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(54) **Title:** DEVICE FOR GENERATING ELECTRICAL SIGNALS FROM GASEOUS FUELS

(57) **Abstract:** Herein is described a device powered by a fuel gas and able to produce electrical signals for use within smart gas-meters enabled for remote reading. Catalysts based on Ir for flameless combustion are also described, such catalysts supported on microporous refractory material.

**Device for generating electrical signals from gaseous fuels****FIELD OF THE INVENTION**

This invention relates to catalysts containing Ir and supported on microporous refractory materials, their use for the flameless combustion of a fuel gas and their use in a device powered by a fuel gas able to produce electrical signals.

**STATE OF THE ART**

The gas distributed to end users, domestic or else, shall be measured in order to enable the correct billing of consumption to the customer; furthermore taxes payable to the tax authorities are calculated considering on the measured values.

The gauges currently installed are based on very traditional and proven mechanical technologies. Worldwide the consumption of typical household is measured using diaphragm meters, also known as metering diaphragm. The patent of the first model of a diaphragm meter was filed in 1816 by Clegg and Malam. Based on these liquid meters on the middle of '800 (1844, Richards and Croll) dry meters had been developed and are still in use. Indeed, without significant innovations, except for the usual upgrading of the materials and the production techniques, this tool is still produced today in millions of pieces. This meter is a tool that measures the volumes of gas through the filling and the emptying of two alternate half-chambers of known volume, divided internally by an elastic diaphragm.

This alternate motion, through simple gearings and crank, is transmitted to a clock that indicates the measured amount of gas. The energy needed for its operation is get from pressure of the gas which passes through the device.

It does not include any external power and any electrical or electronic accessory. The accuracy of measurement is approximate, since it can not take into account parameters that greatly influence the actual amount of energy supplied to the consumer, the pressure, the temperature and the composition of the measured gas. All the more, about half of the amount of meters installed is old, ie built over twenty-five years ago with outdated technology and materials. These tools should be replaced over the next years with a new generation meters containing 'smart' and bi-directional communication capabilities. Certainly these devices must be

electrically powered to perform the new functions. But the current technology, based only on mechanical tools, cannot be used for this purpose.

For higher pressures and gas flow rates different types of meters are used, such as turbine or rotary pistons. In this case the mechanical devices are often associated with electronic accessories for the conversion of gas volumes depending on pressure and temperature, and if required, including modules for remote transmission of the consumptions. Usually these systems are connected to the main power supply or to batteries (that have then to be replaced). For the electrical supplies integrated systems based on Smart Meters and Smart Grids are already in use since years, consisting respectively of devices for the energy measurement and networks for centralized management of the data.

This allows to differentiate the pricing according to the time range of the use and to manage users based on the flows of energy and on the combination of user demand and supply managers. Due to the success of this technology in electricity metering, the Italian Authority for Electricity and Gas after two years of preparatory work has issued the Resolution ARG / gas 155/08 of 22 October 2008 "Guidelines for commissioning meters to measure the gas, containing minimal functional requirements, telemetering and remote control functions, for the delivery of natural gas to distribution networks", in order to introduce smart technologies in the distribution of natural gas.

The above mentioned document requires a gas meter able to measure, provide information via digital display, store, manage some security functions and communicate through the network of transmission in both directions. However, nowadays, except for high load gas flow meters, the existing meter have only measurement capability without any output to external communication. The main difference between the remote reading of gas consumption and of electricity consumption lays in the availability of the energy that powers the electrical devices and the electrical requirements for the new types of electrical meters. However, this is not available for natural gas meters: in almost all cases the connection of the meter to the electricity distribution network is complex, expensive and cause serious security issues, since natural gas is flammable and the connection to a 220 V current may cause explosions. For this reason up to now a limited amount

of devices are available, even at an experimental level, for gas meter associated to an on board electrical equipment, fed by disposable batteries of different capacities, depending on the power and duration required.

5 However, despite the battery technology is continuously increasing, the amount of energy that can be reasonably available is very limited, thus forcing the designers to an extreme reduction in communication skills, management and accuracy of measuring instruments. The limited availability of energy hampers the introduction of innovative technologies for innovative measuring, based on non-volumetric principles, such as ultrasound, thermal mass flow measurement, and others, which  
10 could allow a dramatic improvement of the accuracy and of long-term reliability of gas measurement for everyone is involved: distributors, end customers and control bodies.

#### SUMMARY OF THE INVENTION

This invention relates to a catalyst supported on a refractory material, said catalyst  
15 comprising Ir and one or more transition metals selected from Pt, Pd, Ni, Co, Fe, Rh, Ru, said refractory material having the structure of a porous body whose pores have an average diameter of 5-500 microns.

The catalyst of this invention promotes effectively the flameless combustion of a fuel gas and therefore can be used as reactor in a device that uses the heat  
20 produced by such flameless combustion.

Therefore this invention concerns also a device for generating electricity from fuel gas; said device, referring to Figure 1, includes:

- (a) A Peltier element (1), able to convert thermal energy in electric energy;
- (b) a reactor (2) made by of a catalyst supported on a porous refractory  
25 material; said catalyst being active for the flameless combustion of a fuel gas; said reactor is positioned in thermal contact with one of the two outer faces of the peltier element;
- (c) an electrical resistance (3) in thermal contact with the reactor in order to warm it up to the start up temperatures of the catalyzed flameless  
30 combustion reaction;
- (d) an auxiliary battery (4) for the resistance powering.

The above mentioned device produces a potential detectable inside the Peltier element, when used according with the following method:

- (i) heating of the reactor, by electrical feeding of the thermal resistance, up to a temperature adequate to promote the catalytic flameless combustion of a gaseous fuel;
- (ii) inflow, via an appropriate inlet, of a flow of combustible gas within the refractory support.

The above mentioned method is held in presence of atmospheric oxygen, which otherwise should be sent to the refractory support concurrently with the gas fuel.

The combustion products are released into the atmosphere. If the device is enclosed in a packaging, holes must be provided for the inflow of atmospheric air and/or the outflow of combustion products. That device may be associated with a gas meter, to provide electricity necessary for the powering of the associated electronic accessories suitable for remote transmission of consumptions.

Another object of the invention is thus a smart meter for calculating and reporting the consumption of a fuel gas, said meter comprising the device of the invention.

#### SHORT DESCRIPTION OF THE FIGURES:

Figure 1 shows schematically the device object of the invention and the relative positions of its components.

#### DETAILED DESCRIPTION OF THE INVENTION

Catalysts described in the present invention preferably use as refractory support a material selected from ceramic fiber, silicates (such as rock wool, asbestos), microporous alumina and sintered quartz. The refractory support has a porosity sufficient to ensure an adequate gas permeability for an efficient exchange between reactants and products of the flameless combustion. Preferably the catalysts of the described invention include Ir and Co, and even more preferably with a composition range: 10-50% iridium (the remainder to 100 is cobalt).

These supported catalysts, which consist of finely dispersed metals within the microporous refractory support, may be prepared by appropriate and known techniques, such as impregnation.

The technology covered by this patent is based on the production of electricity from natural gas, available within a gas-meter in not-limited quantities, in order to

power electronic components suitable for the remote transmission of the values measured for the gas itself. In this way, the production of the energy needed for transmission of signals and values makes the gas meter energy-independent, similar to electrical energy meters are currently installed. This allows the increase  
5 of communication capabilities of a gas-meter and the realization of domestic communication platforms, using home display and Internet networks to inform the customer of the energy use in real time, in order to maximize the saving and the use of cheaper sources.

For safety reasons associated to the presence of gas, the production of electrical  
10 signals must be done without open flames. In order to obtain that, it is possible to use catalysts described in this invention or other catalysts selected from among those known to the State of the Art, similarly supported. Among the metals and mixtures capable of promoting the flameless combustion of a fuel gas known to the State of the Art, some of these contain transition metals, such as but not  
15 limited to Ir, Pt, Pd, La, Ni, Co, Fe, Rh, Ru or mixtures thereof (such as those described in Gelin, P., et al. Applied Catalysis B: Environ. 2002, 39, 1-37). These metals and mixtures, suitably supported on refractory porous materials as described above, can be alternately used, in a manner similar to Ir-based catalysts under the present invention, as suitable reactors in the device object of the  
20 invention. In a particularly advantageous method, the device of the present invention contains the supported catalysts object of this invention, as described above.

As a not limiting example one of the techniques used to prepare these catalysts consists in depositing the catalyst metal precursors in appropriate proportions as  
25 aqueous solution on a high porous refractory support and then followed by the pyrolysis in air to a temperature of 600 °C. Preferably these steps of impregnation and pyrolysis may be repeated several times until finding a suitable and sufficient weight gain of the support.

In order to trigger the combustion reaction without open flame it is necessary to  
30 raise the temperature of the catalytic bed at a temperature above 350 ° C. For this purpose, the electrical resistance, to be used during the powering of the device, is allocated into or otherwise in contact with the refractory support.

This electric resistance is powered by an auxiliary battery. Said battery can be disposable battery, and will require periodic replacement, or it can a rechargeable battery. In this case the electricity needed to recharge the battery will be provided directly by means of the Peltier element, once started the gas combustion  
5 reaction. Once the gas combustion reaction is started, then it is possible to interrupt the powering of such resistance.

For the purposes of this invention fuel gas means any hydrocarbon that is in a gaseous state under atmospheric conditions; among these methane, propane and natural gas can be listed.

10 The present invention will be better understood in light of the following example of reduction into practice.

Example A: Synthesis of the catalyst:

5,0 g di  $\text{IrCl}_3$  hydrate and 14,0 g di  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  are solved in 500 mL of distilled water.

15 This solution is used to impregnate a piece of ceramic fiber wool (50x50x10 mm). After impregnation the support is left to dry at room temperature in air and then pyrolyzed in air at 600 °C for 3h. The process of impregnation/pyrolysis is repeated several times to obtain a weight increase of the support of 300 mg.

Example B: Catalytic activity test:

20 The catalyst support, prepared according to Example A, was inserted into a drilled aluminum block containing an electrical resistance of 3 ohms. Adjacent to the aluminum block was placed a micro Peltier mod TE9502/065/012 M (65 pairs, 1.20 Amp-Ferrotec).

25 The temperature of the catalyzed substrate was raised up to 350 °C by heating the electrical resistance and then a stream of methane (50 mL/min) was flown. The potential difference display located downstream of the Peltier module registered a constant voltage of  $0.420 \text{ V} \pm 0.05$ .

## Claims

1. A catalyst supported on a refractory material, said catalyst comprising Ir and one or more transition metals selected from Pt, Pd, Ni, Co, Fe, Rh, Ru,  
5 said refractory material having the structure of a porous body whose pores have an average diameter of 5-500 microns.
2. Catalyst according to claim 1 wherein the refractory material is selected from ceramic fiber, silicates, ceramics, porous alumina, sintered quartz.
3. Catalyst according to any of claims 1-2 comprising Ir and Co.
- 10 4. Use of a catalyst according to any of claims 1-3 for the flameless combustion of a fuel gas.
5. A device for generating electricity from fuel gas, said device comprising:
  - (a) a Peltier element, capable of converting heat energy into electrical energy;
  - (b) a reactor that comprises a catalyst supported on a refractory material, said  
15 catalyst being active for the flameless combustion of fuel gas, said refractory material having the structure of a porous body whose pores have an average diameter of 5-500 microns, said reactor positioned in thermal contact with one of the two outer faces of the Peltier element;
  - (c) an electrical resistance in thermal contact with the reactor in order to warm  
20 it up to the start up temperatures of the catalyzed flameless combustion reaction;
  - (d) an auxiliary battery for the powering of the resistance.
6. Device according to claim 5 containing an active catalyst comprising a metal selected from Pt, Pd, Ni, Co, Fe, La, Ir, Rh, Ru or mixtures thereof.
- 25 7. Device according to any of claims 5-6 in which said refractory support is selected from porous ceramic fiber, silicates, ceramics, porous alumina, sintered quartz.
8. Device according to any of claims 5-6 in which the catalyst is as defined in any of claims 1-3.
- 30 9. Device according to any of claims 5-8 in which the reactor is positioned in thermal contact with all or most of the surface of the Peltier element face.

10. Device according to any of claims 5-9 where the auxiliary battery is rechargeable.

11. Method for the production of electricity from a fuel gas through the device according to any of claims 5-10, said method comprising the following steps:

5

i. heating of the reactor through the powering of a thermal resistance up to a temperature sufficient to promote the catalyzed flameless combustion of a fuel gas;

ii. inflowing, via an appropriate inlet, of a fuel gas flow inside the heated refractory support.

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12. Method according to claim 11 in which the reactor is heated up to a temperature above 350 °C.

13. A smart meter for the measurement and the reporting the consumption of a fuel gas, said meter comprising the device according to any of claims 5-10.

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