid treatment

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THE ELIPSE PROCESS: AN UNDERWATER PLASMA TECHNOLOGY FOR HAZARDOUS ORGANIC LIQUID TREATMENT

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Abstract

Hazardous liquid organic wastes are very various and produced in different quantities. Some of them are treated through specific processes when others are still waiting from outlet to be destroyed and stabilized. Their different composition (chlorinated, phosphate, sulfated, fluorinated …) make their treatment difficult by the same technology.

The ELIPSE process has been designed to propose an innovative solution leading to a global treatment of what is usually called “orphan liquids”. This brand new technology involved a non-transferred plasma torch working under a water column ensuring the cooling, the filtration and the scrubbing of the gases coming from the combustion of the liquids. Furthermore, the water that ensures the global cooling of the system leads to low or to no corrosion in a compact process. Only the nozzle of the torch may be affected by the corrosion and may become a wearing part of the treatment system.

After giving a detailed description of the ELIPSE process, the present paper will focus on the results obtained for the treatment of such different liquids as tributyl phosphate, perfluorinated oil and trichloroethylene. In addition to obtaining destruction efficiency upper than 99%, the corrosion of the reactor seems to have been significantly limited. These features lead to the first conclusion that the ELIPSE process could be a solution for the future to the problem of the hazardous liquid treatment.

Furthermore, if the main objective of the ELIPSE process is the destruction of hazardous waste through instantaneous combustion in oxygen plasma, their gasification could be envisaged through argon and/or water plasma in order to produce Syngas for energy recovery.

1- INTRODUCTION

To incinerate liquid waste with an organic fraction of nearly 100%, the oxidation potential of a plasma torch operating with oxygen was combined with the concept of a submerged plasma jet. The advantage of submerged thermal plasma treatment is the very high temperature obtained in an overall cold reactor, which limits corrosion problems; the high concentration of oxidizing radicals in the oxygen plasma and the intense UV radiation allow almost instantaneous combustion of the organic matter. Recombination reactions are minimized by rapid quenching. Turbulence induced in the water by the plasma jet ensures satisfactory gas-to-liquid transfer and trapping in solution of the waste mineral fraction liable to contain radionuclides. In this operating mode, the solution not only maintains

the process at the ambient temperature but also ensures most of the functions of an off-gas treatment system: cooling, filtration and neutralization.

This process can also be used to gasify organic liquids using argon or possibly water vapor as the plasma gas. In this case, the very high temperatures in the plasma nozzle will limit the amount of soot and tars formed which will be quenched in the water. Afterward, these soots and tars could be reinjected in the plasma torch in order to upgrade their gasification.

2- MATERIALS AND METHODS

The concept of the ELIPSE process consists of implementing a plasma torch at the bottom of a reactor full of water. When organics are fed in the hearth of oxygen plasma, they burn in the nozzle of the torch and form off gases being quenched in the water.

In this way, water is used as off gas treatment: It cools, filters and scrubs the gases. Gas treatment is then replaced by a water treatment system involving a heat exchanger and a filtering system. The pollutants concentrating into the water are likely to precipitate depending on their concentration. They are then recovered thanks to the filter and can be driven toward a cementation or vitrification facility.

In this operating mode the solution not only ensures the gas treatment but maintains the process at the ambient temperature. This is important and pioneering provision to prevent corrosion.

The concept of the process is shown in figure 1.

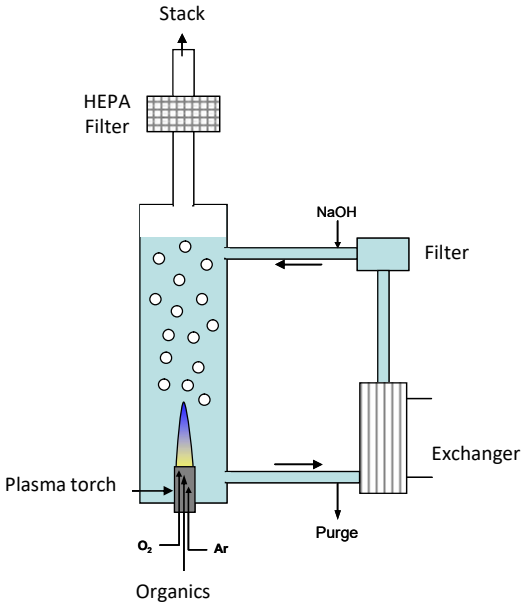

Figure 1: The ELIPSE Process

The design was validated by tests as shown in Figure 2 where one can see plasma working under a water column. A mockup has been built at the Marcoule center in order to assess the treatment of different kinds of organics.

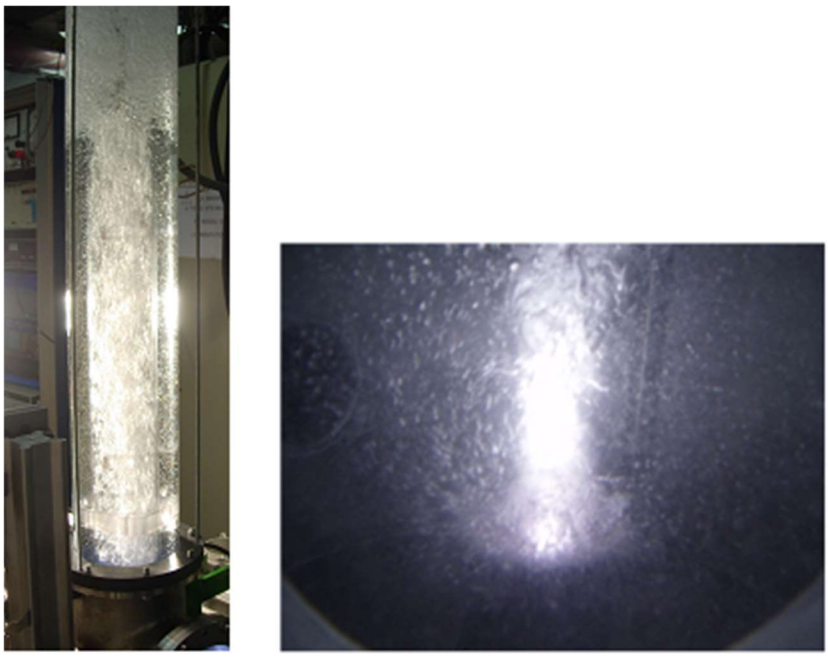

Figure 2: Working underwater plasma

The reactor

The process is based on a non-transferred arc torch of an original design producing a plasma jet of oxygen. The plasma torch is disposed vertically to the base of a water-jacket reactor filled with water as described in figure 1. There is no specific recommendation for the water used to fill the reactor. Its pH must be adjusted around 7 as the treatment progresses for better aqueous corrosion management together with minimization of precipitation.

Initially, the torch was ignited and the jet penetrated into the empty reactor for few seconds before it was filled with around 80L of water. Improvements have allowed to ignite the torch after it has been submerged what avoid an overheating of the empty reactor. The steam condenses and the non-condensable gas phase passing through the solution enters a condenser/demister to trap residual water vapour and stop the water droplets carried over by priming.

Thermocouples indicate the temperature of the water in the reactor and at the condenser outlet. The solution temperature is controlled by a closed-circuit recirculation loop comprising a pump and a plate-type heat exchanger cooled by flowing water. The pH of the water is controlled thank to a probe and adjusted through soda addition. The mineral charges of the liquid are trapped in a filter implemented in the middle of the loop.

All the reactor components (cathode, anode, reactor walls, condenser, …) are cooled by separate and independent water circuits equipped with flowmeters and thermocouples to measure the heat loss in each circuit.

The torch

As described in figure 3, the torch, with gas-vortex stabilization of the arc column, is made of a tungsten cathode, a copper anode and an intermediate diaphragm. The cathode tungsten tip is protected by a stream of argon. Oxygen, the main gas, is injected downstream the diaphragm. The change in diameter inside the nozzle anode creates a zone of recirculation of the flow. It is colder thus more electrically resistive, fixing the anodic spot behind the ledge [1]. At around 200 A, the voltage is about 250 V meaning the effective power dissipated is about 30 kW.

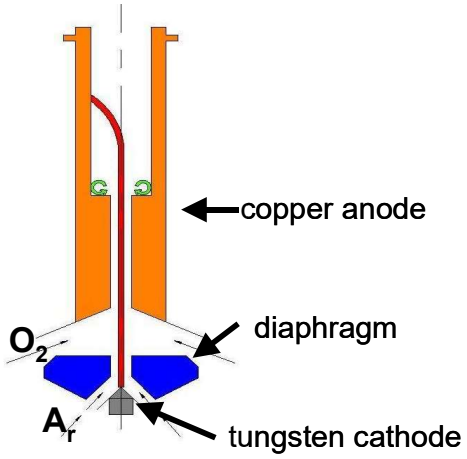

Figure 3: *Schematic view of the torch.*

Combustion Zone

The liquid is injected into a stage attached to the anode outlet as described in figure 4. If we assume that the dissociation and oxidation reactions are rapid enough to ensure that thermodynamic equilibrium is reached at the outlet of the injection stage, the amount of CO should be high at a temperature ranging between 3000 and 4000 K. If the gases are directly driven toward the solution, the quenching rate estimated by NV.Alekseev [2] as around 2.10^7 $K.s^{-1}$ is fast enough to ensure that the gas composition does not change from the equilibrium what has been confirmed through experiments.

Measurements during the treatment of 3 L/h of TBP/dodecan have shown that quenched gases contained about 10 %(vol) of CO.

In order to decrease the CO content, a dilution stage using water injection was designed and implemented downstream the liquid injection as described in figure 4. Measurements performed during similar treatment as those mentioned above have shown CO content less than 0.2 % (vol). In order to upgrade the process it has been decided to inject water coming from the reactor. This option has the advantage of passing the solution several times through the plasma ensuring a better destruction of any residual organic compounds.

Finally, a last stage of cooling has been added to increase the residence time of the gases before quenching. This allows us a better control of the cooling of the mixture. This stage is optional and could be removed if required.

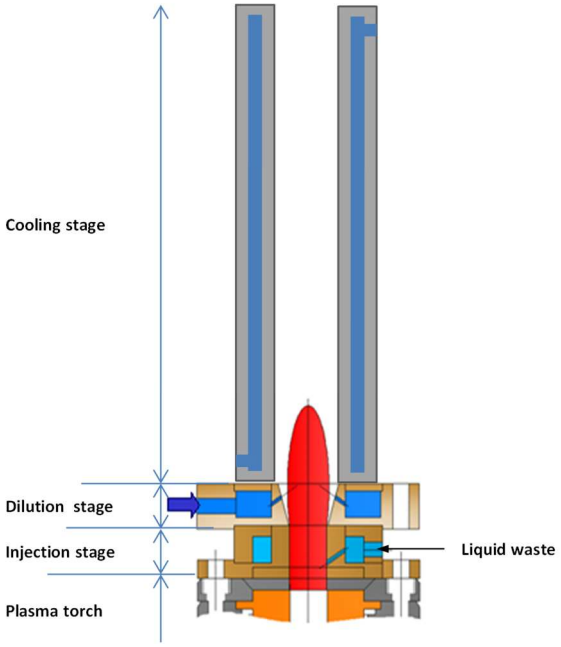

Figure 4: *Schematic view of the combustion zone.*

The mockup

The whole mockup implemented at the Marcoule Research Center is shown in figure 5. It has been designed for a throughput of around 3 $L.h^{-1}$. Depending on the experimental results, this objective may be increased and optimized. The reactor equipped with several windows appears in the foreground of the picture. The background shows the closed-circuit recirculation loop including the filter, the heat exchanger, the different pumps, instrumentation and the neutralizer.

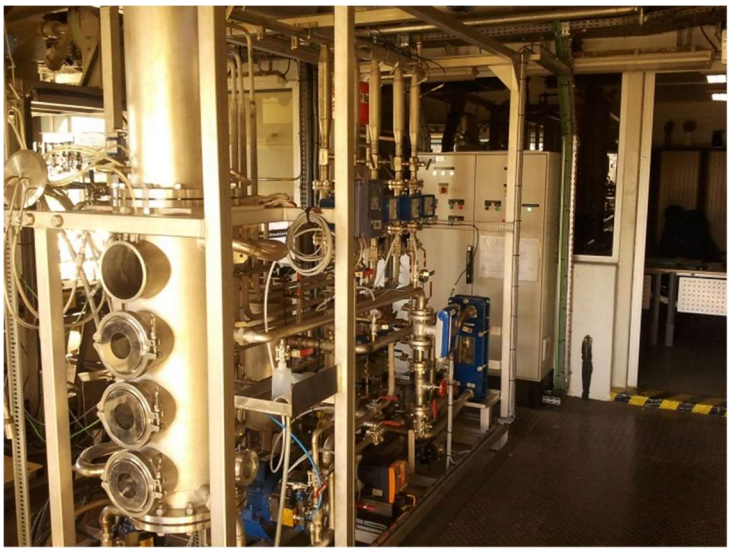

Figure 5: ELIPSE mockup

3- RESULTS AND DISCUSSION

Assessment on TBP-Dodecan extractant

The first experiments have been carried out with the extractant TBP-dodecane containing traces of uranium that have not been re-extracted in the form uranyl nitrate, the overall calculation for the destruction of one liter of mixture with the molar ratio of 0.9 mole of TBP for 3.3 moles of Dodecane (70 % weight of Dodecane) may be proposed in the following format:

$$0.9\ C_{12}H_{27}O_4P + 3.3\ C_{12}H_{26} + \zeta\ UO_2(NO_3)_2 + 77.25O_2 \rightarrow 50.4\ CO_2 + 53.7\ H_2O + 0.9\ H_3PO_4 + 2\zeta\ HNO_3 + \zeta\ UO_2 \quad (1)$$

Input organic charge ***Aqueous solution in the reactor***

In this example (not totally balanced with additional 2ζ H coming from water for NO_3 protonation and ζ O coming from oxygen plasma), the speciation of uranium remains to be studied, as it may be freed in oxide form after the uranyl has passed through the plasma. It may also be freed in the form of uranium phosphate, or eventually be solvated as uranium nitrate.

From a thermal point of view, the oxidation of the mixture will dissipate a total energy that is close to the standard reaction enthalpy because the mixture is introduced at ambient temperature, and the reaction products are at the temperature of the solution in the reactor. The enthalpy for the TBP formation is estimated at 1457.1 $kJ.mol^{-1}$ [3], and the calculation for the overall reaction enthalpy (1) corresponding to 1 liter of solution is approximately -33819 kJ. It can easily be deduced that the dissipated power for a rate of $1L.h^{-1}$ of mixture will be approximately 9.4 kW. In general, for the treatment of any given liquid, the power developed in the system will be the power injected by the plasma (P_{Plasma}), plus the power exchanged during the treatment of 1 liter per hour of liquid ($\Delta H_{r/L}$) multiplied by overall processing rate D:

$$P_t = P_{plasma} + \frac{\Delta H_{r/L}}{3600} D \quad (2)$$

The dissipated power will be evacuated via the various process involved in the cooling systems, including all the internal circulation lines of the torch and its nozzle, the cooled reactor walls, the condenser-demister and the heat exchanger on the process water circulation loop.

The curve shown in Figure 6 represents the power balance for a test conducted with a plasma torch supplied with 52 kW of stabilized electrical power, and in which different feeding rates of TBP-Dodecane mixture were used. These experiments were performed with simple chemicals without radioelements. The feeding rates were provided by a calibrated peristaltic pump and checked thanks to the monitoring of the mass of the supply cylinder. The red curve represents the power injected into the torch over time; the black curve represents the total dissipated power in all the cooling systems, measured with the test instrumentation that can be seen in the foreground of Figure 5. The difference represents the power dissipated in the torch by combustion of the organic liquid feed.

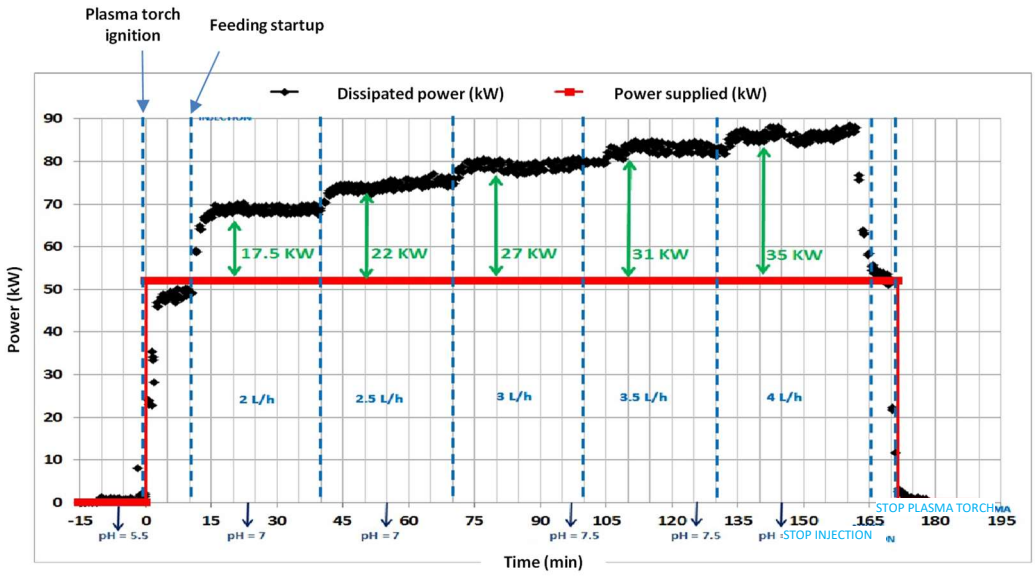

Figure 6: *Power balance during treatment of TBP-Dodecane mixture at variable feeding rates.*

The deviations measured between the red curve and the black curve for different feed rates correspond to the power dissipated by the combustion of the organic mixture. Figure 7 shows the close correspondence between the theoretical power calculated based on the equation (3) and the measurement taken on the treatment facility.

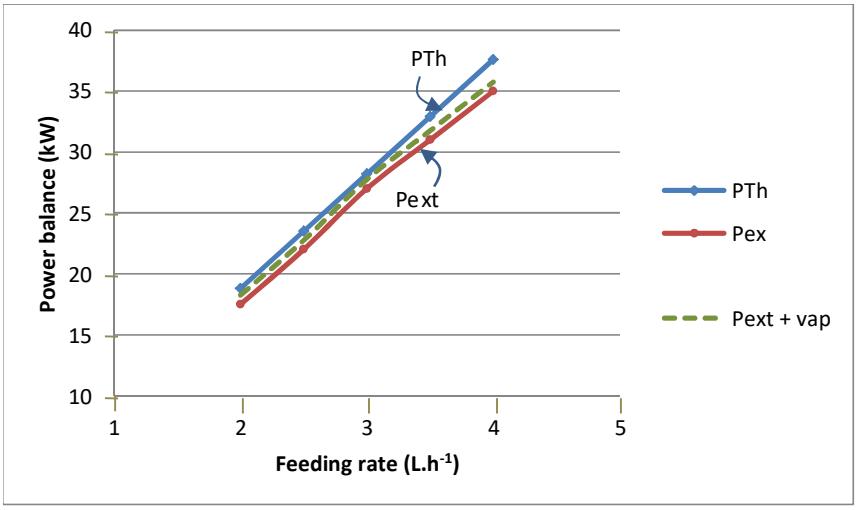

Figure 7: Comparison between theoretical power dissipated during treatment with variable TBP-Dodecane feeding rate and the measured power.

A hygrometry measurement of the gases at the condenser outlet shows a relative humidity of 100 %, representing a total water loss for the 155 minutes of treatment of approximately 2.5 L (quantity

measured after performing a material balance). Considering the enthalpy of the water vaporization (2675 $kJ \cdot kg^{-1}$) applied to this quantity and the treatment time, it appears that this continuous process absorbs approximately 0.75 kW, which provides an even more accurate power balance as shown in Figure 7.

These thermal balances, which demonstrate the excellent efficiency of the experimental pilot facility, made it possible to evaluate its capability of destroying the three categories of the described liquids above.

Validation on other liquids

To evaluate the potential of ELIPSE to treat a wide variety of liquids, its effectiveness for the destruction of 3 compounds cited in the general process description was investigated:

- The TBP/Dodecane mixture widely used in the nuclear industry as an extractant in the PUREX retreatment process. The thermal power generated by its oxygen combustion is 9.4 $kW \cdot h \cdot L^{-1}$.
- Trichloroethylene (TCE), a slightly flammable solvent whose use is now prohibited for safety reasons. The thermal power generated by its oxygen combustion is 3.0 $kW \cdot h \cdot L^{-1}$.
- A perfluoropolyether (PFPE) product from Fomblin® used as a lubricant in UF_6 transfer pumps. The thermal power generated by its oxygen combustion is 4.8 $kW \cdot h \cdot L^{-1}$.

The respective molecules are shown in Figure 8.

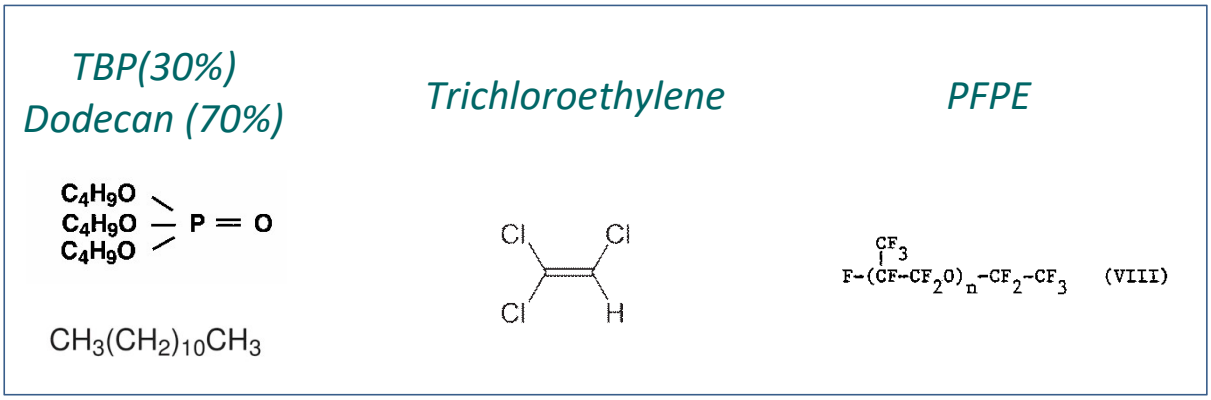

Figure 8: 3 molecules with varying charges undergoing ELIPSE treatment.

The treatment of each liquid was initially evaluated at a treatment rate of 2 $L \cdot h^{-1}$ for 1 hour, in the operating mode specified in the general process description.

The destruction efficiency was evaluated by analyzing the Total Organic Carbon (TOC) in the residual solution. The TOC is measured with a SHIMADZU analyzer, model TOC-L, using the 680°C combustion catalytic oxidation method. The analysis time for the device is between 3 and 7 minutes, and the detection limit is between 0.5 μg/L and 20,000 mg/L.

The destruction efficiency is calculated using the following equation:

$$\eta_d = \frac{C_i - C_f}{C_i} \quad (3)$$

where C_i is the TOC introduced in the process and C_f is the final TOC analyzed at the end of treatment.

The results obtained using this method are indicated in table 1.

Liquid	TBP/Dodecan	TCE	PFPE
η	99.90%	99.99%	99.80%

Table 1: Destruction efficiencies obtained for different liquids

The post-test inspection performed on the components of the plasma nozzle described in the general process description did not reveal any visible extensive corrosion on their surface (as shown in Figure 9). The choices made in terms of geometry, cooling and materials were therefore validated.

Figure 9: Appearance of torch outlet nozzle components following treatment of TBP/Dodecan, TCE and PFPE liquids at a rate of $2 L \cdot h^{-1}$.

This evaluation demonstrates an excellent response by the process for treatment of the liquids mentioned above. The effective destruction rates obtained in these initial experiments was better than 99 %, and may be improved by certain upgrades that are currently being studied.

Additional tests which are not covered in the present article were also conducted to test the treatment of TBP/Dodecan at rates of up to $5 L \cdot h^{-1}$. The results currently show effective destruction rates that remain above 99 %, with no or very little corrosion.

4- GASIFICATION ASSESSMENT

The ELIPSE process could also be used as gasifier to produce Syngaz in the frame of a waste to energy scenario. A pure argon plasma torch or a water plasma torch could be used instead of an oxygen torch. In the first case, the plasma enthalpy could be to weak to ensure the pyrolysis of the organics and that is why it is better to work with a water plasma torch. Research is currently underway to develop such torches that can be used for the treatment of organic matter under oxydative or reductive condition [3].

If we consider the valorization of cellulosic waste that can be considered as glucose, the two recovery routes can be considered as being either a direct combustion or a pyrolysis generating a syngas that can be burned afterwards. Figure 10 illustrates these two paths.

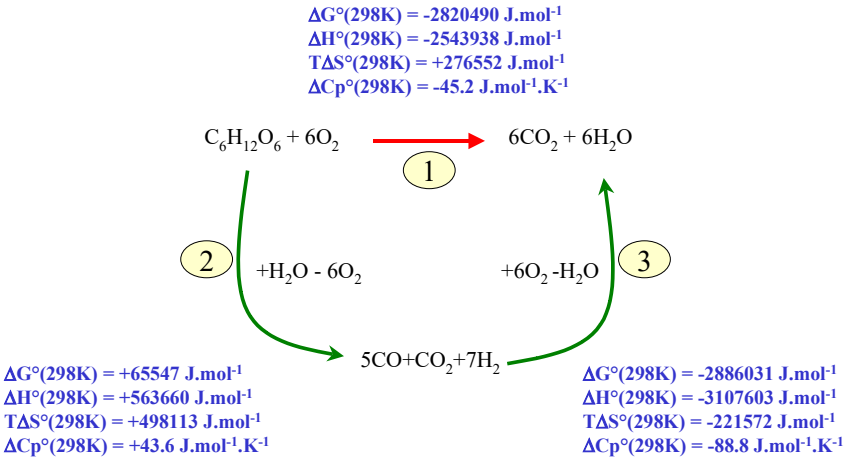

Figure 10: Two paths for heat production from cellulose.

According to the available data, for a water flow rate of around 2.6 $g.s^{-1}$, the water torch operates with U-I characteristic around 215 V – 180 A or about 40 kW. For this power, the plasma temperature is around 2700 K and water is partially dissociated in H_2 and O_2 according to the graph shown in the figure 11.

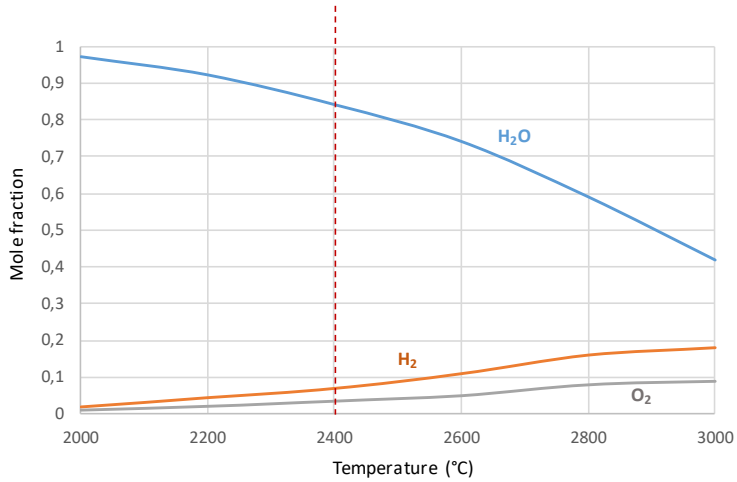

Figure 11: Two paths for heat production from cellulose.

Figure 11 shows a dissociation rate of around 16 % following the reaction:

$H_2O \rightarrow H_2 + O_2$ $\Delta H°(2400\ °C) = 265176\ kJ$ (4)

The required power for the dissociation of 2.6g.s^{-1} of water should be around 6.1kW according to a reaction enthalpy at 2400 °C.
It can be considered that at 2400 °C the gaseous chemical equilibria are reached in a few milliseconds. Furthermore, the gas quenching due to their bubbling in the reactor avoid any further recombination.
A chemical equilibrium calculation performed on software Factsage [4] shows that a cellulose molecule breaks down according to (2) into 6.3 H_2 and 5.9 CO that can be used as fuel according the two following reactions:

$H_2 + 1/2O2 \rightarrow H_2O$ $\Delta H°(25°C) = -242588\ kJ$ (5)
$CO + 1/2O_2 \rightarrow CO_2$ $\Delta H°(25°C) = -283388\ kJ$ (6)

Taking into account the additional hydrogen input coming from the dissociation of the water in the plasma torch, it is possible to calculate for different treatment flow rates of a cellulosic compound, the different powers used or developed during the path 2 and 3 described in Figure 10. Figure 12 shows, versus the treatment flow, the evolution of the thermal power P1 consumed to ensure the degradation of the cellulosic compound, the evolution of the thermal power P2 developed during the combustion of the gases produced from P1 and the ratio of this second power on the thermal power of the plasma torch (40 kW in the present case). It can be seen that the process may become thermally interesting for a treatment flow greater than 7 kg.h^{-1}.

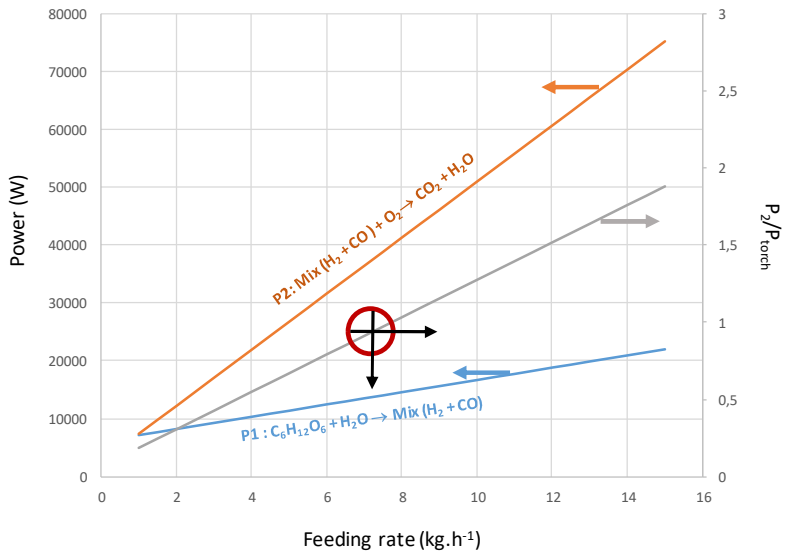

Figure 12: Two paths for heat production from cellulose.

These results show that the ELIPSE process could be an intersting way forward for the gasification of liquid organic materials. It has the additional advantage of having a good management of soot and tar since they are supported by the aqueous solution.

4- CONCLUSIONS

We presented an overview of the scientific and technological progression leading to the design of a submerged plasma process for the treatment of organic liquids. After demonstrating that cooling the gas before it

penetrates into the reactor guarantees a composition with an acceptable CO/CO_2 output ratio, tests were conducted to evaluate the destruction of a TBP/dodecane mixture.

The tests substantiated the process efficiency: the TOC destruction efficiency always exceeds 99 % regardless of the type of waste, and the trapping yields for inorganic materials such as chlorine are near 100 %, within the measurement uncertainty margin. Only fluorine shows a lower capture that has to be investigated.

The very good behavior of the process regarding treatment efficiency and maybe above all the lack of corrosion opens considerable perspectives for the destruction of various liquids. We can then already conclude that the process now being developed has very strong potential. Versatility, compactness and robustness are the terms that best describe it.

This quite satisfactory set of results also makes possible to envisage the use of such a process for gasifying liquid organic materials. On the basis of a process using a water torch of 40kW, it was assessed that the technique would be thermally cost-effective from a cellulosic waste flow equivalent glucose of 7 kg.

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