A study on combustion characteristics under enriched-oxygen condition by exergy analysis

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Abstract. The object of this paper is to investigate the effect of operating parameters on Oxygen-enriched combustion (OEC) by exergy balance analysis during methane combustion process. In this work, the specific exergy value of fuel, feed gas and products were calculated on the basis of the second law of thermodynamics in different reaction conditions, so that availability destructions and exergy efficiencies of OEC process can be obtained based on exergy balance, and the influence of initial fuel temperature, oxygen concentration, exhaust gas recirculation ratio and equivalence ratio were addressed. It is observed that during methane OEC process, the exergy efficiency is mainly affected by products temperature, in the case of products temperature lower than 1870K, exergy efficiency of combustion increase with products temperature, and opposite changes was appeared when the products temperature higher than 1870K. Meanwhile, appropriate control of equivalence ratio can also be used to improve exergy efficiency by suppressing the dissociation of product.

1. Introduction

As a result of the rapid depletion of fossil fuel reserves and excessive emissions of greenhouse gases, it is necessary to exploit effectively natural energy resources and release the pollutants emissions at present, which are available for the science progress and the sustainable development. In 2007, almost 83.8% of total 495 quadrillion kJ energy is produced from fossil fuel. Ignoring the exhaustion of the natural resource, up to 2030, the total energy consumption will reach almost 739 quadrillion kJ, 86% of which will still be acquired from fossil fuel [1]. Hence, it is vital to increase the energy conversion efficiency through improving the combustion systems in the next several decades.

Oxygen-enriched combustion (OEC) is one of the useful energy-saving technologies for combustion systems. By concentrating the oxygen in the feed gas, the amount of inert nitrogen contained in flue gases is lowered, and many benefits may be realized: higher thermal efficiency, increased productivity, enrich the concentration of CO2 in flue gas etc. Historically, OEC has been the conventional technology used in nearly all industrial heating processes, such as glass smelting furnace, metallurgic furnace and etc[2]. In the last decade, OEC systems are becoming more common in a variety of industries because of growing concern about CO2 emissions [3, 4]. The power generation industry have done a considerable amount of work on oxy-fuel combustion (oxygen typically of greater than 95% purity), and many benefits have been demonstrated: increased power generation, lowering the energy cost for CO2 capture and capital cost [5-7]. Moreover, the comment production
industry also achieved similarly benefits by using of oxy-fuel technology [8]. In industrial heat treating processes, the application of OEC can realize the use of low valuable gas (such as blast furnace gas), reducing the energy consumption and CO2 emissions [9-10]. In this paper, the fundamental research on oxygen-enriched combustion technology process is practical interest.

The concept of exergy is a direct outcome of second law of thermodynamics, which can be used to reveal the depletion of energy in energy conversion process and to evaluate the work potential of a system. Several studies have indicated that the conventional combustion process involves inherent exergy loss by 20~30%, which is attributed to both internal heat and mass transfer and chemical reactions in flame sheet.

Historically, two methods were developed to evaluate exergy efficiency in combustion process: one way of analyzing the performance of a combustor is base on the exergy balance during combustion process; the other way is to calculate the rate of entropy generation in the physical and chemical process, the rate of exergy destruction is calculated with Gouy-Stodola equation($E_{loss}=T_0 \times dS$). E, T and S are the exergy, reference environment temperature and entropy) [1].

In recent papers, some researchers have analyzed the rate distribution of entropy generation inside the several combustor by numerical simulation and gained the effects of operating parameters in the laminar and turbulent combustion process. It is showed that 72~77% of exergy destruction in combustion process was due to the inner heat transfer, chemical reaction (15~18%), and mass diffusion (5~10%) in CH4-air laminar flame. Then in the same way, more than 95% of the exergy destruction was due to turbulent parts in CH4-air turbulent flame.

Meanwhile, some other researcher analysis the exergy efficiency of combustion process by the exergy balance in the combustor. It is proved that reactant conditions (such as the equivalence ratio, initial temperature and pressure) may affect the exergy efficiency, and the implications of exhaust gas recirculation on exergy efficiency was also evaluated. Due to this, exergy efficiency is a important parameter to evaluate the performance of the combustion technology, but there were hardly any investigation on exergy analysis of oxygen-enriched combustion technology.

In this paper, the exergy efficiency can be obtained by exergy balance analysis after calculating the specific exergy value of fuel, feed gas and products on the basis of the second law of thermodynamics in different reaction conditions. The initial fuel temperature, oxygen concentration, exhaust gas recirculation and the equivalence ratio will affect the exergy efficiency greatly, and exergy efficiency diagram can be gained in the oxygen-enriched combustion, and a strategies that reduces the exergy loss in the combustion process were introduced, which will provide a theoretical guidance to design oxygen-enriched combustor and combustion system.

2. Theoretical basis

2.1. Basic concept of exergy

Thermodynamically, the exergy is defined to its”work potential” in the reference environment. The work potential implies physically the maximum theoretical obtainable work of the system, and the term exergy is sometimes replaced by availability. In general, the availability of a closed system is a composite property of the system in the reference environment, which is expressed as Eq. (1).

$$a = K + a_{im} + a_{ch}$$  

Where, a is the total specific availability (J/mol); K is the specific kinetic energy (J/mol); atm is the specific thermomechanical availability (J/mol); ach is the specific chemical availability (J/mol).

The specific thermomechanical availability is estimated as the sum of two components, thermal availability and pressure exergy. For open systems (subscript 0 denotes the parameters of reference environment):
\[ a_{im} = (h - h_0) - T_0(s - s_0) = C_p(T - T_0) + RT_0 \ln \left( \frac{P}{P_0} \right) - C_p T_0 \ln(T / T_0) \] (2)

For closed systems:

\[ a_{im} = (u - u_0) - T_0(s - s_0) + P_0(u - u_0) - C_p T_0 \ln(T / T_0) + RT_0 \left[ \ln \left( \frac{P}{P_0} \right) - \left( 1 - \frac{P}{P_0} \right) \right] \] (3)

\( T \) is the temperature (K); \( P \) is the pressure (Pa); \( s \) is the specific entropy (J/ (K mol)); \( u \) is the specific internal energy (J/ (K mol)); \( C_p \) is the constant-pressure specific heats, (J/ (K • mol)); \( R \) is the perfect gas constant (8.314 J/mol K).

The subscript 0 represents the reference state.

Chemical availability of species is expressed as the sum of the standard Gibbs free energy of formation and the Gibbs free energy of elements. The specific chemical availability of a species is given as:

\[ a_{ch} = \Delta g_f(T_0, P_0) + \sum_{i} n_i g_i(T_0, P_0) \] (4)

Where, \( \Delta g_f(T_0,P_0) \) is the standard Gibbs free energy of formation(J/mol); \( g_i(T_0,P_0) \) is the Gibbs free energy of elements(J/mol).

In most cases, the reactants and products of combustion systems are mixture of different species, so it is necessary to estimate the availability destruction during the mixing process. The specific availability of mixture is evaluated as:

\[ a_{mix} = \sum_{i} x_i a_i + RT_0 \sum_{i} x_i \ln(x_i) \] (5)

Where, \( a_{mix} \) is the specific availability of mixture (J/mol); \( x_i \) is the mole fraction of \( i \) species in the mixture.

2.2. The exergy balance in the combustion process

In order to find the relations between the reactants condition and the exergy efficiency in the oxygen-enriched combustion process, a zero dimensional model is raised to simulate the combustion process, and methane is used as fuel and consider the combustion process as isobaric.

During combustion reaction, medium products are considered, generally, including the following 7 species: CO2, CO, H2O, H2, CH4, O2, and N2. Other medium products are ignored because of its lower concentration. The equilibrium products state are characterized by the equilibrium constants and minimum Gibbs free energy. The generalized combustion reaction formulas can be presented as follows:

\[ \begin{align*}
CH_4 + \frac{2}{\Phi} O_2 + \frac{2}{\Phi} \left( \frac{X_{O_2}}{Y_{O_2}} - 1 \right) \sum_{i} n_i Y_i = 1 - \frac{F}{1 - 2F} \sum_{i} n_i Y_i \\
\sum_{i} n_i Y_i = n_1 CO_2 + n_2 CO + n_3 O_2 + n_4 H_2O + n_5 H_2 + n_6 N_2 + n_7 CH_4
\end{align*} \] (6) (7)
Where, Yi is the constituents of product i; ni is the number of moles of elements i.

The equilibrium product temperature is obtained from the energy balance equation in the combustion process (Eqs (8)-(10)). According to Eq (6) and Eq (8), the equilibrium product temperature and constituents concentration of products have to be solved simultaneously.

\[ E_r = E_p + Q \]  

\[ E_r = h_{cH_2}(T_r) + \frac{2}{\Phi} h_{O_2}(T_r) + \frac{2}{\Phi} \left( \frac{1}{X_{O_2}} - 1 \right) h_{N_2}(T_r) + \frac{F}{1 - 2F} \sum_i n_i Y_i h_i(T_r) \]  

\[ E_p = \frac{1 - F}{1 - 2F} \sum_i n_i Y_i h_i(T_p) \]  

\( E_r \) is the total energy of reactants(J); \( E_p \) is the total energy of products(J); \( F \) is the exhaust gas recirculation ratio, defined as the ratio of recirculated exhaust gas to total exhaust gas; \( T_r \) is the temperature of feed gas(K); \( T_p \) is the equilibrium temperature(K); \( \Phi \) is the equivalence ratio; \( X_{O_2} \) is the oxygen mole fraction in feed gas; \( Q \) is the heat loss in the combustion process(J).

![Fig. 1 Diagram of the exergy transfer in a combustion system](image-url)

Fig. 1 is a diagram of the exergy transfer in a combustion system. It can be seen from Fig.1 that the availability of reactants (Ar) is divided into three parts in the combustion process, the availability of products (Ap), availability lost in the heat loss (\( \Delta A_{Q\text{loss}} \)) and availability destruction in combustion process (Acomb).

\[ A_r = A_p + A_{\text{comb}} + \Delta A_{Q\text{loss}} \]  

\[ A_p = A_{p,\text{th}} + A_{p,\text{chem}} \]  

Exergy efficiency (\( \eta_e \)) of the combustion process can be defined as the ratio of thermomechanical availability of products (Ap tm) to the the availability of reactants (Ar). It can be expressed as:

\[ \eta_e = \frac{A_{p,\text{th}}}{A_r} \]  

3. Results and discussions

In the oxygen-enriched combustion process, the concentration of species in product and the equilibrium temperature are changed with the increasing of oxygen concentration. As is expected,
equilibrium temperature and species concentration have a great effect on exergy efficiency of the combustion process. In this section, we are able to find the effect of oxygen concentration in feed gas, reactant temperature, exhaust gas recirculation (EGR) and equivalence ratio on exergy lost during OEC process. Finally, some methods to improve the exergy efficiency of OEC are provided.

3.1. Effect of oxygen concentration in feed gas
The effects of oxygen concentration on exergy efficiency are investigated by using oxygen mole fraction in feed gas ($X_{O_2}$). As previously mentioned, products temperature increases with oxygen mole fraction $X_{O_2}$, higher products temperature has great impact on the availability destruction ($A_{comb}$) and chemical availability lost ($A_{chem}$). However, the chemical availability lost increases with products temperature. The effect of $X_{O_2}$ on exergy efficiency is shown in Fig.2 (a).

![Fig. 2 The effect of oxygen enrichment on (a) exergy efficiency $\eta_e$, (b) CO and H2 mole fraction in products and the products temperature $T_p$[Tr=298, F=0, Q=0J, $\phi$=1, $P=P_0$].](image)

As Fig.2(a) shows, exergy efficiency ($\eta_e$) rises firstly, and then drops sharply with the increases of $X_{O_2}$ and hits a maximum at $X_{O_2}=15\%$, the products temperature is about 1868.7K at this point(shown in Fig.2(b)). The reasons mainly include: in the range of lower oxygen concentration, exergy efficiency of combustion increases due to decrease of availability destruction ($A_{comb}$); and in the range of higher oxygen concentration, exergy efficiency decreases due to the enhanced dissociation reactions at higher temperatures produce more moles of CO and H2 (shown in Fig.2(b)). In Fig.2, when $X_{O_2}=40\sim100\%$, the increase of $X_{O_2}$ only slightly increase the products temperature but largely enhance the generation of unburned species, therefore, reasonable choice of oxygen concentration in OEC process is very important.

3.2. Effect of exhaust gas recirculation ratio
Historically, exhaust gas recirculation is widely used to improve the temperature uniformity in oxygen-enriched combustion chamber, so that it is important to evaluate the influence of EGR on exergy efficiency of OEC process. It is investigated with a factor F defined in section 2.2. The conditions ranging from F=0(no flue gas recirculation) to F=0.45 are studied, and oxygen concentration $X_{O_2}$ is considered at $X_{O_2}=10\%$, 21% and 50%, as depicted in Fig.3.
As Fig.3(a) shows: for $X_{O_2}=10\%$, exergy efficiency ($\eta_e$) decreases continuously when raising $F$, due to the lower product temperature; for $X_{O_2}=21\%$, exergy efficiency rises slowly with the increase of $F$ in the range of $0 \sim 0.18$, then drops sharply and reaches a maximum around $F=0.18$; for $X_{O_2}=50\%$, exergy efficiency has a similar trend just as $X_{O_2}=21\%$, which hits a maximum at $F=0.37$, and the products temperature at this point is about 1867.4K. Fig.3 (b) depicts the relations of products temperature and CO, H2 concentration with variation of the exhaust gas recirculation ratio $F$ in the case of $X_{O_2}=50\%$. Naturally, the products temperature is lowered by increasing $F$, and the low temperature is also attributed to the reduction in the amount of combustible species (mainly CO and H2).

![Fig. 3](image)

**Fig. 3** The effect of flue gas recirculation ratio on (a) exergy efficiency $\eta_e$ [Tr=298, Q=0J, $\phi=1$, $P=P_0$], (b) CO and H2 mole fraction in products and the products temperature $T_p$ [ $X_{O_2}=50\%$, Tr=298, Q=0J, $\phi=1$, $P=P_0$].

Meanwhile it can be shown that the exergy efficiency difference decreases between $X_{O_2}=21\%$ and 50% with the increase of $F$ in the range of $F=0 \sim 0.45$ and exergy efficiency for $X_{O_2}=21\%$ is lower than that for $X_{O_2}=50\%$ when $F>0.3$ from Fig.3 (a).

Combining with the previous analysis in section 3.1, the main reasons caused this changes were listed as follows: when the products temperature is below 1870K, availability destruction ($A_{comb}$) play a major role in total exergy lost in combustion process; and when the temperature is higher than 1870K, exergy efficiency is mainly affected by the chemical availability lost ($A_{chem}$).

In conclusion, reasonable exhaust gas recirculation is necessary in the oxygen-enriched combustible process. On one hand, it can increase the temperature uniformity in combustion chamber and on the other hand, the exergy efficiency can also be improved.

### 3.3. Effect of feed gas temperature

Actually, waste gas can be recovered to preheat the feed gas via heat exchanger, and feed gas can be heated up to 1400K with the regenerative exchanger. In this paper, the relations between the exergy efficiency and the temperature of the feed gas (Tr) ranging from Tr =298K up to 1400K are studied, Fig.4(a) shows the variation of exergy efficiency with feed gas temperature in the cases of $X_{O_2}=10\%$, $X_{O_2}=21\%$, $X_{O_2}=50\%$. 

![Fig. 4](image)
21% and 50%. The curve for $X_{O_2}=10\%$ in Fig.4(a) first increase and then decrease, and hit the maximum at $Tr=870K$, products temperature at this point is about 1867K (very close to 1870K that mentioned in section 3.2). In contrast, the other two curves continuously decrease with increase of the feed gas temperature.

The products temperature rises relatively as the temperature of the feed gas is raised. The temperature difference between the reactant and products diminish and cause decrease of the inner exergy loss ($A_{comb}$). The higher products temperature also result in dissociation of product species (as show in Fig.4 (b)). For $X_{O_2}=21\%$ and 50%, the products temperature is higher than 1870K at the starting point ($Tr=300K$). Hence, two curves continuously decrease with increase of the feed gas temperature.

![Fig. 4](image)

**Fig. 4** The effect of feed gas temperature on (a) exergy efficiency $\eta$ [F=0, Q=0J, $\Phi=1$, P=P0] , (b) CO and H2 mole fraction in products and the product temperature $T_p$ [ $X_{O_2}=10\%$, F=0, Q=0J, $\Phi=1$, P=P0].

### 3.4. Effect of equivalence ratio

The equivalence ratio is an important parameter in the process of the combustion control, and has great impact on the products temperature and components. Referring to Fig.5(a), the exergy efficiency for $X_{O_2}=10\%$, 21% and 50% first increase and then decrease with the increase of $\Phi$, and the peak of curves shifts towards the smaller $\Phi$ as $X_{O_2}$ increase.

It leads to a conclusions that the temperature of product and concentration of combustible product in flue gas hit their maximum around $\Phi=1.05$ for all $X_{O_2}=10\%$, 21% and 50% after research. In contrast, the maximum exergy efficiency point shifts towards to smaller $\Phi$ as $X_{O_2}$ increase. The main reason is that the dissociation of product can be suppressed significantly by increasing oxygen concentration in flue gas, as shown in Fig.5 (b).
Fig. 5 The effect of equivalence ratio on (a) exergy efficiency $\eta_e [T_r=298, Q=0J, \phi=1, P=P_0]$, (b) CO and H2 mole fraction in products and the products temperature $T_p [X_{O_2}=21\%T_r=298, Q=0J, \phi=1, P=P_0]$.

4. Conclusion
As demonstrated in this paper, the effect of important parameters on exergy efficiency of combustion is investigated to improve the efficiency of oxygen-enriched combustion system, several important conclusions drawn from the results of this work are as follows:

1) For methane, exergy efficiency of the isobaric combustion process is mainly affected by products temperature: when products temperature is below 1870K, exergy lost in the combustion process includes inner combustion exergy lost $A_{comb}$, exergy efficiency $\eta_e$ rises with the increase of the products temperature: when the temperature is higher than 1870K, exergy efficiency is mainly affected by the chemical incomplete combustion exergy lost $A_{chem}$, so that exergy efficiency $\eta_e$ will decrease with the increase of the products temperature.

2) In OEC process, exhaust gas recirculation ratio $F$ and feed gas temperature $T_r$ have great impact on exergy efficiency. For the lower oxygen concentration $X_{O_2}$, exergy efficiency can be improved by increasing $T_r$. At the same time, the exhaust gas recirculation can significantly improve the exergy efficiency in the higher range of $X_{O_2}$.

3) The reasonable equivalence ratio in the oxygen-enriched combustion process is also important to improve exergy efficiency $\eta_e$ by reducing the generation of the intermediate product.

Acknowledgments
This study is supported by the Foundation of Shaanxi Provincial Department of Education (Grant 17JK0604).

References
[1] Som SK, Datta A. Thermodynamic Irreversibilities and exergy balance in combustion processes [J]. Progress in energy and combustion science, 2008; 34: 351-376.
[2] Zhang X, Tong LG, Wang L. The application and analysis of oxygen-enriched combustion [J]. Energy for Metallurgical Industry 2007; 26: 41-46.
[3] Yewen T, Eric C, Mark A. Combustion characteristics of coal in a mixture of oxygen and recycled flue gas [J]. Fuel 2006; 85: 507-512.
[4] Yewen T, Mark AD, Kelly VT. CO2 capture using oxygen enhanced combustion strategies for natural gas power plants [J]. Fuel 2002; 81: 1007-1017.
[5] Buhre BJP, Elliott LK. Oxy-fule combustion technology for coal-fired power generation [J]. Progress in Energy and Combustion Science, 2005; 31: 284-305.

[6] D Singh, E Croiset, L Douglas. Techno-economic study of CO2 capture from an existing coal-fired power plant: MEA scrubbing vs. O2/CO2 recycle combustion [J]. Energy Conversion & Management, 2003;44: 3073-3091.

[7] Yang HQ, Zheng HF, Mao H. Progress in carbon dioxide separation and capture: A review [J]. Journal of Environmental Sciences 2008; 20: 14–27.

[8] Frank Z. Oxygen combustion in cement production [J]. Energy Procedia 2009; 1: 187-194.

[9] Wu KK, Chang YC, Chen CH. High-efficiency combustion of natural gas with 21-30% oxygen-enriched air [J]. Fuel 2010; 89:2455-2462.

[10] Giacomo B, Alessandro B, Giuseppe R. Thermodynamics applied to oxygen enrichment of combustion air [J]. Energy Conversion & Management, 2002;43:2589-2600.