What makes a thermal plasma suitable for hazardous waste disposal

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(ricevuto il 10 Aprile 1997; approvato l'8 Maggio 1997)

Summary. — The basic transport and thermodynamic characteristics of a thermal plasma are analysed in order to emphasize those properties that make a high-temperature source profitable and suitable over the conventional devices for hazardous waste treatment. In addition a survey of the basic reaction sequence and apparatus units is made together with the different approaches to thermal plasma waste treatments.

PACS 52.75.Hn - Plasma torches.
PACS 52.75.Rx - Plasma applications in manufacturing and material processing (etching, surface cleaning, spraying, arc welding, ion implantation, film deposition etc.)
PACS 82.40.Ra - Plasma reaction (including flowing afterglow and electric discharges.
PACS 51.20 - Viscosity diffusion and thermal conductivity.

1. - Introduction

The disposal of toxic and hazardous waste materials due to increased quantity and consequently increased environmental pollution risk, must be avoided and replaced by destruction or decomposition processes. As conventional incinerators are mostly unable to reach temperatures above 1500 K, an increase in residence time, or post-combustion treatments, for effective thermal destruction of chlorinated organics, is required. Plasma arc processing is particularly well suited to treat those wastes due to its capability of obtaining determined chemical composition and independent realisation of its high temperature level. The plasma can decompose complex molecules into simple compounds like nitrogen, hydrogen, carbon monoxide and hydrochloric acid. Polychlorinated biphenyl isomers, with the general formula \( \text{C}_{12}\text{H}_{10-14}\text{Cl}_n \) requires relatively high temperature for complete decomposition. Under normal conditions of thermal destruction (combustion at about 1500 K in air) the residue often contains a quantity of undecomposed PCBs, even up to a few percent [1]. Burning PCBs in ordinary incinerators can cause more problems than it solves, because highly toxic dioxins and dibenzofurans are formed if combustion temperatures are too low. In this paper the basic transport and thermodynamic features of thermal plasmas are underlined in order to shed light on those properties that make these high temperature sources profitable over the conventional devices.
2. - Equilibrium and non-equilibrium plasma

A plasma can be generated with many possible techniques: by electrical discharges between two electrodes, by RF inductive coupling, microwaves, shock waves, lasers and heating gases in a high-temperature furnace. The most widely used methods are those that employ high intensity arcs and inductively coupled high frequency discharges.

Plasmas can be classified in two wide groups: cold or non-equilibrium plasmas and hot or thermal plasmas (fig. 1).

Non-equilibrium plasmas are characterised by electronic temperatures of the order of some tens of eV and much higher than those of heavy species (atoms and ions). The characteristic particle density for these types of plasma produced in glow discharges, radio frequency discharges at low pressure and corona discharges is less than $10^{20} \text{m}^{-3}$.

Thermal plasmas feature high energy density and a thermodynamic state close to kinetic equilibrium. In thermal plasmas the particles density ranges between $10^{22} \text{m}^{-3}$ and $10^{28} \text{m}^{-3}$ with an electronic temperature of the order of 1-2 eV, corresponding (assuming a Maxwell-Boltzmann distribution of velocities) to a particle temperature between 7500 and 15 000 K.

In a dense, collision dominated, high temperature plasma each species is supposed to assume a Maxwellian distribution. This leads, in general, to the definition of at least two different temperatures one for the electrons $T_e$ and one for the heavy particles $T_h$. Because of their high mobility, the electrons pick up the energy fed into the arc from the electric field and transfer it to the heavy particles through collisions. Due to this energy flowing from the electrons to heavy particles, a temperature difference has to be supposed and it tends to become closer as the collision rate and hence the pressure grows.

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**Fig. 1.** Typical ranges of temperatures and electron densities for thermal and non-equilibrium plasmas.
If we consider the energy balance equation and assume that the kinetic energy exchange by elastic collisions is equal to the energy gained by electrons from the electric field, we can estimate the degree of equilibrium between the two species. The energy transfer in an elastic collision between electrons and heavy particles is [2]

\[
\Delta E = \frac{3}{2} k \Delta T \Delta \xi = \frac{3}{2} k(T_e - T_h) \frac{2m_e}{m_h}.
\]

The energy gained by an electron from the electric field between two collisions is

\[
\Delta E = \frac{eE l_e \bar{v}_0}{\bar{v}_e},
\]

where \(\bar{v}_e = (8kT_e/\pi m_e)^{1/2}\) is the electron mean velocity, \(e\) is the electron charge, \(E\) the electric field and \(\bar{v}_0 = \mu_e E = eE l_e/m_e \bar{v}_e\) is the mean drift velocity and \(\mu_e\) is the electron mobility; the term \(l_e/\nu_e\) represents the mean time between two collisions of electrons with heavy particles.

Assuming steady-state conditions we get

\[
\frac{T_e - T_h}{T_e} = \frac{3\pi m_h}{32 m_e} \left( \frac{eE l_e}{(3/2) kT_e} \right)^2.
\]

If the quantity given in (2) is much less than the electrons mean kinetic energy (high temperature), from (3) we can see that the difference between the heavy particles and electrons temperature become small, and as \(l_e \sim p^{-1}\), this condition is verified when the ratio \(E/p \ll 1\). The parameter \(E/p\) represents the characteristic value to estimate the kinetic equilibrium degree in a thermal plasma.

Typical values of the \(E/p\) ratio for a glow discharge are of the order of \(10^6 \text{V/m-Pa}\), while in arcs at atmospheric pressure of the order of \(10^{-2} \text{V/m-Pa}\).

3. - Local Thermodynamic Equilibrium (LTE)

A more restrictive form of thermal equilibrium is known as Local Thermodynamic E quilibrium (LTE). In this equilibrium, generally found in optically thin plasmas, despite the CTE case, the radiation field does not correspond to that of the black body at the system temperature. In this case the following conditions must be met [2]:

i) The species forming the plasma have a Maxwellian distribution of velocity.

ii) The \(E/p\) ratio is small enough and the electron temperature is adequately high to assume the same temperature for every species.

iii) The principle mechanism for ionisation is the electron collisions and, as a consequence, the particle density of the species forming the plasma are described by the Saha equation.

iv) Electron collisions are the principal mechanism for excitation; the corresponding particle density is given by the Boltzmann distribution.

v) Local gradients of plasma properties (temperature, density, heat conductivity, etc.) are sufficiently small to give to diffused particles enough time to get to equilibrium conditions.
These requirements are not satisfied in the following situations:
- near plasma generator walls (not enough collisions in the boundary layer),
- on the plasma fringes (electrons diffuse more rapidly than heavy particles),
- in regions of low electron density \( n_e < 10^{22} \text{ m}^{-3} \),
- during the injection of cold gas (the energy transfer between heavy particles takes place in a few collisions whereas between heavy particles and electrons it needs thousands of collisions).

4. - Thermodynamic properties

The composition of a gas depends strongly on its temperature. This is a result of the energy balance between the electrical energy dissipated and the heat losses (conduction, convection, radiative) in the plasma arc fringes. The total energy content depends on the energy of the different species (frozen energy) and the on the chemical reaction among them (reactive energy). For this reason thermodynamic properties are strictly tied to the plasma composition.

Species concentrations in a plasma volume are generally determined at fixed temperature and pressure. The method consists in finding the chemical composition that minimises the Gibbs free energy under the limitations imposed by the conservation of charge and mass:

\[
\begin{align*}
G &= G(T, p, n_i) \text{ minimum }, \\
\sum_i \alpha_{ii} n_i - b_0^I &= 0, \\
\end{align*}
\]

where \( T, p, n_i \) are, respectively, the temperature, the pressure and the number of moles of the \( i \)-th species, \( \alpha_{ii} \) and \( b_0^I \) the number of gram atoms of element \( I \) in the specie \( i \) and the number of gram atoms of the element \( I \) present in the closed volume.

5. - Specific heat at constant pressure

The specific heat at constant pressure is defined as

\[
C_p = \left( \frac{\partial h_g}{\partial T} \right)_p,
\]

where \( h_g \) is the gas enthalpy and is expressed as

\[
h_g = \frac{\sum_{i=1}^{K} x_i H_i}{\sum_{i=1}^{K} x_i M_i}.
\]

In this equation \( M_i, H_i \) and \( x_i \) are, respectively, the mass, enthalpy of one mole and the molar fraction \( (N_i / N_T) \), of the \( i \)-th chemical specie. The specific heat can be written as
Fig. 2. - Specific heat at constant pressure (1 atm) as a function of temperature for hydrogen.

The specific heat is therefore expressed by the sum of two terms:

\[ C_p = \frac{1}{m_g} \sum_{i=1}^{K} x_i C_{p_i} + \sum_{i=1}^{K} x_i (H_i - M_i h_i) \left( \frac{\partial \ln x_i}{\partial T} \right). \]  

\[ C_p = C_{p_f} + C_{p_r}, \]

\( C_{p_f} \) is called the frozen specific heat and it represents the contribution of the specific heat of all the plasma components in the absence of chemical reaction; \( C_{p_r} \) is the reactional specific heat connected to a chemical reaction at a given temperature and often it is the main contribution. The frozen specific heat \( C_{p_f} \) linearly increases with the temperature, while \( C_{p_r} \) exhibits a non-linear behaviour due to the dissociation reaction (7600 K for nitrogen), first ionisation (14500 K for nitrogen) and second ionisation (\( \approx 30000 \) K for nitrogen) (fig. 2 and 3).

6. - Enthalpy

The enthalpy function can be obtained through eq. (6), or if the specific heat as a
Fig. 3. – Specific heat at constant pressure (1 atm) as a function of temperature for different gases.

function of the temperature is known, by the following integral:

\[ H_g - H_g^0 = \int_0^T C_p(T) \, dT, \]  

where \( H_g \) is the total enthalpy at the temperature \( T \) and pressure \( p \), and \( H_g^0 \) is the total enthalpy at the reference state \( T = 0 \, K \) and \( p = 10^5 \, Pa \). The enthalpy can be reckoned introducing the frozen and reactive enthalpy. In the case of one mole of \( N_2 \) (two moles of atomic nitrogen) at temperature \( T_0 \) and pressure \( p_0 \), the composition at temperature \( T \) and pressure \( p \) is given by

\[ N_2 \rightarrow n_{N_2} N_2 + n_N N + n_{N^+} N^+ + n_e e^- \]  

where \( n_x \) is molar fraction. Two conditions have to hold: conservation of moles number and neutrality of charges:

\[ 2 = 2n_{N_2} + n_N + n_{N^+} \quad \text{and} \quad n_{N^+} = n_e; \]

the possible reactions are

- dissociation \( (N_2 \rightarrow 2N) \). The corresponding enthalpy variation is

\[ 2H_N - H_{N_2} = H_N^0; \]
Fig. 4. - Enthalpy at constant pressure (1 atm) as a function of temperature for different gases.

- ionisation ($N \rightarrow N^+ + e^-$). The corresponding enthalpy variation is

$$H_N^+ + H_e^- - H_N = H_{N^+}.$$  

The total enthalpy at temperature $T$ and pressure $p$ is (6)

$$H = n_{N_2} H_{N_2}^0 + n_N H_N + n_{N^+} H_{N^+} + n_e H_e.$$  

The required enthalpy change $\Delta H = H - H_{N_2}^0$ is deduced by the conservation of moles number and the neutrality of charges

$$\Delta H = \Delta H_{N_2} + \left( \frac{n_N}{2} + \frac{n_{N^+}}{2} \right) H_N^0 + n_{N^+} H_{N^+}.$$  

The first is the frozen term corresponding to the enthalpy change necessary to heat a nitrogen molecule from temperature $T_0$ to $T$; the last two terms (reactive) correspond to the dissociation and ionisation enthalpy. The presence of the reactive terms (heats of reaction) makes a high-temperature gas assume values of specific enthalpy higher in some cases of two orders of magnitude than the same gas at ambient temperature. Figures 4 and 5 show the specific enthalpy for different gases as a function of temperature at atmospheric pressure. These figures show how a plasma can represent a profitable means to supply energy to a process. Supposing to use an oxygen-fuel flame at 3000 K (temperature determined by the chemical reaction of combustion) to
heat a body to 2500 K, only a small fraction of its enthalpy \( \Delta H / H \equiv 20\% \) is exploited in the process, whereas using an oxygen plasma at 10,000 K the 92% of its energy is exploited and in case of nitrogen it goes up to 95%. This high energy efficiency may more than offset the economic convenience that combustion energy has over electrical energy; such advantage will increase as electrical energy gets cheaper and fossil energy more expensive [3].

7. - Transport properties

The main industrial applications exploit the high heat transfer capability of thermal plasmas, capability that strictly relies on the transport properties such as thermal conductivity and viscosity and convective heat transfer. In general in most transport processes there exists a linear relation between fluxes and driving forces (provided the force is not too large). The coefficients of proportionality when the driving force is a gradient are called transport coefficients.

7.1. Electrical conductivity. - The electrical conductivity is connected to the motion of charge carriers and charge mobility in the presence of an electric field. In particular one finds by integrating the equation of motion and taking the average
Fig. 6. - Electrical conductivity as a function of temperature for different gases.

behaviour of an arbitrary chosen particle:

\[ \vec{V}_d = \frac{q\vec{E}}{m\tau_q}, \]  

(16)

where \( \vec{V}_d \) is the mean drift velocity, \( \vec{E} \) is the electric field, \( q \) is the particle charge, \( m \) its mass and \( \tau_q \) is the mean time between two consecutive collisions. Substituting \( \tau_q = l/\vec{V}_q \), where \( l \) is the mean free path length and \( \vec{V}_q \) is the thermal velocity we can write

\[ \vec{V}_d = \mu \vec{E}, \]  

(17)

where \( \mu \) is the mobility. In a plasma, electrons and ions drift in opposite directions under the influence of an external electric field and this gives rise to an electric current of density:

\[ \vec{J} = \vec{J}_i + \vec{J}_e = e(n_i \vec{V}_{di} - n_e \vec{V}_{de}) = e(n_i \mu_i + n_e \mu_e) \vec{E}. \]  

(18)

Ohm's law assumes the form

\[ \vec{J} = \sigma \vec{E}, \]  

(19)

where \( \sigma = e(n_i \mu_i + n_e \mu_e) \) is the electrical conductivity. This expression can be
Fig. 7. - Thermal conductivity for different gases as a function of temperature.

furtherly simplified accounting for neutrality of plasma and being $\mu_i \ll \mu_e$

\[ \sigma_e = e n_e \mu_e = \frac{n_e e^2}{\sqrt{2\pi} m_e n_a \sigma_{en}}, \]

where $n_a$ is the neutral particle number density and $\sigma_{en}$ is the electron-neutral cross-section (it is tacitly assumed that the electron and ion density are low compared to neutrals so that $l_e$ is due to collision with neutrals).

The plot of the electrical conductivity as a function of temperature (fig. 6) shows that for most commonly used gases: ar, $H_2$, $O_2$, $N_2$, air, Ar-$H_2$, Ar-He, CO$_2$,..., with the exception of pure helium, $\sigma_e$ has a value sufficient enough to sustain a thermal plasma (arc) at temperature above 6000–7000 K.

72. Thermal conductivity. - The thermal conductivity holds an important role in thermal plasmas because it is responsible (together with the convective coefficient) of the heat transfer from the arc and superheated gas (plasma jet) to the material to be processed (powder, solid, gas). If $q_z$ is the heat flux due to temperature gradients in the $z$ direction, the thermal conductivity $k$ is defined by the Fourier equation:

\[ q_z = -k \frac{\partial T}{\partial z}. \]
In fig. 7 the thermal conductivity for different gases as a function of temperature is plotted. In general the thermal conductivity contains different contributions that can be written as sum of three terms:

\[ k = k_{tr} + k_{r} + k_{int}, \]

where \( k_{tr} \) accounts for the translation of particles, \( k_{r} \) for reactions of dissociation and ionisation and \( k_{int} \) for the degrees of freedom of the particles.

### 73. Viscosity.

The viscosity is the result of a friction force produced in the transport of momentum.

In fig. 8 the viscosity for some gases as a function of temperature is reported, showing that for temperatures above the temperature of ionisation, the viscosity decreases. This reason is to be attributed to the interactions between particles that, beyond certain temperatures, are dominated by Colombian forces. Due to the increase of charged particles with temperature, their mobility decreases, thus producing a lowering of the momentum transport.

The knowledge of the viscosity of an interacting system of gases is of great importance in order to have complete mixing, this being the condition to attain the higher heat transfer from the hot source to a cold gas.
8. - Chemical processes under thermal plasma conditions

Plasma chemistry is concerned with reactions occurring in plasmas. The presence of ions, electrons and atoms in highly excited states may give origin to reactions whose compounds are unlikely to be formed in conventional chemical reactions. The upper limit of flame temperatures is about 3500 K. At this value molecules begin to dissociate. The lower limit of plasma temperatures is about 7000 K, since only at these temperatures there is enough ionisation to assure the required electrical conductivity.

A plasma jet is a relatively new means to achieve temperatures beyond the limit imposed by chemical-combustion flames.

In principle, for reactions within the bulk plasma and reactions of the plasma with the confining material walls, two distinct processes are present:

a) destruction or decomposition of existing bonds, leading to creation of simpler molecules or free radicals and

b) formation of new bonds, resulting in the synthesis of bigger molecules.

According to the two steps described, two different types of chemical reactions can be carried out by the use of plasma jets:

- The decomposition of compounds into their elements or less energetic compounds as for example:

  \[2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2, \quad \text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2, \quad \text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + \frac{3}{2} \text{O}_2.\]

- The formation of endothermic compounds by freezing the chemical equilibria obtained at high temperature by the use of fast quenching techniques.

The formation of exothermic compounds, such as ammonia from nitrogen with hydrogen, is not probable, since the equilibrium at high temperature is more favourable for nitrogen and hydrogen than ammonia.

Chemical synthesis which involves rearrangement of electron distributions to form new bonds (molecules) may frequently be achieved more efficiently in glow discharges at low pressures. However, sometimes a high yield can be obtained in spark discharges, and for particular chemical reactions the arc discharge may be most suitable (as in the case of destruction of existing bonds and dissociation of complex molecules).

Low-temperature plasmas can be used in chemical reactions because they offer the following unique advantages [8]:

- The high energy density and temperatures associated with thermal plasmas and the corresponding fast reaction times offer the potential of large throughputs in a small reactor.

- The high temperatures can also be used to obtain very high quench rates allowing the attainment of metastable states and non-equilibrium compositions.

- The high heat fluxes at the reactor boundaries lead to fast attainment of steady state conditions allowing rapid start-up and shut down times compared to other thermal treatments such as furnaces.
- The use of electric energy reduces gas flow needs and off-gas treatment requirements and offers control over the chemistry, including the possibility of generating saleable co-products.

- A source of positive and negative ions, potential precursors for ion and ion-molecule reactions.

- A source of luminous radiation for photochemical reactions.

Plasma temperature has to be high to insure rather high dissociation rate of reagent molecules, but if new compounds have to be synthetised in marked quantities thermodynamic and kinetic factors have to be taken into account. The quenching seems to play a significant, if not deciding, role in the technology of quasi-equilibrium type plasma chemical processes. The character of chemical conversions that occur at temperatures of the order of several thousand degrees is largely determined by thermodynamic properties of substances which take part in a reaction. Given reliable thermodynamic constants it should be possible to determine, in most cases, optimal temperature conditions for reactions and values of product yields expected. The description of the system is difficult: the high velocities of chemical reactions at the temperatures under consideration can depend to a considerable extent on velocity of physical processes such as the diffusion (molecular) and turbulent transfer and the microscopic mixing of the reacting system's components.

There are two types of reactions in a plasma jet where composition of products depends on quenching conditions. The first type includes reactions which produce in succession a number of intermediate products, some of which should be frozen. An example of such reactions is the conversion of methane into acetylene. It is natural that not only the quenching velocity, but also the moment when temperature starts to decrease, is of prime importance for such reactions.

In reactions of the second type the desired compounds are final products of a reaction which proceeds only at high temperatures, the product molecules being sufficiently stable at room temperature. The purpose of quenching, in this case, is to cool a product of reaction as soon as possible so that the product has no time to decompose within the intermediate range of temperatures. This type of reaction includes, for example, thermal formation of nitric oxide in air. In this case, it is necessary to insure the required rate of quenching, which should observe a definite law \( \frac{dT}{dt} = f(T) \) [3]. The violation of this law in any temperature range cannot be offset by an increase in the quenching rate in another range. In some cases, it is important not only to remove heat rapidly from a system but also to utilise as much of it as possible.

In principle, under ideal conditions of thermodynamic equilibrium, it might be possible to determine the products of a given reaction. In addition, the knowledge of the chemical composition as a function of temperature is essential for the evaluation of thermodynamic and transport properties.

The problem is to know to what extent a real system can be described by a model that assumes complete thermodynamic equilibrium. Consider a flowing plasma (plasma jet): in this case thermodynamic equilibrium can be applied if the chemical reaction performs at a rate higher than that of the physical phenomena involved (time related to the relaxation of energy or Maxwellianisation of velocity). An estimate of the order of magnitude of reaction times to attain chemical equilibrium can be given considering the temperature distribution of a typical DC plasma jet. Along its axis we can get a
Table I. – Characteristic times for various processes at temperatures between $3 \cdot 10^3$ and $1.5 \cdot 10^4K$.

<table>
<thead>
<tr>
<th>Characteristic times</th>
<th>Seconds</th>
</tr>
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<tbody>
<tr>
<td>Molecular interaction mean time</td>
<td>$10^{-14}$</td>
</tr>
<tr>
<td>Mean time for molecular free path run ($\approx$ Maxwellisation time)</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Relaxation time for molecular rotation</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Relaxation time for vibrational processes</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>Relaxation time for dissociation of oxygen</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>Mean time for an effective collision to occur with a barrier energy of $E = 2.5$ eV</td>
<td>$10^{-5}$</td>
</tr>
</tbody>
</table>

Temperature variation of 1% in $2.5 \cdot 10^{-5}m$ and with a flow velocity of 250 m/s this corresponds to a residence time in the considered region of $10^{-7}s$. Hence reaction times should be smaller than this value.

Various calculations have demonstrated that this reaction time exists at temperatures above 5000 K.

Table I shows typical times for various processes at temperatures between $3 \cdot 10^3$ and $1.5 \cdot 10^4K$.

In general chemical changes (chemical reactions, ionisation,...) in a flowing plasma mixture depend on typical different relaxation times to reach the equilibrium state. If $t_m$ represents the typical mechanical time of a molecule associated to the residence time in a reactive volume, the value of the ratio $D_I = t_p / t_m$ (Damköhler parameter), where $t_p$ is the vibrational relaxation time, contains information on the evolution of the molecule in the given physical conditions.

1) If $D_I << 1$ the evolution time associated to the process is lower than the typical mechanical time, the flow is then considered in equilibrium.

2) If $D_I >> 1$ no chemical changes occur during the time $t_m$ (flow frozen).

3) If $D_I \approx 1$ the flow is said to be “relaxed” and this relaxation needs a chemical kinetics description.

Therefore given certain physical conditions, the composition of a chemical system can be determined by thermodynamic means if the transformation is realised as a sequence of equilibrium states (1). In this situation time does not need to be taken into account and thermodynamic laws provide the real composition of the chemical system. In case (3) the time evolution of the typical parameters of the flowing plasma (mainly temperature $T(t)$) requires kinetic models to predict the influence of physical conditions on the reaction rates.

High energy, high temperature and intensive light enable to realise refractory chemical reaction and to increase the reaction rate. Figure 9 shows how to reduce the reaction time compared with a combustion gas whose temperature ($T_c$) is assumed to be 2000 K. In this case, the reaction [5]

$$A + M = B + C + M$$
is assumed, and then the reaction time ($\tau$) is given as

$$\tau \approx \frac{1}{k_f[M]}$$

where $k_f$ is the reaction rate constant.

The ordinate of fig. 9 is the ratio of the reaction time in a thermal plasma ($\tau_p$) to that in a combustion gas ($\tau_c$). The ratio is strongly dependent on the plasma temperature ($T_p$) and the activation energy of the reaction. For example, the decomposition reaction of methane has an activation energy of about $10^5$ cal·mol$^{-1}$, and the reaction time is largely reduced to $1/10^{10}$ if the thermal plasma of $10^4$ K is used.

9. Reaction sequence and apparatus

The main components of any apparatus used in low-temperature plasma chemistry are power supplies and feeding devices for any form of reactant materials. A general scheme of the apparatus assembly and the functions of each unit are shown in fig. 10. A three-stage sequence is often followed: plasma generation, injection, quenching.

Plasma generation. The first stage in the process involves the generation of the plasma state.

Injection flow-patterns. Two usable flow-pattern possibilities are available in fig. 10: pregenerator mixing and postgenerator injection.

In premixing reagents upstream of the plasma generator, problems of intermixing a cold reagent gas with a hot plasma are avoided. This assures that all reagent species to be exposed to the plasma temperature. Premixed feeds are not convenient for systems in which heated reactants would corrode the generator electrodes. Premixing is not applicable for systems in which solid or liquid feeds would short-circuit the generator operation. In some systems premixing may hamper yield optimisation at minimum
power consumption, which would be achieved by only partial exposure of the reactants to the plasma arc.

Figure 10 also shows this flow pattern, where the reagent gas A is sent to the generator, which produces a highly reactive plasma stream. The other reagent B is intermixed with this plasma downstream, to induce A-B combination reactions. In the particular case in which the application precludes the feeding of any reactants through the generator, the enthalpy carrier is represented by an inert gas. The reactant gases are then intermixed downstream with the inert gas plasma to induce high temperature reactions. Introduction of a cold reactant gas obviously chills the plasma. The extent of cooling is a function of the heat capacity of the reactants and the ratio of flow rates. If the mixing is achieved and sufficient enthalpy is carried from the plasma generator, high temperature can be attained in the plasma mixture.

The successful injection of various substances into the plasma is an important and crucial practical aspect of a plasma-chemical process. In fact the injection of cold materials has to occur gradually enough to prevent the destruction of the electrical conduction channel, but rapidly enough to raise the materials to plasma temperature. In electrode plasma generators, jets normal to the plasma flow are used for feeding material either into the arc region or beyond the arc into the plasma. Injecting materials into arcs is more difficult because of the presence of electrodes and the small available volume of plasma. For injecting hot gases, hollow cathodes, porous and volatile anodes are currently used.

Quenching. The method most extensively employed is the cooling of hot gases in a water-cooled pipe, which is used to cool gases having temperatures up to 4000 K. When diameter of the pipe is $\approx 3$ mm, the quenching rate is of the order of $\approx 10^6$ K/s at
3000 K. The method of quenching by injection of water is also widespread. The estimates show that the quenching rate amounts to $10^8$ K/s, at pressures of 10 atm, ratio of water and gas flows is 1:1 and initial gas temperature of about 3000 K.

10. – Waste treatment installation

For chlorinated organics a postgenerator injection is required in order to avoid electrodes from a dramatic wear. The introduction of the gaseous or liquid waste is then obtained downstream the torch into the plasma jet making it flow through a reaction tube. The process requires an intensive mixing between the plasma process gas and the waste (requiring high velocities and small diameters of the nozzle in the mixing chamber), an almost constant temperature, velocity and concentration distribution along the reaction tube, consisting of a refractory lined hot channel. The exhaust products are then passed to a larger holding tank and from here a part is sent to an analysis system for the residual waste detachment (gascromatography + mass spectrometry) whereas the remaining is vented to a scrubber (fig. 11).

11. – Different approaches to waste treatment

Depending on the availability of oxygen the process can be classified as follows [6]:

<table>
<thead>
<tr>
<th>O$_2$</th>
<th>Process name</th>
<th>Plasma gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>presence of free oxygen</td>
<td>combustion</td>
<td>O$_2$ or air</td>
</tr>
<tr>
<td>with partially free oxygen</td>
<td>gasification</td>
<td>CO$_2$ or steam</td>
</tr>
<tr>
<td>without oxygen</td>
<td>pyrolysis</td>
<td>noble gases, N$_2$, H$_2$, CO mixtures</td>
</tr>
</tbody>
</table>
The first process, using air, is economically convenient, but the presence of nitrogen is disadvantageous absorbing a large amount of energy without participating (actively) in the destruction process with the possibility of forming nitrogen oxides.

The second process, when using water steam, is advantageous due to its dissociation and forming atomic oxygen and reactive OH radicals. In addition, the presence of hydrogen promotes the destruction of halogen-carbon bonds. Carbon dioxide decomposes into oxygen and carbon monoxide but this latter is not involved in the destruction process.

In the third process hydrogen holds a peculiar position due to the fact that its dissociation produces a high enthalpy content (energy density) and delivers atomic hydrogen that drives substantially the decomposition process.

12. - Conclusions

The high temperature of the plasma can give rise to considerably high reactivity, material heating and quench rates (in the order of $10^5$-$10^7$ K/s) which are characteristics of thermal plasma processing. The fact that energy is generated through electrical coupling into the plasma and not through a combustion process also provides the additional means for the independent control of the chemistry of the reaction mixture and its specific energy level, which is a unique and important feature of plasma processing, with important implications in plasma-chemical synthesis. The thermodynamic and transport properties of most common gases at high temperature (over 3500 K) and atmospheric pressure give to a thermal plasma some peculiar characteristics over the conventional heat source generators. Those characteristics, in some cases, are combined to the economy of the process because of the higher energy efficiency that can offset the convenience that combustion has over the electrical energy.

REFERENCES