

# Application of Zirconia Analyzer in Combustion Control

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**Abstract:** the paper introduces the factors affecting combustion efficiency, how to realize optimized combustion, working principle of zirconia analyzer and typical application of it in electric power, iron and steel, petrifaction and other key occasions.

**Key Words:** energy conservation and emission reduction, optimized combustion, air-fuel ratio, zirconia.

## Foreword

The Government of China reaffirmed the commitment that energy consumptions per GDP in energy conservation and emission reduction field reduces by 20% at end of the “11th Five-Year Plan”. Along with the intensive release of the more and more severe energy conservation and emission reduction policy, combustion monitoring and optimization gain more and more attentions as the key monitoring target for energy consumption and greenhouse gases emission. As a key control meter of combustion control rapidly developed and applied in recent years, intelligent zirconia is quickly promoted right now with its accurate measurement results, convenient installation and less maintenance, and has gains good economic benefit and social benefit.

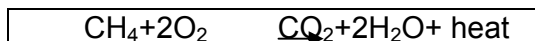
## I. Combustion

### 1.1 Basic definition of combustion

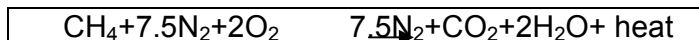
Combustion is defined in various modes, and the topical one is described as below:

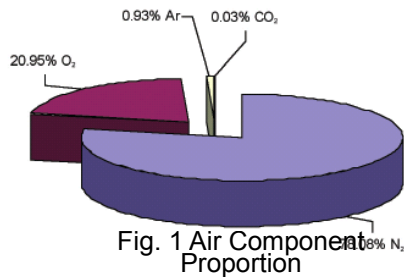
“The rapid oxidation process between combustibles and oxide at certain temperature accompanied with heat release, shining, etc.”

In definition above, combustion can be deemed as a oxidation process of fuel, especially hydrocarbon, and the main purpose is to generate heat that is utilizable. Take methane as the example, methane reacts with oxygen to generate carbon dioxide, water and heat:



However, in most combustion, oxygen comes from the air. Oxygen accounts only about 21% of the air, as shown in Fig. 1 (Oxygen is simply considered accounting 21% of the air, and others are nitrogen). Thus, the formula above can be changed into:





Obviously, an ideal combustion process is hard to achieve, and combustion in practice is a complex reaction process which always fails to realize complete combustion. If methane burns incompletely, CO will be generated. If sulphur exists in fuels (most chemical fuels contain sulphur, such as coal and oil), SO<sub>2</sub>, NO, NO<sub>2</sub> and others will be generated after combustion. All those are considered as harmful gas.

## 1.2 Combustion efficiency

In an ideal combustion process, appropriate amount of oxygen is fed and burns with the combustibles, which is the well-known stoichiometric air-fuel ratio. Different fuels have distinct air-fuel ratio, and the exact air-fuel ratio is determined by ratio of hydrocarbon in fuel. Take methane as the example again, 9.5 units of air (2 units of oxygen and 7.5 units of nitrogen) is required for completely burning 1 unit of methane, 9.5 is the ideal air-fuel ratio of methane; as shown in Fig. 2.

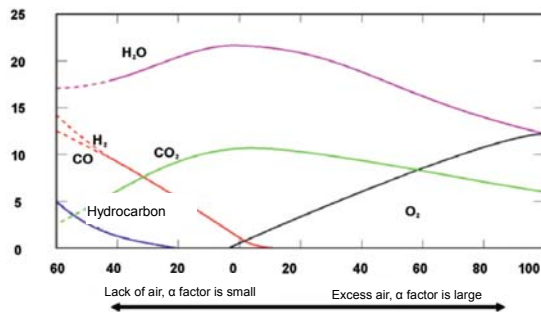


Fig. 2

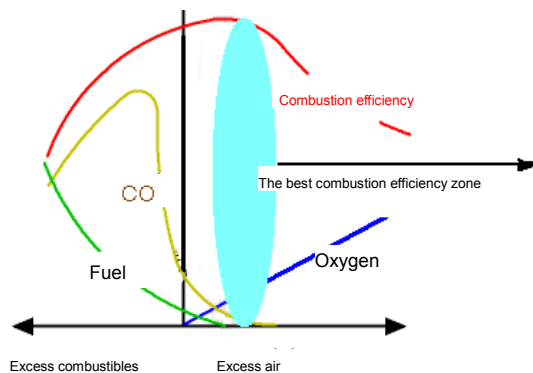


Fig. 3

However, it is impossible in practice. Most combustion processes have the efficiency of 30-50%. In a combustion process, heat is lost in following aspects: ① Heat lost due to incomplete combustion of combustibles  $Q_1$ ; ② Heat lost in smoke evacuation  $Q_2$ ; ③ Heat dissipation  $Q_3$ ; ④ Heat lost in ash of combustibles  $Q_4$ . Combustion efficiency is:  $\eta = [1 - (Q_1 + Q_2 + Q_3 + Q_4)] \times \%$ .

If quantitative air that conforming to ideal air-fuel ratio is supplied exactly, since the air can not mix quickly and completely, the combustion is always incomplete, which will cause  $Q_1$  and  $Q_4$  increase, and the combustion efficiency  $\eta$  is lower than the ideal value. To change the situation, excessive air will be fed into combustion process. The theoretical value of the actual oxygen supply and complete combustion of combustibles are called as excess air factor  $\alpha$ . When  $\alpha$  is large, viz. too much

combustion-supporting gas is supplied, heat taken away by excessive high-temperature gas will increase, viz.  $Q_2$  increases, combustion efficiency  $\eta$  will reduce. As shown in Fig. 3.

Combustion efficiency is the key parameter to calculate the whole combustion process/equipment. In short, combustion efficiency reflects the energy to be provided and promotion space after reducing energy carried in smoke and improving combustion efficiency and other measures.

Combustion efficiency is commonly metered with Siegert formula:

$$H = 100 - [k(T_1 - T_2)] / (20.8 - \%O_2)$$

$T_1$  = combustion temperature of fuel

$T_2$  = entry air temperature

$\%O_2$  = oxygen content of smoke  $\%O_2$

$K$  = combustion constant, determined by combustion type

With the formula above, we can obtain combustion efficiency when knowing the temperature difference, fuel type and residual oxygen content.

### 1.3 Combustion optimization

It can be seen from two chapters above that to ensure the optimized combustion process, accurate monitoring on excess air factor  $\alpha$  is required. Residual oxygen in combustion air after combustion is directly related to excess air factor, air-fuel ratio and combustion efficiency.

It is considered in the typical theory that 1% combustion air will probably cause 0.25% combustion efficiency difference. Ideal combustion environment of different combustibles is shown in Table below. The optimized combustion can be realized in excess air atmosphere shown as following. Furthermore, residual oxygen has a similar linear relation with excess air, which provides possibility to optimizing combustion through obtaining excess air by ways of measuring residual oxygen.

Combustible type	Excess air	Residual air
Natural gas	5-10%	1-2%
Propane	5-10%	1-2%
Heavy oil	10-15%	2-3%
Pulverized coal	15-20%	3-4%
Lump coal	20-30%	4-6%
Biomass fuel	15-40%	3-8%

Table 1

## II. Measurement of Oxygen

### 2.1 Technological evolution

In the past, combustion efficiency is monitored by measuring  $CO_2$ , which has the following disadvantages:

1) Curve of  $CO_2$  is unimodal curve (refer to Fig. 1), and it is difficult to participate automatic control.

- 2) It is hard to measure CO<sub>2</sub>, and has higher requirements on pre-treatment.
- 3) CO<sub>2</sub> content is greatly affected by fuel variety.

After 1940s, paramagnetic oxygen measurement technology appeared and became the mainstream technology quickly at that time. With the technology, oxygen content is measured based on the difference of other magnetic susceptibility of oxygen to other components, however, the same as the measurement of CO<sub>2</sub>, smoke must be extracted before measurement, and the pretreatment is complex and response is slow. The technology is now replaced by zirconia analyzer gradually.

## 2.2 Measurement principle of zirconia

According to installation and measurement mode, zirconia analyzer can be divided into direct plug-in analyzer and suction-type analyzer. Suction-type analyzer adopts current type sensor, and is mainly applied in following cases:

- 1) Combustion control of clean fuel
- 2) The case with temperature variation exceeds 600 °C
- 3) The case measuring CO<sub>e</sub> at the same time

Owing to complex installation and high price, suction-type analyzer is rarely applied. Direct plug-in analyzer is used in most cases (unless otherwise specified, zirconia below in the text refers to direct plug-in zirconia).

Direct plug-in zirconia adopts the conducting mechanism utilizing solid electrolyte (zirconia crystal added with calcium oxide and yttria). When oxygen partial pressure measured inside and outside zirconia measuring body (deformed as tubular shape generally, as shown in Fig. 4) is different, oxygen ion will diffuse from high concentration side to low concentration side, thus potential difference is generated by platinum electrode at both sides of zirconia

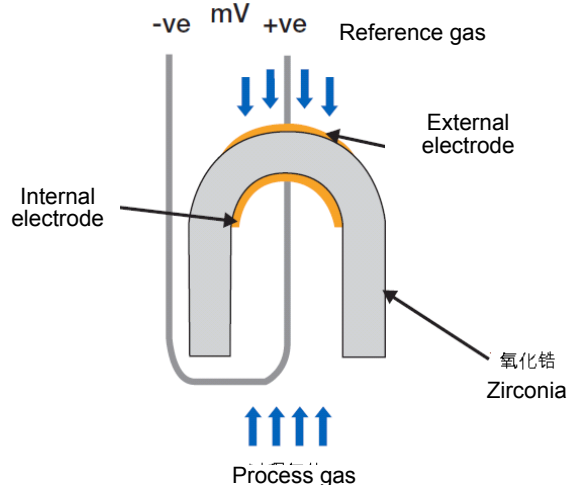


Fig. 4

measuring body. Under certain temperature (above 600 °C), the potential difference has a linear relation with the oxygen partial pressure, which conforms to Nernst equation:

$$mV = 0.0496 \times (0^\circ C + 273) \times (\log_{10} P_0 / P_1) \pm CmV$$

Wherein,

**mV**= micro volt output of probe

**0.496**= Faraday gas constant

**P0**= oxygen concentration at reference side

**P1**= other concentration at reference side

**CmV** = sensor constant (zero off-set)

Sort and amplify the signal on secondary meter, and display and output oxygen content in percent.

### 2.3 Structure of zirconia analyzer

The typical low temperature zirconia probe is shown in Fig. 5 as below: the following parts are included:

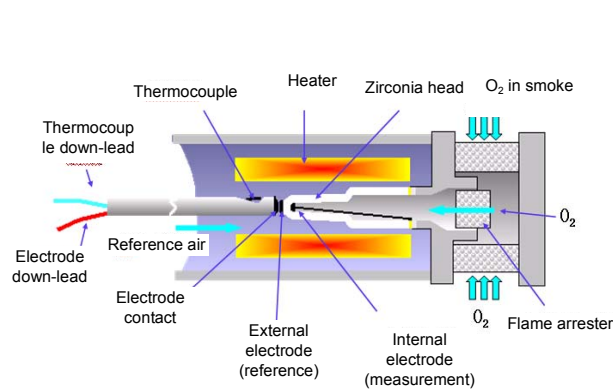


Fig. 5

- 1) Core measurement parts: zirconia head
- 2) Heater: constant temperature of head exceeds 600 °C
- 3) Thermocouple: measure and control heater humidity
- 4) Filter: filter dust in smoke
- 5) Flame arrester: prevent detonation in side

6) Other wire connectors, etc.

Secondary meter is generally installed near probe. Intelligent transmitter at present supports automatic calibration, HART communication and other advanced functions at the same time, which greatly reduces maintenance workload on field.

## III. Practical Application of Zirconic

### 3.1 Boiler in thermal power plant

Combustion control effect of boiler in power plant directly affects the generation efficiency and economic benefit of the whole plant. Thermal power plant has been the major client of zirconia. Oxygen content of smoke ejected by furnace is directly measured with direct plug-in zirconia, which can ensure to keep excess air factor  $\alpha$  at best status to efficiently adjust coal-air ratio, control smoke exhaust, lower exhaust gas temperature, prolong service life of combustor and improve combustion efficiency.

Typical installation place includes front and rear air flues of air preheater, tail flue or/and chimney (vertical flue) of secondary economizer, etc. The second one is rarely applied in recent years. Installation position is shown in Fig. 6.

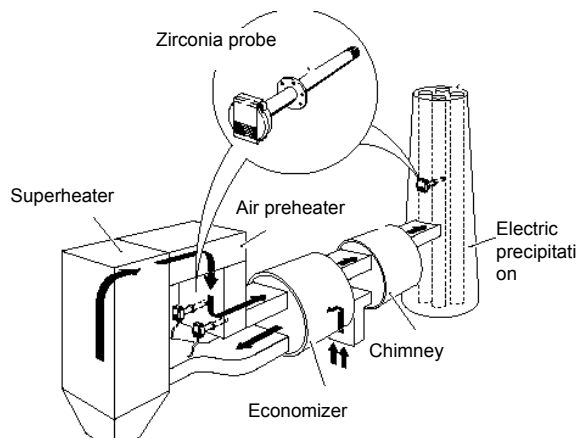


Fig. 6

Generally, large-scale thermal power plant is equipped with intelligent zirconia, which is configured with 4-20mA signal output and Profibus, Hart as well as other advanced communication function to participate automatic combustion adjustment of boiler. The whole combustion automatic adjustment has the basic

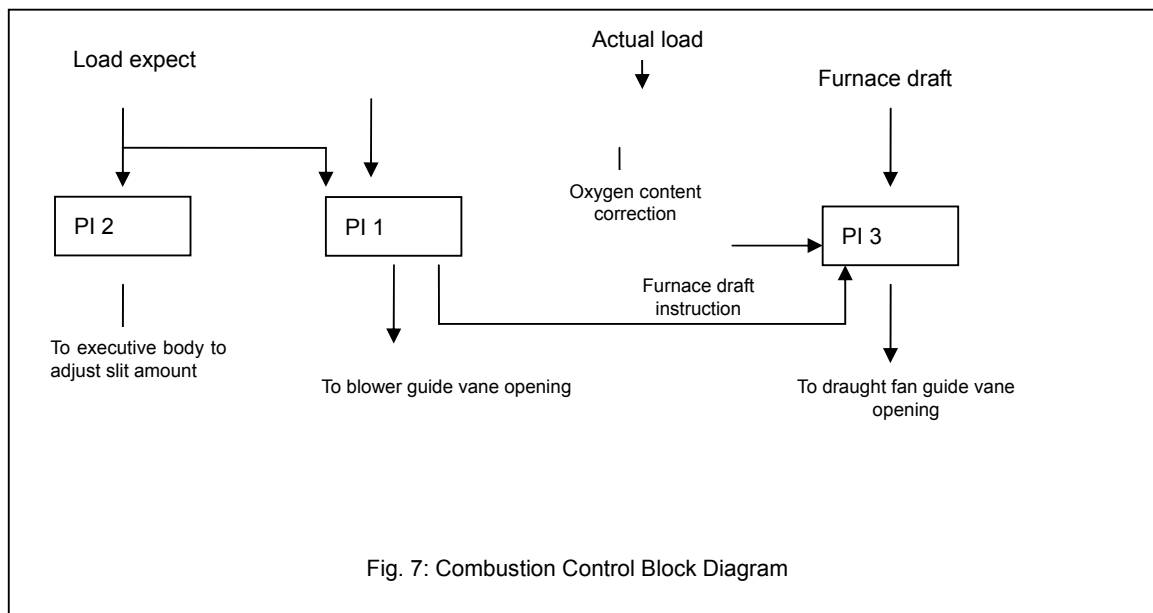
requirements as following:

- 1) Zirconia measures exactly and has good dynamic performance
- 2) Adjustment device and execution mechanism has good dynamic performance
- 3) Adequate adjustment allowance is provided for boiler
- 4) Adjustment device has automatic feedback and automatic correction function

Typical combustion automatic adjustment system is composed of the following subsystems:

- 1) Fuel adjustment system (shown as master vapour pressure)
- 2) Air output adjustment system (shown as blower opening)
- 3) Draught fan adjustment system (shown as furnace draft)

It is respectively slit, air output and air input in turn to be adjusted. Generally, smoke oxygen content (viz. zirconia measuring value) is taken as signal for adjusting air output, and an oxygen correction signal will be additionally added on a large scale boiler of 400t/h. The system is shown in Fig. 7 below, smoke oxygen content is induced from zirconia analyzer and corrected through oxygen expected value for adjusting load; load expect is induced at the same time to correct the ratio of fuel amount and air output; open/close signal is sent to blower guide vane execution mechanism through adjuster PI1 to control opening of the guide vane to further adjust air output. Meanwhile, PI1 sends associative instruction to PI3 to combine with pressure signal of furnace to adjust draught fan and further adjust furnace draft. Then adjust combustion environment in furnace furthermore.



In addition, besides participating combustion optimization control, it can judge air leakage of air preheater based on zirconia reading in front and rear sections of air preheater. In certain working conditions, if residual pulverized coal detonation exists in flue, residual oxygen in tail flue will be lower than oxygen content at inlet. Thus, smoke combustion at tail can be judged.

### 3.2 Hot-blast stove of iron and steel industry

Heating furnace is the major custom of energy consumption in iron and steel industry. Generally, mixed gas of blast furnace or coke oven is used to heat checker brick to store energy, and then send hot wind to blast furnace through fan for combustion-supporting. Compared with other combustion monitoring modes, it has the characteristics of simple realization, accurate measurement and small maintenance workload for monitoring residual oxygen content after combustion; it is rapidly promoted at present.

Typical zirconia position is shown in Fig. 8. Zirconic installed at position 1 is used to detect oxygen content of combustion air, that installed at position 2 is used to detect oxygen content of waste gas. It can judge combustion effect, adjust proportion of combustible gas and combustion air based on the zirconia installed respectively before and after combustion process to realize complete combustion in combustor.

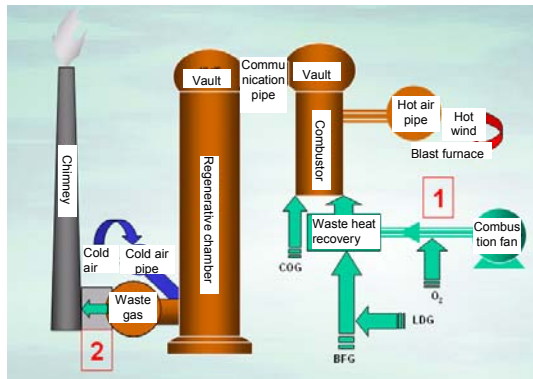


Fig.8

Typical hot blast heater automation combustion control system includes:

- 1) Control of combustible flow and combustion air flow
- 2) Control of air-fuel ratio
- 3) Control of vault temperature and waste temperature

The most important part is the control of air-fuel ratio. Calculate the air-fuel ratio setting value of steam through measuring residual oxygen after combustion, combine feedback adjustment with setting adjustment, and meanwhile pay attention

to the special case heat absorption on vault of hot blast heater to prevent superheat of vault to damage equipment.

Take the hot blast heater of Maanshan Iron and Steel Co., Ltd. as an example, by adopting combustion optimization control system, oxygen content of waste gas is controlled at about 0.2%, and gas consumption is reduced by 8%, which greatly improves efficiency of hot blast heater and reduces emission ratio.

### 3.3 Cracking furnace

Pyrolysis is the key technology in petrochemical industry. Raw material of petrochemicals in the world mainly comes from cracking furnace. Cracking furnace takes light hydrocarbon, naphtha and others as cracking raw material to finish cracking reaction in short time (0.2s or less) at about 800 °C accompanied with steam to form hydrocarbon of low molecular weight, and then to obtain triene, benzene, toluene and dimethylbenzene as well as the by-product (pyrolysis fuel oil, etc.) after separation and purification.

Vertical tubular cracking furnace is used in industry, which, as the same as steam boiler, has many alloy steel tubes arranged in certain rules in furnace. Cracking raw material is supplied in tubes. When furnace box temperature reaches 1,000 °C after combustion of combustible gas and combustion air, cracking reaction occurs in tubes. The high temperature smoke after combustion will heat furnace pipe at convection section

continuously and then is ejected from chimney.

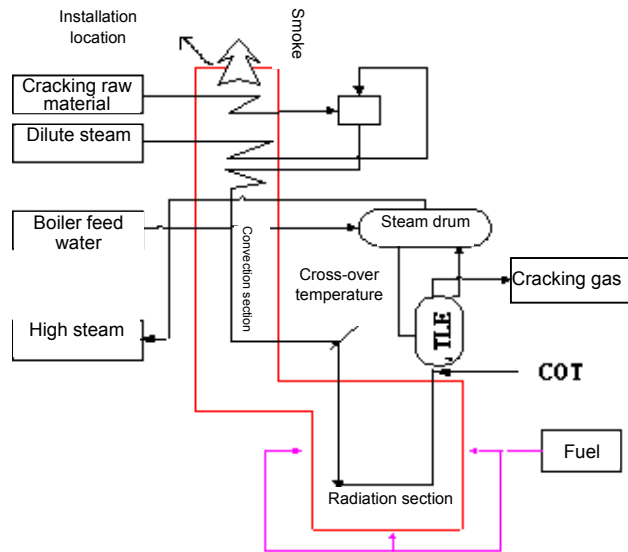


Fig 9

Explosion proof type zirconia is generally required in such occasion; the typical position of the zirconia is installed at chimney, as shown in Fig. 9. Residual oxygen content hereby is measured, and is used in combustion control of the whole cracking furnace, which can realize accurate supply of fuel and combustion air of cracking furnace, optimize accurate control of combustion and furnace temperature. It increases ratio of superior grade cracking product and prolongs service life of furnace tube and other quick-wear parts. Meanwhile, zirconia can be used to monitor pressure environment inside furnace and judge seal situation of system.

It is noted that temperature at measuring point for installing cracking furnace is higher than 600 °C, so non-electrically heated high-temperature zirconia must be adopted, and heat resisting ceramic bushing will be used. Furthermore, sulfur tolerance type must be selected.

#### IV. Development of Zirconia technology in China

Nernst put forth the basic principle of zirconia electric conduction in 1900. The first commercial direct plug-in zirconia emerged in Europe after 1960. In recent years, zirconia is widely applied and promoted. In China, Atomic Energy Research Institute firstly researched and developed ZO series online zirconia in 1980s. At present, the main manufactures of zirconia in China include ZO series of China Atomic Energy Research Institute, ZO4 series of Shanghai Institute of Ceramics, JGY series of Shanghai Haining Instrument Company, ZO3 series of Shanghai Solid State Ionic Conductors Co., Ltd., which still have long distance to international brand in terms of head manufacturing technology, head service life, measurement accuracy, secondary meter circuit design of zirconia. Presently, it occupies mainly the medium-and low-end market.

Zirconia of imported brands entered China since 1990s, including ABB, Rosemount, Fuji, Yokogawa and Ametek. It occupies electric power, petrification and other medium-and high-end market at beginning. Now, products mainly depend on import; part of brands is planning for localization production.

Contributing to years of marketing and enhancement of awareness on energy conservation and emission reduction, online combustion monitoring equipment will be used in more and more combustion cases. In China, there are a great number of medium and low size industrial boilers and heating furnaces, and coal consumption in unit and energy consumption of per ton steel are largely lower than the internal level. Zirconia with stable



low price will be more and more applied on Chinese market.

## **V. Conclusion**

Online zirconia analyzer is an analysis meter with mature technology, which has become indispensable equipment for users to control combustion and operation in many cases. It can effectively reduce emission of NOX and SO<sub>2</sub> pollutant and reduce environmental pollution, and has huge development potential.

Advanced zirconia is only a kind of monitoring equipment. It is still necessary to cooperate to make combustion optimization control system according to present combustion status of user so as to obtain maximum combustion efficiency and bring huge economic benefit and social benefit.