



DEVELOPMENT OF PYROLYZER FOR OBTAINING CONDUCTIVE SUBSTRATES TO GLASS BASE TO APPLY TO OPTOELETRONICS

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Abstract. *The development of Electronic Industry depends on machines and systems that are used to obtain electronic devices and inputs. However, Brazil still has imported this kind of machine, as it is the case of the spray-pyrolysis process. Therefore, a new concept of pyrolyzer was built in order to achieve a low-cost high-efficiency device that works through the natural gas burning. For the design development of this pyrolyzer, the filtration combustion principles were employed in order for the pyrolyzer's combustion chamber to reach 900 K, maintaining low CO and NOx emissions. The spray system, positioned in the ante-chamber of the pyrolyzer, requires this temperature to be triggered. This allows the system to scatter on the glass surface a tin chloride ($\text{SnCl}_2 \cdot \text{H}_2\text{O}$), that is converted into ($\text{SnO}_2:\text{F}$) by the heat. Combustion in the porous medium happens in steady state regime, and the main operation parameters are: equivalence ratio, gas flow rate and inlet pressure. The pyrolyzer operation is controlled with the equivalence ratio \times temperature chart. The natural gas passes through the burner constituted of ceramic material (Al_2O_3), structured on layers, in which heat losses are reduced by refractory material. Thus, conductive glasses have been obtained with electrical resistance of less than 20Ω through the use of this pyrolyzer.*

Keywords: *spray pyrolysis, tin dioxide, porous burner oven, filtration combustion.*

1. INTRODUCTION

The conversion of solar energy into electricity through photovoltaic cells has emerged as a promising alternative technology to restructure the national energy matrix, considering the natural vocation of Brazil in this area. In this context, the technology diffused in the market is based on photovoltaic collectors made of silicon, even though with relatively high cell costs. Due to the growth of researches about renewable energy sources, there has been interest in the study of physical processes relevant to the conversion of sunlight into electricity, in an efficient and inexpensive manner. In this context, the Grätzel cell arose as a new technology for the production of photovoltaic cells at lower costs when compared to silicon cells (Ohring, M., 1992).

The Grätzel cell belongs to the class of called activated dye solar cells (or photoelectrochemical cells). It is presented as an alternative technology due to the fact of that the semiconductor has its photosensitivity, i.e., absorption of photons of energy increase by the adsorption of a dye on its surface. The Grätzel cell is composed of semiconductor layers with transparent conductive oxide (TCO) and titanium dioxide (TiO_2); dye photosensitizer and electrode with redox electrolyte, having a transparent substrate as a support. The dye ideal for use in this type of cell must have an absorption spectrum in the visible region, ranging from the spectrum of radiation to be stable for several years exposure to sunlight, and connect strongly and stably to the semi-conductive surface (Will et al, 2000).

In the literature, it is reported that thin films of $\text{SnO}_2:\text{F}$ have been deposited on transparent substrates using the technique spray-pyrolysis. The technique involves thermal stimulation by chemical reaction between atoms of different chemical species (Perednis, G. and Gauckler, L., 2004). The technique consists in spraying the chemical solution containing soluble salts of a metal on the preheated substrate. Thermal energy of the substrate provides the energy for the thermal decomposition and subsequent recombination of atoms, sintering the formed product and providing the recrystallization. This technique is an inexpensive method of deposition, which allows the production of films on large surfaces for industrial applications.

Experiments have shown that thin films growing at temperatures lower than 600 K are amorphous, while those that are formed at higher temperatures are polycrystalline. The factors that are involved in the film quality are, for example, nature and temperature of the substrate, solution composition, flow rate of gas and solution deposition time, etc.. The technique of spray-pyrolysis allows the growth of films on substrates resistant to high temperatures ($>600\text{ }^\circ\text{C}$) as silicon, quartz, borosilicate glass, plain glass and other types of substrates (Perednis, G. et al, 2005). However, for achieving the

best efficiency of this method, it is required deposition of a film of tin dioxide doped with fluorine (SnO₂:F) on the conductive glass, occurring at a temperature of 900 K, approximately, from a precursor solution.

The special heating processes can be performed by combustion reaction, ohmic heating, microwave and infrared heating. Nevertheless, among the emerging technologies of heating, the infrared heating process has been very promising, i.e., heat transmission by radiation, which produces vibration in particular intra- and intermolecular bonds of the component materials (Gomes, A.F, 2002). Thus, this heating process is based on the heat wave from an infrared radiation source, which interacts with the internal structure of the sample, increasing its temperature. Moreover, the infrared energy is transferred from the heater element to the sample, without air circulation. As a result, the material exposed to the electromagnetic radiation, under the wavelength range of infrared, is heated directly by absorption of energy (Setoguchi, G. et al).

Then, all these features have motivated the development of a novel heating device dedicated to the spray-pyrolysis technique in order to obtain high quality thin films, in industrial scale. Therefore, the development of the pyrolyzer's prototype was initiated seeking to build a low-cost heating system, burning natural gas and, also, maintaining reduced manufacturing and maintenance costs as well as without causing significant environmental impacts.

In this context, the principles of filtration combustion (FC), also known as porous media combustion and considered as a clean combustion technology, was applied to the development of this pyrolyzer, which is basically a kind of a porous burner oven. The interest for this experimental investigation was justified not only by the economic features, due to the low fuel consumption, but also, by the environmental ones, due to the very low emissions of toxic gases, especially carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO_x). In addition, the FC can provide safe operation conditions, with process temperatures well defined, in a wide equivalence ratio range, beyond those practiced in conventional ovens.

2. BASE TECHNOLOGIES: FILTRATION COMBUSTION

Filtration Combustion

In general, conventional combustion processes, characterized by operating at equivalence ratio ranges restricted and relatively high temperatures. Consequently, the thermal combustion systems, in addition to producing toxic gases and impacting the environment, require materials of high thermal resistance for mounting the equipment, which increases the cost of manufacture and maintenance of the reactor / burner and reduces the life of the installation. Using the technology of "Combustion Filtration" (CF), the flammability limits of the fuel can be significantly expanded, since air-fuel mixtures ultra-poor to ultra-rich ($0.1 < \Phi < 1.0$). In addition, this technology has proven high relative efficiency and enabled the redesign of reactor designs.

CF is basically the reaction occurring in the interstices of a porous material (inert or catalytic), eliminating the traditional burner nozzle of conventional reactors installed inside the combustion chamber. In CF, the flame front to travel freely along the interior of the combustion chamber, which is filled with a porous material (fully or partially), significantly changing the phenomena present in the process. The porous medium, which can consist of different materials: alumina, quartz, silicon carbide, etc modifies the effect of convection and radiation heat into the chamber and introduces another process of heat transfer driving.

As an internally self-organizing process heat recovery, combustion of air-fuel mixtures premixed in a porous medium, differs significantly from the homogeneous flame. This difference can be attributed to two main factors: the highly developed internal surface of the porous medium, resulting in efficient heat transfer between gas and solid and the process of intense mixing during the gas flow in the porous medium which increases the effective diffusion gas-phase (Zhdanok et al. 1995).

The reaction occurring in the porous medium acts as a heat recovery process in which part of the energy that would normally be released by the exhaust with the exhaust gases is recirculated in the reactor chamber through porous cradle. The porous matrix acts in the process as store heat recirculating it to the flow of working fluid that is coming to the reaction zone.

It stores this energy which is absorbed by the conduction and radiation in regions close to the reaction zone and is transported by the convection via the flue gases, passing through a porous medium high heat capacity, performs a process of intense heat transfer (Kennedy et al. 1995; Contarin et al, 2003a).

With the heat being stored in the chamber, the temperature of the exhaust gases is lower and, consequently, the thermal efficiency of the system becomes higher. With the heat storage in porous media, has an activation energy enough to burn blends ultra-rich or poor, which would be impossible in conventional reactors and burners (Barcellos, 2003; Contarin et al, 2003b ; Kennedy et al, 2000). The Figures 6 and 7 show the ability of a porous cylindrical reactor operating with different equivalence ratios in good process stability.

An intense heat transfer interstitial provides a lower degree of non-thermal equilibrium between gas phase and solid-phase resulting in the coupling of the thermal wave reaction. This situation generally corresponds to a low speed regime of propagation of the combustion wave according to the classification given by (Babkin 1993). The CF technology

applied to the generation of new types of burners, heaters, boilers and furnaces becomes then by promising smaller temperature gradients within the chamber which tends to benefit the speed and efficiency of conversion of fuel. For these types of burners / reactors, commonly called superadiabatic reactors, the level of operating temperature is usually between 1400 and 1750 K, depending on the equivalence ratio and flow velocity of the mixture entering the reactor (Barcellos et al. 2006). The term superadiabatic, which also has some association to the term employed by excess enthalpy, can be explained by the reaction heat stored in the porous medium, which is not exhausted in the discharge, which can maintain a temperature higher than that which corresponds to the condition ultrapoor burning mixtures often impossible to apply the conventional burners.

3. EXPERIMENTAL APPARATUS AND PROCEDURES

3.1 Prototype Design

As previously mentioned, the basic technology is CF in that the combustion chamber is completely filled with ceramic balls of alumina (Al_2O_3), which acts as a heat storer means participant heat inside the reactor. The temperature in the reaction zone varies in the range from 1300 to 1600 K and operate with fuel-air mixtures to emit ultra-poor very low emissions of nitrogen oxides (NOx) and carbon monoxide (CO).

Figure 3 shows the constructive features, with some details external pointing including some dimensions by drawing in perspective and side views, front and top. It is noted that the format of the furnace is rectangular to meet its functionality, which is located in the rear combustion chamber and channels of heat transfer to the central chamber where the process occurs radiation heat drying of the film. In fact, the oven has two key regions as the combustion process: the first is the cylindrical part that is below the oven, which constitutes a porous cylindrical reactor, filled ball, where the wave of combustion must be installed, traveling within the physical boundaries of cylindrical porous body. The part of the porous burner which effectively radiates heat into the central chamber of drying the thin film, as can be seen in Figure 3 (longitudinal) has a rectangular shape, partition bulkhead working as the main chambers. Observing Figure 3, which identifies the three chambers constituting the furnace, namely: i) the rear chamber - where there is a porous medium and through which the flame front propagates to keep the drying temperature thin film through a radiant wall which infrared waves are emitted continuously in continuous operation. In this figure, it is observed that the camera is preceded by a central chamber in the front (right side of the drawing), through which the material is accessed, and where deposition occurs by spraying the material in a controlled and relatively low temperature (slightly above room temperature), for safely handling the material. Between the drying chamber and the antechamber there is a sliding door that allows insertion of the sample to the center of the central chamber for drying (cure) the material deposited on the substrate (glass). Both in the antechamber and in the central chamber there are rails, on which the table that holds the substrate slides from one chamber to the other.

Noting Figure 3 in detail, it turns out that the hole which is in the rear of the furnace is intended to allow the ignition. As can be seen between the porous cylindrical body and the plane, there is a gap through which is inserted into the ignition device, which may be a commercial gas lighter or a spark as well. This change in geometry of the porous body of the reactor, with an empty space separating them, aims to restrict freedom of forward spread over the burner, though, the flat part of the burner can perform a post-combustion of a hydrocarbon remaining combustion process occurring in the cylindrical portion of the porous burner, which is in the oven development.

Combustion gases to pass through the porous flat part of the burner are led out of the oven where the residual heat is transported by convection in the exhaust temperature is relatively low compared to conventional ovens, is captured by a heat exchanger. This exchanger, in addition to protecting the exhaust pipe on leaving the outlet temperature of the gases in the atmosphere near value, recovers heat to be recycled in the process, aiming to reduce fuel or to generate steam for other utilitarian purposes (heating or cogeneration).

The central chamber, as can be seen in the figures 5 and 6, is the environment of the semiconductor heat treatment where the temperature is controlled to be maintained at the value of 600° C, heat radiation function of the bulkhead walls radiating from the rear camera. In principle, this bulkhead is operating at a temperature range between 1000 and 1200 ° C approximately, that can be controlled by injecting more or less fuel, varying the equivalence ratio in the reaction range of 0.3 to 0.8 which allows to obtain very low emissions, CO and NOx.

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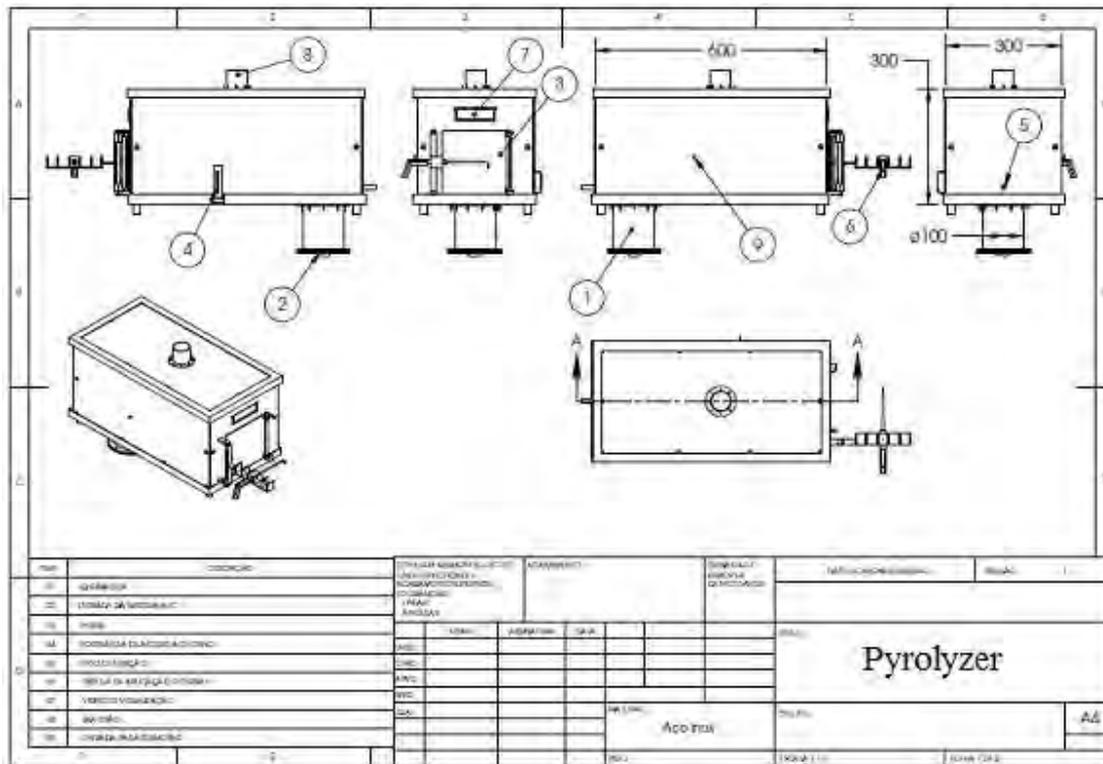


Figure 3 – Side section view of the pyrolyzer

3.2 Operational Procedures

It will be developed a prototype of the furnace to be constructed in a laboratory scale with a porous burner consisting of a cylindrical quartz tube ($L = 150$ mm, $ID = 50$ mm) filled with balls of alumina (Al_2O_3) of approximately 5, 5 mm in diameter, creating a porosity of 40%, on average, through which the air-fuel mixture along the entire length of the burner.

The ignition of the mixture into the burner is carried out by a spark (or pilot flame) to the end of the burner orifice accessed by the rear wall of the oven. The flame front propagates naturally created for the burner center and is there installed in position for operation control arbitrated with a function of equivalence ratio and flow velocity of fuel-air mixture which feeds the burner. Experimentally, the selected speed range is between 0.2 and 0.6 m / s, under a range of equivalence ratios between 0.2 and 1.0. The flow rates of fuel and air are measured and controlled by rotameters. The flow pressure is slightly above atmospheric, differing by 15 mmHg to 30 mmHg, mainly due to pressure losses through the porous cradle.

The fuel flow joins the air at a point forward, with reasonably long length of tubing, associated with a relatively high velocity gas, provide a good mixing process. The pressure and temperature of the flow of air-fuel mixture are measured in a position close to the flange to each end of the reactor.

All output signals of instruments are scanned by a system of National Instruments AT-MIO-16 board. He shows, in real time, as output data: the temperature distribution within the reactor, the temperature of the intake and exhaust gases, water temperatures etc, and samples of these variables monitored are saved to file every 5 seconds.

Emissions of NO and NO_2 are measured with an analyzer chemiluminescência and CO are determined by an infrared analyzer. A volumetric pump draws a constant sample of the products of combustion discharge flow, injecting them into the analyzer. The readings (online) on both analyzers, performed with the other instruments are transformed to standard analog signals are digitized by an analog (Analog Instrument's Board), that displays and records the samples every 10 sec.

As soon as the peak temperature is reached at any point of the porous medium, mixing a certain speed and a certain air-fuel equivalence ratio desired is then implemented so that the combustion process is started automatically. The temperature distribution assumes a shape gradually trapezoid, wherein two temperature peaks begin to grow at the vertices of the profile outlined above, corresponding to the location of the combustion zones, for a given direction of gas flow.

Naturally, the temperature distribution within the reactor will form a trapezoidal profile, wherein the heat exchangers contribute greatly to this configuration. Observing the distribution profile, it turns out that the extraction effectively ends the reactor results in a large temperature gradient.

It is important to note that the emission values indicate the strong influence that this process of energy extraction has on emissions with reasonable fidelity. On the other hand, when some instability that occurs in the combustion process, it is observed instabilities in the process of vaporization of the water flowing in the heat exchangers. Therefore, the combination of the speed range of the flow of the fuel-air mixture, the range of equivalence ratio and the flow of water selected becomes dominant to obtain stability of both processes, combustion and vaporization.

3.3 Instruments

It will be used the thermocouple type J in the Pyrolyze to measure the internal temperature, which mandatorily should be 600 °C. In this case the temperature control was manual.

The cooling water of the reactor is supplied by the bottom edge of the reactor section, with a working pressure range of 500 kPa to 800 kPa. The system pressure is maintained constant, by using a upstream pressure regulator, which is installed in the boiler outlet piping, after the steam pipe joint the flow of air in the mixture was controlled by rotameter (Dwyer – model MMA-37, total range $1,00 \cdot 10^{-5} \text{m}^3/\text{s}$), making it rich or lean mixture depending on the temperature reached.

It will be used a manometer to take the pressure measurement at specific points of the piping. The mainly pressures that should be measured are the heat exchanger and steam piping pressures. There is another “U” tube double column manometer. This equipment was installed to give relative pressure of the exhaustion gas flow, which will allow to know the pressure drop of the gas crossing de porous media.

4. RESULTS AND DISCUSSIONS

The start of the pyrolyzer occurred so as to obtain a heating rate of about 3°C /min, thus showing that the filtration combustion technology can set the desired needs it. Figure 4 shows the behavior of the ignition process of the pyrolyzer.

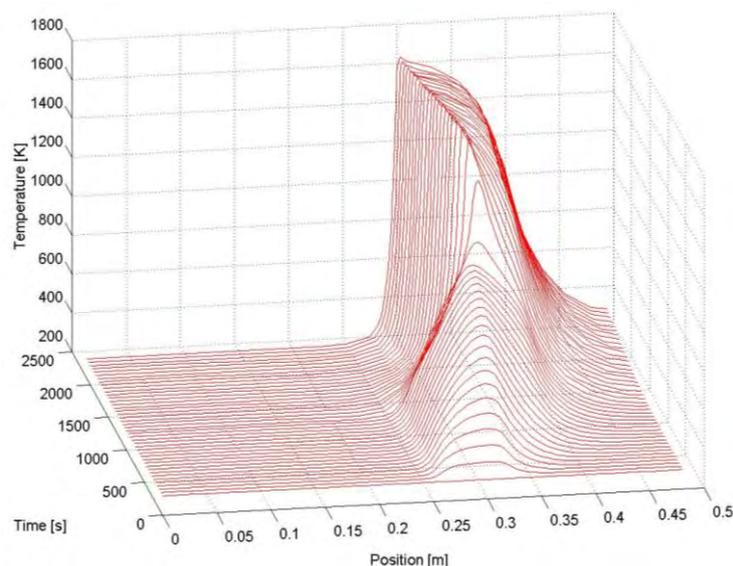


Figure 4 - Temperature Distribution from ignition over time.

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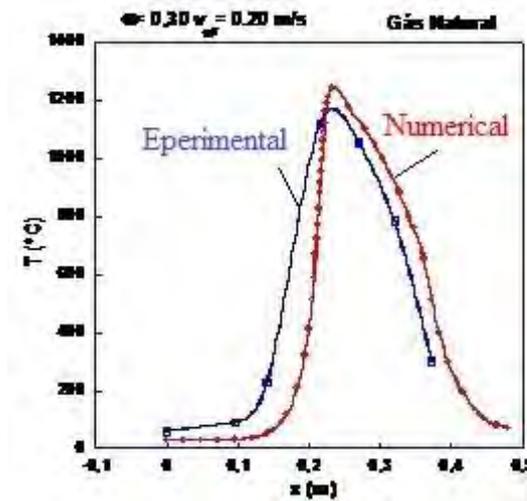


Figure 5 - Profile of temperature distribution with $\Phi = 0.30$ and $v_{gf} = 0.20 \text{ m/s}$ (x Numerical Experimental).

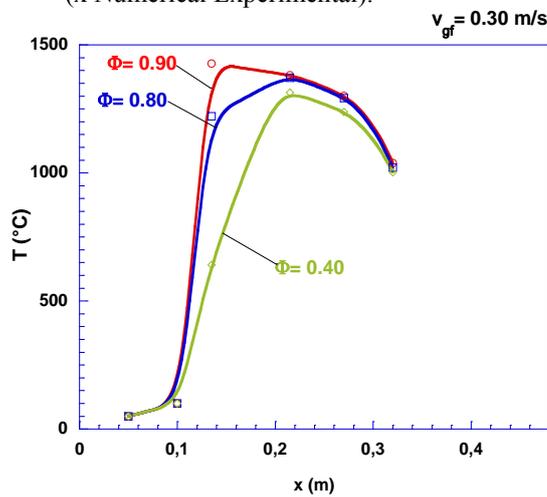


Figure 6 - Profile of temperature distribution with $v_{gf} = 0.30 \text{ m/s}$ (Natural Gas).

4.1 Produced Thin Films

It was made a test with the pyrolyzer in which heating curves chart was obtained with various equivalence ratios. To obtain these curves it was operated with a specific air-fuel flow rate until the oven temperature reach 120 °C, then the maximum flow rate supported by oven was applied. The figure 7 shows the curves obtained.

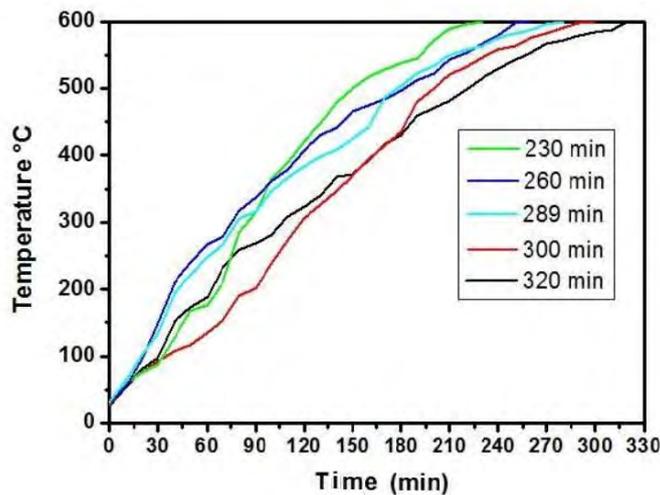


Figure 7 – Pyrolyzer heating curve.

It was verified that there was heat losses in the oven walls, however the covering thickness and the pyrolyzer material was changed. The reactor covering material was changed for refractory ceramic to avoid heat losses between the walls. The pyrolyzer will be heated by ionizing radiation. With this change, it is expected to decrease the heat losses in the walls, to reach the project temperature, to lift up the calibration curve for pyrolysis ($\phi \times t$) and to automate the pyrolyzer with a programmable logic control.

5. CONCLUSIONS

The pyrolyzer was adequate to obtain substrates (glass conductive), increasing the operating (600°C) for 200minutes and mantencing this temperature. The use of natural gas a fuel can be considered essential because the atmosphere inside the pirolyzer is extremely corrosive, if it were used as a source of electric resistance heating in short time the same woud be completely rusted.

This work showed that it is possible to use filtration combustion technology applied to the development of an innovative product and the result of the work was the filing of the patent, preliminary tests showed substrates with electrical resistance around 20Ω.

A new technology was presented using filtration combustion and may possibly be marketed for use in various arms of industry sector, include optoeletronics.

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