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Ceramic fuel cells to replace metal burners

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Global warming is thought to result from emissions largely caused by combustion reactions. Designs of burners and specifications of their materials are therefore of primary importance in restraining the warming phenomena. This paper proposes a new type of ceramic burner which incorporates many of the innovations which are needed to improve burner performance, including catalytic combustion, premixed fuel/air, recuperation of combustion heat, recycling of reaction products, electric-ignition and electron extraction. The key problems of fuel variation and thermal shock resistance of the ceramic are addressed through the concept of 'reaction gradient' in which the rich sequence of oxidation reactions during combustion is spread through three extended catalytic regimes along the isothermal ceramic device. It is evident that ceramic burners are necessary to provide catalytic activity and to promote electron transfer. The conclusion is that ceramic will ultimately replace metal in burners requiring low emissions and high exergy output.

1. Introduction

Combustion is the most important man-made chemical reaction occurring on earth, with approximately 8 gigatonnes of fuels used annually [1], from substances as diverse as coal [2], oil, natural gas, wood, and hydrogen. This reaction can take place in the open, where oxygen penetrates a porous fuel mass in a burning bonfire, for example. More often, the combustion is performed in an enclosure or burner, where fuel and oxygen are contacted in a controlled manner, for example in an engine cylinder, a gas turbine flame tube, or a burner/heat exchanger assembly. Usually this burner is made of metal.

The main problem with conventional flame burners is emissions. With the exception of carbon dioxide and water (CO_2 and H_2O) which are the natural products of hydrocarbon oxidation, these emissions stem from three sources:- poor oxygen penetration, giving toxic partial oxidation products such as carbon monoxide (CO); inadequate time for reaction, which allows unburnt organic compounds to escape; and excessive reaction temperature which promotes side reactions, for example forming nitrogen oxides (NO_x). It is clear that such emissions can be damaging to the environment. Consequently, regulations are increasing, especially since the 1969 US edict on automobile clean-up [3, 4]. For example, a new regulation has appeared in Hamburg, demanding NO_x levels below 10 ppm in burner exhausts [5]. Such regulations require either end-of-pipe catalysis, or more desirably, improved burners. This paper suggests that the new regulations will tend to inhibit conventional metal burners and instead will favour ceramic burners, promoting a substantial thrust in burner materials development.

2. Theoretical aspects

Paradoxically, it was the processing of platinum metal by Wollaston [6] and the first demonstration of flameless combustion by Davy [7] in 1817 which pointed the way to the devices described here. Davy passed fuel gas over a platinum wire in air and found that the oxidation reaction would proceed at low temperature without the need for flame. Active metal nanoparticles thus became more important in this type of "flameless burner" than the material forming the tube wall, though this was beneficially an oxide catalyst support to inhibit sintering of the platinum particles. The problem was that, without high temperature heat output, an ordinary combustion reaction was not beneficial because the exergy, that is the recoverable energy, produced by the burner went to zero. Thus, such catalytic burners wasted the valuable chemical energy stored in the fuel by converting it into heat at low temperature. However, such burners were safe because they could not ignite litter. Consequently, flameless heaters using natural gas over platinum supported on ceramic wool are still used commercially to provide low grade heat in chicken houses [8].

A further advance was made by Bunsen [9] who showed that premixing of air and fuel using a simple venturi could provide much improved control of flame chemistry by contacting the fuel first with primary air, then with secondary air. Earlier, with Playfair, he had also studied recycling of product gases such as CO_2 and H_2O which facilitate many fuel reactions to improve efficiency. Such heat recuperation and exhaust gas recycle have been used in several burner designs but have not yet become generally utilised, even where there is significant efficiency benefit, as in small gas turbines [10].

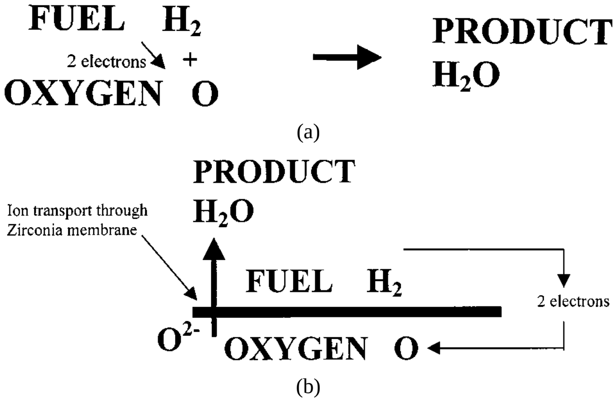

Figure 1 (a) Fuel burning with oxygen, dissipating electrons as water is formed; (b) zirconia membrane forcing the electrons around the external circuit as oxygen combines electrochemically with hydrogen.

Electrical ignition was also an elegant advance noted by Davy [7], allowing facile starting of the flame through sparking electrodes or glowing hot wires sitting in the gas stream. Unfortunately, these electrodes generally remained in the flame and corroded substantially, causing unreliability after some thousands of hours operation.

But the most important deficiency of metal burners is the electron loss. All conventional burners waste the electrons which are transferred uncontrollably from fuel to oxygen atoms in the intense flame front, as shown in Fig. 1a. Thus the only useful product of ordinary burners is heat exergy, the amount of useful work extractable from the hot gas, which is proportional to temperature [11]. The efficiency of a burner can therefore be written as

$$\text{Efficiency} = \text{exergy/input energy}.$$

Therefore, catalytic burners operating at low temperatures are doomed to low efficiency. Davy's flameless platinum burner had almost zero efficiency by this definition. However, the exergy can be improved through extraction of the chemical potential by inserting an ion conducting membrane to restrain electron transfer directly from fuel to oxygen, forcing the electrons to pass around an external circuit where external work can be done. This is the fuel cell principle illustrated in Fig. 1b. Fig. 1a shows normal burner combustion where the electrons are wasted whereas Fig. 1b shows schematically the ion conducting zirconia membrane which forces the electrons round the external circuit, where the 1 volt Nernst potential can drive an electric motor, for example. In this paper, we describe the fabrication and testing of yttria stabilised zirconia membranes which are used in typical solid oxide fuel cells (SOFCs).

3. Ceramic burner/fuel cell design

The objective of the present study was to build a low emission burner which would incorporate all the advances above, to provide a ceramic burner incorporating a zirconia fuel cell. Fig. 2 shows the evolution of the concept starting with the simple tube burner, moving to the Davy catalytic burner, incorporating the Bunsen premix, providing preheat and recycle, inserting the electrical igniter and finally separating the electrons using a zirconia membrane fuel cell tube to replace the Bunsen metal tube.

In terms of burner operation, the main design requirement was the temperature of operation. This was chosen to be between 700 and 800 °C for natural gas and other hydrocarbon operation [12, 13]. Lower temperatures apply for alcohol reactions which can proceed at 250 °C, and higher values would be needed for coal and other carbon based fuels which could operate at 1000 °C. The idea was to maintain the burner tube under approximately isothermal conditions, to spread the reaction gradient from a few micrometres in a conventional flame to 30 millimetres in the new device, a factor of 30,000 in distance to provide controllability of the complex fuel/oxygen chemistry [14]. This spread of reactions was achieved by using three catalysts over the length of the tube as shown in Fig. 2. Oxygen entered in three stages; premix air in the primary zone, electrolytic oxygen in the secondary zone and total oxidation air in the tertiary zone.

The first catalyst, shown in Fig. 3, was ruthenium on zirconia, to give partial oxidation of the fuel preventing carbon deposition downstream, and also to provide an exotherm to maintain the upstream temperature around 700°C [15]. The next catalyst was nickel on zirconia to reform any remaining hydrocarbon and to transfer oxygen ions from the zirconia electrolyte tube into the fuel atoms, releasing electrons into the nickel. A nickel wire current lead was used inside the tube to collect these electrons and transfer them to the negative terminal outside the burner. On the outside of the zirconia tube in this section, surrounded by preheated air, was a layer of lanthanum strontium manganite to catalyse the oxygen reduction and transfer electrons from the wire current leads into the oxygen atoms [16, 17]. The interesting point about this catalyst was that it could be controlled electrically by allowing different amounts of oxygen through the zirconia membrane. Thus there was much potential for tuning the chemistry of this burner by electrical means.

Finally, at the top end of the tube was a platinum on ceria/zirconia catalyst to provide full oxidation of any remaining fuel molecules. At this stage tertiary air was allowed to diffuse back down the tube to maintain the operating temperature condition. Overall, the burner has evolved from Bunsen's concept to bring in secondary oxygen through the zirconia membrane, providing extra control of hydrocarbon reaction along the tube, in addition using the premix air (primary air) to react controllably in the upstream region. This spreading of the reaction gradient is essential to separate the many complicated hydrocarbon reactions and to allow electron transfer.

A key materials problem of this new ceramic burner concept was thermal shock of the oxide parts. In contrast to Bunsen's metal tube, zirconia is notorious for its high thermal expansion coefficient and poor thermal conductivity, which allow large stresses to build up in the ceramic, thus promoting cracking failure. It was found that reducing the burner tube diameter, from 10 mm for a Bunsen tube to 1 or 2 mm for this device,

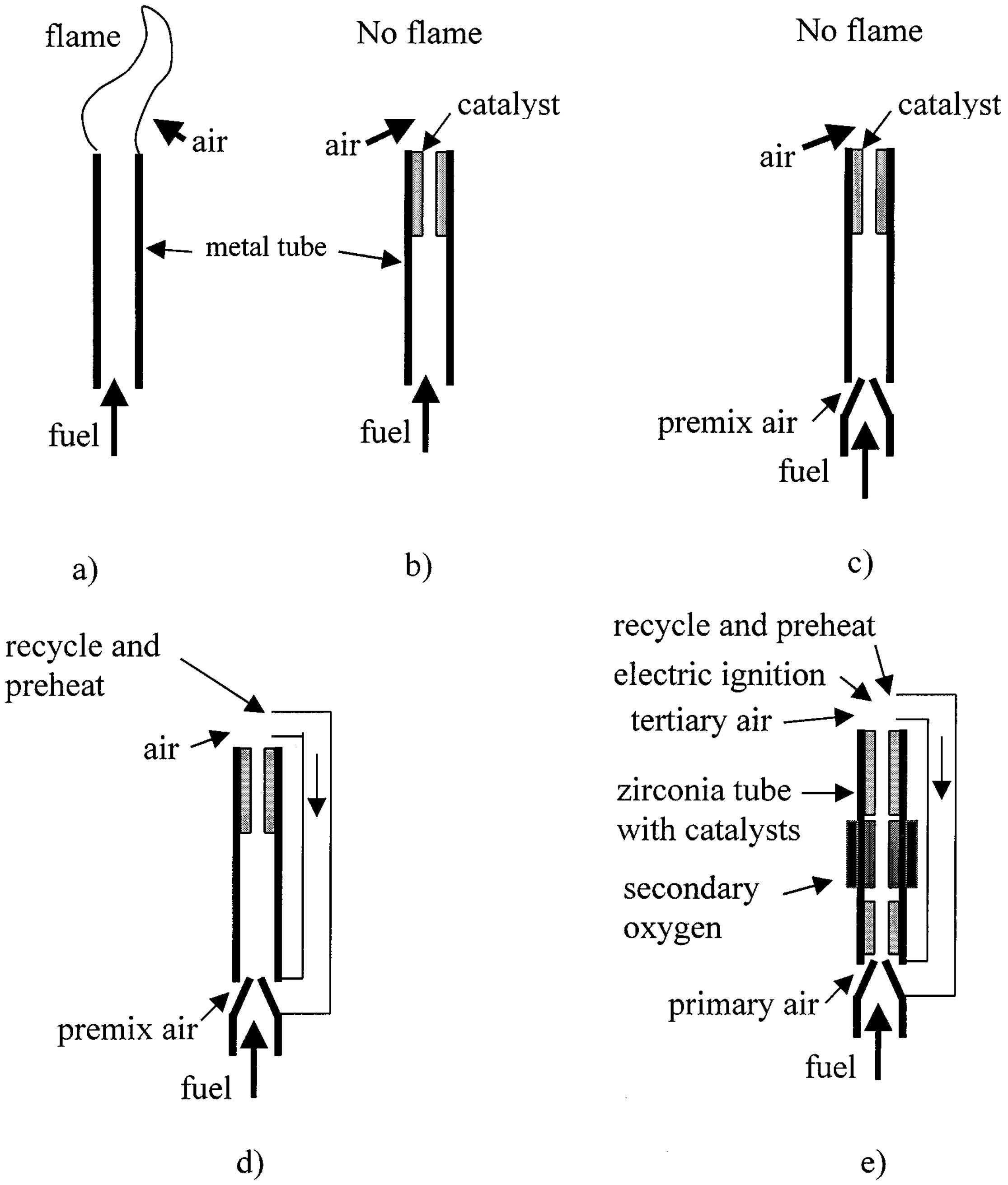

Figure 2 Schematic showing the evolution of an SOFC burner from a simple metal tube:- a) metal tube burner; b) Davy catalytic flameless burner; c) Bunsen premix burner with catalytic oxidation; d) addition of recycle and preheat; e) final electron transfer through zirconia tube, showing three air paths into the burner, one for premix, second through the zirconia SOFC, and third into the final oxidation catalyst.

was sufficient to prevent thermal shock cracking [18, 19]. Rapid warm-up was then possible for the new device, together with cool-down in a few seconds. Although this is slower than a flame warm-up, which occurs in microseconds, it is acceptable for many burner applications, especially the rapid start-up required in domestic, leisure or transport applications.

4. Experimental materials and method

Zirconia powder stabilised with 8 mol% yttria was provided by MEL Chemicals. Its particle size measured by Malvern Mastersizer was 0.5 μm. By mixing this powder with polyvinyl alcohol (KH17s, Gohsenol) then adding water, in volume proportions 55/20/25 respectively, a plastic dough could be formed using a twin roll mill to produce a mouldable sheet which was pressed overnight in a plastic bag at 5 MPa pressure to remove any air bubbles. This plastic sheet was ram extruded through a tube die 2.5 mm outside diameter and 200 μm wall dimension to provide lengths of tube which were dried and fired to 1450°C giving full density. This resulted in an essentially defect free membrane, though an occasional pore about 100 μm in diameter could be seen by micro-focus X-ray inspection (Fig. 4). Striations indicating the flow direction could also be observed, demonstrating slight (e.g. 1%) density differences through the thickness of the membrane. Despite such defects, none of the tubes showed any leaks. Leaks can readily be detected by a drop in open circuit voltage of the cells. Typically, this was maintained at 1.153V for all the membranes when tested at 900 °C on 20 ml/min hydrogen flow in air.

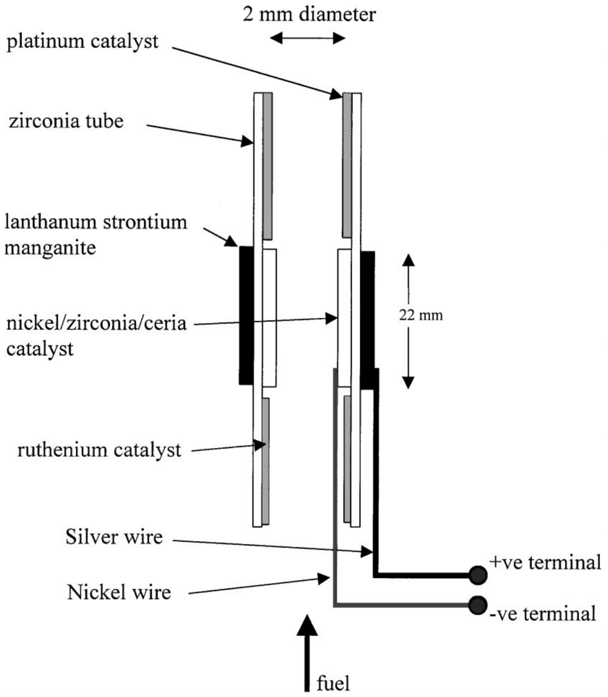

Figure 3 Cross-section through the zirconia tube containing the three combustion catalysts, and the oxygen reduction catalyst outside the tube.

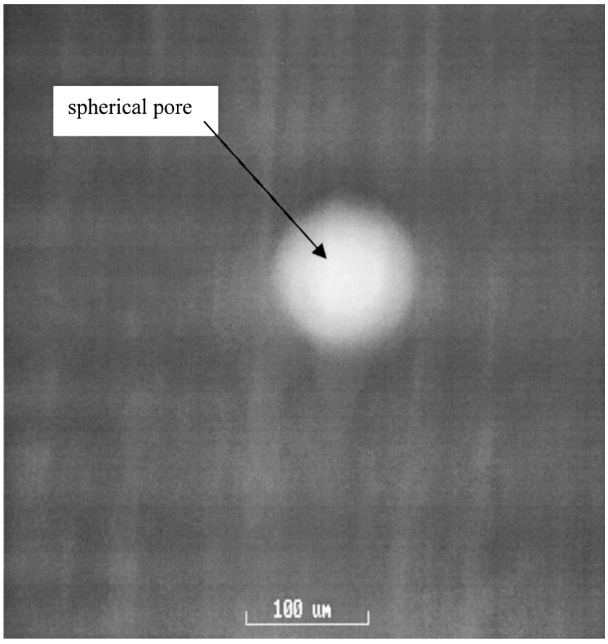

Figure 4 Micro-focus X-ray picture of a zirconia tube showing a spherical pore in the 200 μm wall thickness.

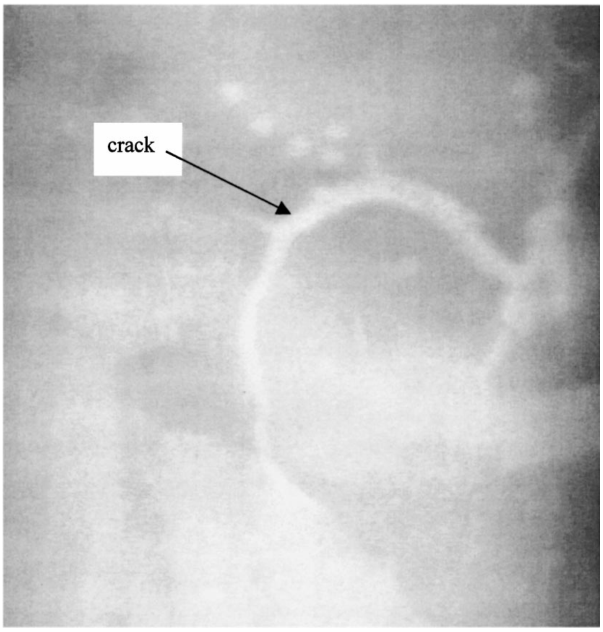

Figure 5 Microfocus X-ray picture of crack defects in the lanthanum strontium manganite cathode layer.

An inner electrode, or anode, was made by vibro-milling green nickel oxide powder (Aldrich) with acetone and dispersing agent (KD1, Avecia) to give a fine dispersion at 20% volume fraction, then adding 9.5Y-zirconia powder of 8 μm diameter (MEL Chemicals) to produce anode cermet ink containing equal volumes of nickel and zirconia. This was sucked into the zirconia electrolyte tube with a syringe, then allowed to drain out, leaving a 50 μm layer dried on the inner surface. A second layer containing 90% nickel was laid on top to improve the current collection from the electrode. This was also viewed by microfocus Xray inspection (Xtek) and sometimes cracks were observed as shown in Fig. 5, although generally, the electrodes were flaw free.

The outer air electrode, or cathode, was made from lanthanum strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, SSC) by milling the powder in acetone/KD1 and painting the dispersion onto the outside of the zirconia tube. A second layer of coarse LSM was coated on top to improve conductivity. Then the cell was fired at 1300°C and the current collection wires attached to the electrodes. Nickel was the anode wire, wrapped into a spiral and pulled into the tube; silver was the cathode wire, twisted several times around the outside of the black cathode. Catalyst compositions were painted onto the inner tube surfaces as illustrated in Fig. 3. The cell was then heated in an oven to 900°C and hydrogen flowed down the inside of the tube to reduce the nickel oxide anode. After 15 minutes, the SOFC was performing adequately and the characteristic current curve could be plotted as shown in Fig. 6. The open circuit voltage was 1.153 V and the current density at 0.5 V was

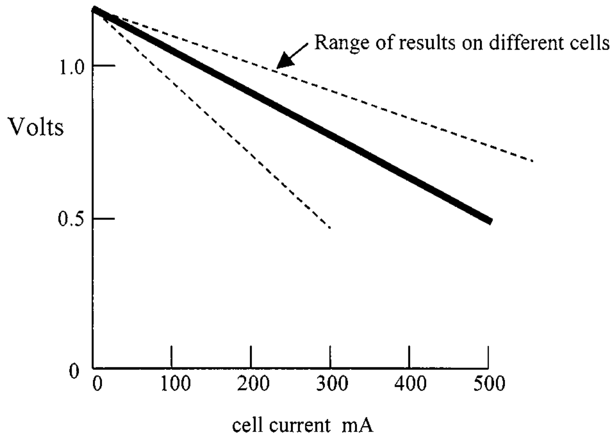

Figure 6 Voltage/current characteristic for tubular SOFCs.

between 300 and 800 mA for a cell area of 1.3 cm^2. This variation in cell output depended greatly on the contact between the anode wire and the nickel cermet, and was a function of the precise assembly method. Cells below 300 mA output were discarded and reworked.

5. Results for burner/SOFC operation on methane

Having calibrated the device on hydrogen, the cell was inserted in the apparatus shown in Fig. 7. Various gases could be injected into the burner/SOFC from the gas inlet system. The tube was contained in a thermally controlled furnace and the inside gas composition was sampled along the tube using the mass spectrometer probe. Meanwhile, oxygen flow through the zirconia membrane was controlled by the potentiostat [20, 21]. Methane was the hydrocarbon fuel used in the experiments described here. The initial gas composition entering the tube was methane and oxygen derived from the premix air. Two different ratios are shown in Fig. 8A and B. Nitrogen and other inert gases are not shown. During partial oxidation on the ruthenium the oxygen and methane diminished and CO and H increased. Then, over the nickel reforming catalyst of the SOFC more methane was converted, oxygen fell to near zero and CO plus H_2 were converted by electron transfer. Finally, over the platinum oxidation catalyst, tertiary oxygen was introduced and methane, H_2 and CO decreased to zero.

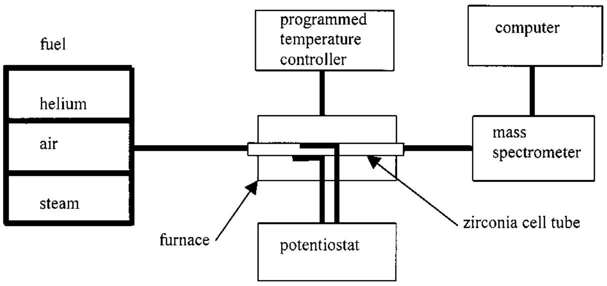

Figure 7 Test apparatus for measuring the performance of the zirconia fuel cell/burner.

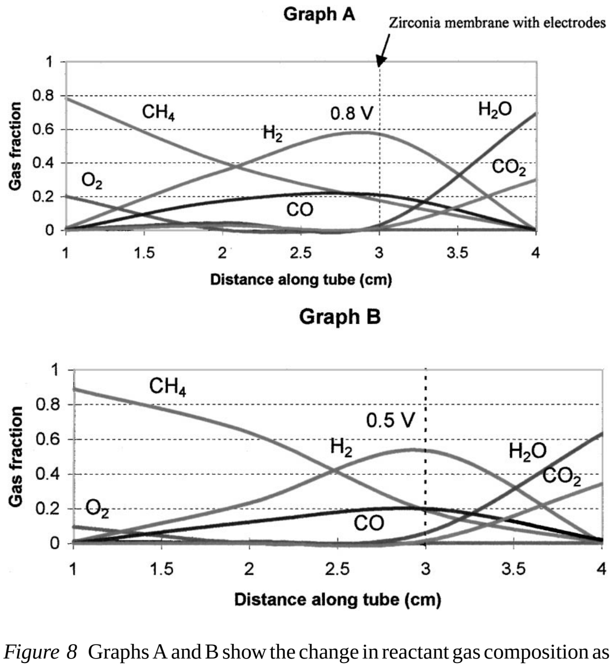

Figure 8 Graphs A and B show the change in reactant gas composition as it passed through the catalytic burner device from left to right. Graph A shows the gas composition change for a starting mixture with a 4 : 1 methane/oxygen ratio. An electrical load of 0.8 V was applied to obtain the desired reactant mixture for total combustion. Graph B shows the gas composition change for a starting mixture with a 9 : 1 methane/oxygen ratio. A load of 0.5 V was applied to obtain the desired reactant mixture for total combustion.

Start-up of the burner was an important question because the equilibrium running condition described above cannot be achieved easily. Either electrical preheating of the device, or flame start-up was necessary to get the new ceramic burner going. Electrical preheating was simplest because there was then no need to adjust the air/fuel conditions in the burner. A current was passed along a nichrome heater wire until the device reached its operating temperature of 700°C, then the fuel flow was started. Alternatively, an electric igniter was positioned just downstream of the tube and this ignited a small flow of fuel and air to produce a starter flame. Within a few seconds, the heat from this flame had warmed the system to 700 °C and the flame then went out and the catalytic device glowed red. The metal ignition electrodes were then not excessively hot and remained reliable after many hours of operation.

6. Conclusions

In conclusion, a new ceramic burner concept has been demonstrated to improve the emissions from hydrocarbon oxidation reactions, while simultaneously raising the efficiency. The burner incorporates the benefits of catalytic combustion, premixed fuel/air, preheat and recycle, electric ignition and electron capture within a ceramic structure. The burner has operated using hydrocarbon fuels such as methane, propane and butane and has potential efficiency (output exergy/input energy) of 70% compared to 35% for a conventional metal burner used in a diesel or gas turbine engine. Such a burner could make a significant contribution to reduction of global warming.

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