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THERMODYNAMIC ANALYSIS AND EXPERIMENTAL INVESTIGATION INTO NONFLAME COMBUSTION TECHNOLOGY (NFCT) USING THERMAL CYCLIC CARRIER

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ABSTRACT The utilization of fossil fuels causes serious negative impacts on the environment and human life. To mitigate greenhouse gases and other pollutants, a novel combustion process—nonflame combustion technology using thermal cyclic carrier of molten salt is introduced. And the technological concept of this technology is pointed out. Four types of combustion systems, in which $\text{Cu}_2\text{O-CuO}$, $\text{Na}_2\text{O-Na}_2\text{O}_2$, $\text{Na}_2\text{S-Na}_2\text{SO}_4$ and $\text{FeO-Fe}_2\text{O}_3$ are involved as oxygen carriers respectively, are examined thermodynamically, and the thermodynamic data of the redox reactions are calculated. The metal oxides scattered into molten salts play the roles of oxygen carriers, and they can constantly gain and give oxygen element from air to fuels during combustion process. There are not environmental-unfriendly gases such as NO_x , CO_2 and SO_x discharged in the whole combustion process because N_2 is separated from O_2 in the section of producing oxide, sulfur and heavy metals elements are absorbed into molten salts, and pure CO_2 is easily recovered in the section of combustion. Combustion processes realizes zero emission through this technology. Experimental studies are carried out in a mini-scale stainless reactor. Results indicate that the nonflame combustion process is going on as it is expected. But the reaction rates are not as quick as we anticipated. It seems that the kinetics and the mechanism of combustion process are still to be investigated.

[Key words] nonflame combustion technology, thermal cyclic carrier, molten salt, thermodynamic analysis, zero emission

1. INTRODUCTION

Combustion of fossil fuels is and will probably continue to be an important part of the heat and power production systems of many countries^[1-3]. However, the utilization of fossil fuels, such as coal, oil and natural gas, has been and is causing negative impacts on the environment and human life locally and globally^[45]. Under traditional combustion technologies, a large number of exhausted wastes are discharged during combustion process. Especially CO_2 , NO_x and SO_x are released in large quantities. These gases have led to serious air pollution and greenhouse effect. It was researched that the air compositions have changed dramatically after Industrial Revolution. One of an air pollutant

important resources is SO_x which is emitted during industrial production. It is generally believed that SO_x and NO_x are the initial substance which can originate acid rain. Fig. 1^[6] demonstrates the percentage contribution to the world's total CO_2 emissions. As above-mentioned, the consumption of fossil fuel can make great environmental impacts. Thus, lots of scientists and engineers have made great efforts to develop new combustion technologies aiming to reduce the pollution derived from combustion of nonrenewable fuels. Some new combustion processes such as high-performance regenerative combustion system, high temperature air combustion technology and pulsating combustion have been developed in western countries^[7, 8]. Fortunately, these technologies make substantial

contribution to decrease the emission of environmental-unfriendly gases. Unfortunately, all over the technologies cannot fundamentally eliminate the emission of the hazardous gases. So it is necessary to develop clean and environmental friendly combustion technologies. The technology introduced in this paper is developed by

combining the knowledge of energy chemistry, fuel cell and combustion science & technology. This technology is a novel revolutionary combustion process based on thermal cyclic carriers of molten salt. It is supposed that zero emission can be realized during combustion process through the technology^[9].

Fig. 1 Percentage contribution to the annual world CO₂ emission

2. CONCEPT OF NFCT

Fig. 2 is the conceptual schematic of the NFCT.

Fig. 2 Conceptual schematic of nonflame combustion technology

As shown in Fig. 2, the first part of the process is the section of producing oxide, and there are molten salts and oxides in this reactor. Air is driven by an air compressor or other equipment going through the reactor. When air contact with the molten salts and oxides, the O₂ in the air is absorbed by the molten salts and oxides through physical and chemical reactions. Theoretically, if the air flow is controlled properly, all of the O₂ in the air can be absorbed by the media. So, as the only outlet gas, pure N₂ can be recycled as commercial products. And then the molten salts and oxides are pumped into another reactor, namely the section of combustion. In this chamber, fuels are blown into the molten bath, i.e. the

media of carrying heat and oxide, and the oxygen element absorbed by the media at first stage is released and interacted with fuels when the fuels come across the oxides. In many cases, if the fuels react completely with oxide, only three kinds of productions are formed: water vapor, CO₂ and thermal energy in this stage. CO₂ can be easily separated from water and used as a commercial product or chemical raw material, and heat is stored in the media of heat carrier. In the heat exchanger, heat is transferred from heat carrier to water, air or other media, and made come into utilization. It is necessary to point that nitrogen and sulfur elements are absorbed into molten salt instead of being fired in

the section of combustion. This can partly be explained by the fact that the fuels react with oxide through chemical reactions rather than react with O_2 directly. From the conceptual schematic, we can see that there are no hazardous gases discharged into air during the whole combustion process. So this combustion system is a clean, zero emission combustion process.

It is worth to mention that heat exchanger is not placed after the section of combustion in some cases. Where the heat exchanger should be placed depends on the exact combustion system. In some conditions the heat discharged in section of producing of oxide is more than that of section of combustion, and in these conditions, the heat exchanger should be positioned following the section of producing oxides. In many cases, the heat energies discharged in the two sections are comparable, and then two heat exchangers are needed.

Generally speaking, NFCT enjoys several apparent advantages. They can be summarized as following points: (a) There are only two kinds of by-product CO_2 and water vapor to be discharged when fuel combust completely in the section of combustion. Thus the greenhouse gas is fundamentally eliminated to emit into air because pure CO_2 can be easily recycled as a chemical raw material. (b) NO_x are prevented to form due to the lower temperature in section of producing oxide and there is not nitrogen element in section of combustion. (3) The sulfur and heavy metals are absorbed into molten salt instead of being fired during combustion due to fuels do not directly contact with O_2 . (d) The technology realizes zero emission during combustion process.

3. THERMODYNAMIC ANALYSIS

The mechanism of NCT is still not entirely clear at present. It is believed that oxygen transfer theory can partly explain the combustion process in some extent. According to oxygen transfer theory, some additives, such as M_xO_y (M represent a metal element) can play the role of oxygen transfer media during combustion.

Take Cu_2O as an example. In the section of producing oxide, if Cu_2O is involved in molten salts, Cu_2O will react with oxygen as the following

equation at certain temperature range.

The standard Gibbs free Energy change ($\Delta_r G$) of reaction (1) is no more than zero until at temperature above 1745K. That means this reaction can spontaneously carry out at temperatures below 1745K. Thus Cu_2O will combine with O_2 in the section of producing oxide and CuO will be formed. The enthalpy change ($\Delta_r H$) of the reaction is $-379.858 \text{ kJ.mol}^{-1}$ at 900K. It is evident that this reaction is exothermic, and heat is released in large quantities during reaction. And then the molten salts and oxide are pumped into the reactor of combustion. When CuO meet fuels, such as coal, reaction will take place as following:

The standard Gibbs free Energy change ($\Delta_r G$) of reaction (2) is lower than zero over a wide temperature range. Thus, at temperature above 298K, $\Delta_r G < 0$ and the reaction will go spontaneously to the right. The enthalpy change of reaction (2) is about $-(10\sim 20) \text{ kJ.mol}^{-1}$ over the entire temperature range of interest. The reaction is also exothermic at this temperature range. Actually, in the whole process Cu_2O and CuO play the roles of oxygen carriers, and they act respectively as oxygen receptor and donor during reaction process. On the other hand, O_2 and fuel may correspondingly serve as oxidant and reducing agent. In this combustion system, the variation of $\Delta_r H$ for reaction (1) is much more than that of reaction (2); Thus, heat exchanger will be positioned following the section of producing oxides.

Take Na_2O as another example. In the section of producing of oxide, Na_2O will react with oxygen as following:

At about 1229K and 1 atm, the standard Gibbs free Energy change ($\Delta_r G$) goes to zero, and at temperature below 1229K, the reaction proceeds spontaneously to the right. The enthalpy change ($\Delta_r H$) of the reaction is about -190 kJ.mol^{-1} and almost constant over a wide temperature range. Na_2O_2 , is brought into contact with fuel in section of combustion, can act as an oxidant and react with fuel, and Na_2O will be reformed again. This reaction can be represented as:

Similarly, $\Delta_r G$ of reaction (4) decreases with temperature, and less than zero at a wide temperature range. Thus, the reaction is thermodynamically favorable at operational temperature of combustion system. The enthalpy change ($\Delta_r H$) of reaction (4) changes from about -198 to -210 $\text{kJ}\cdot\text{mol}^{-1}$ at temperature from 500 to 1300K . In this combustion system, the enthalpy changes ($\Delta_r H$) of reactions (3) and (4) are comparable. From an economical point of view, it is had better to equip two heat exchangers into this combustion system.

Another two examples are given as following:

Fig. 3 The variations of $\Delta_r G$ and $\Delta_r H$ with temperature for reactions (1) through (8)

Tab. 1 The $\Delta_r G$ and $\Delta_r H$ of reactions (1) through (8) at different temperatures ($\text{kJ}\cdot\text{mol}^{-1}$)

reaction	2 Cu ₂ O + O ₂ = 4 CuO		4 CuO + C = 2Cu ₂ O + CO ₂		2Na ₂ O + O ₂ = 2Na ₂ O ₂		2Na ₂ O ₂ + C = CO ₂ + 2 Na ₂ O		Na ₂ S + 2O ₂ = Na ₂ SO ₄		Na ₂ SO ₄ + CH ₄ = Na ₂ S + CO ₂ + 2H ₂ O		4FeO + O ₂ = 2Fe ₂ O ₃		2Fe ₂ O ₃ + C = CO ₂ + 4FeO	
	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$	$\Delta_r G$	$\Delta_r H$
298	-321.26	-387.42	-79.08	-6.09	-150.01	-198.00	-244.37	-195.51	-912.51	-1018.36	111.73	216.05	-428.66	-578.80	33.88	184.89
500	-276.42	-384.88	-128.56	-8.81	-117.49	-195.04	-277.49	-198.65	-840.75	-1021.18	41.02	220.85	-326.89	-581.35	-68.49	187.26
700	-232.01	-382.37	-177.54	-11.50	-85.28	-192.11	-310.28	-201.75	-769.71	-1023.96	-28.10	225.00	-226.12	-583.88	-169.84	198.62
900	-187.61	-379.86	-226.53	-14.18	-53.07	-189.19	-343.07	-204.85	-698.66	-1026.74	-99.01	230.36	-125.35	-586.41	-271.19	191.97
1000	-165.41	-378.60	-251.02	-15.53	-36.97	-187.72	-359.46	-206.41	-663.14	-1028.13	-134.02	232.73	-74.97	-587.69	-321.86	193.15
1100	-143.21	-377.35	-275.51	-16.87	-20.87	-186.26	-375.86	-207.96	-627.62	-1029.52	-169.02	235.11	-24.59	-588.94	-372.53	194.32
1200	-121.01	-376.09	-300.00	-18.21	-4.77	-184.79	-395.25	-209.51	-592.10	-1030.92	-204.03	237.48	25.80	-590.20	-423.21	195.50
1300	-98.81	-374.83	-324.50	-19.56	11.34	-183.33	-408.64	-211.06	-556.57	-1032.31	-239.03	239.86	76.18	-591.46	-473.88	196.68

4. EXPERIMENTAL

The mini-scale tests were carried out in a reactor designed by the authors, which size is $\phi 120 \times 480\text{mm}$. The media of carrying heat and oxide involved in the experiments are 1083 (g) Li_2CO_3 - 1254 (g) K_2CO_3 and 1444 (g) Na_2SO_4 respectively, and the

fuel used is CH_4 . Experiments were performed under temperature at $800 \pm 5^\circ\text{C}$. All over the reagents used in the experiments are analytically pure, and produced by Shanghai Medicines Company Group. At the beginning, the reactor is filled with Li_2CO_3 - K_2CO_3 - Na_2SO_4 mixture salts. When the reactor is heated up to 800°C in a tube furnace, it is

necessary to reside a period of time to guarantee the salts molten down. And then, CH_4 is blow in the molten bath. It is expected that CH_4 will react with Na_2SO_4 as represented as the reaction (6). The waste gas out of the reactor is analyzed with an on-line automatic gas analyzer. This is the first half cycle of the combustion process.

At the second half cycle, the CH_4 is shut off, and the air is blow into the molten bath. Also, the exhaust gas is analyzed. The whole experimental flow diagram is schematized as Fig. 4. It is worth noting that the flow rates of CH_4 and air are equally $0.2\text{m}^3\cdot\text{h}^{-1}$, and copper oxides are used as catalyzer in the experiments.

Fig. 4 Schematic diagram of the experimental procedure

5. RESULTS AND DISCUSSION

In the first half combustion cycle, if the practical process in the reactor is going on as it is expected,

there is only CO_2 which can be only detected in the waste gas. Analysis results of the waste gas after CH_4 combustion in the molten bath are shown in Tab. 2.

Tab. 2 exhaust gases analysis results of the two sections of a whole combustion process

Molten salts system	fuel	Experiments number	catalyzer	Experimental results					
				Section of combustion			Section of producing oxide		
				$\text{CO}_2/\%$	$\text{CO}/\text{mg}\cdot\text{l}^{-1}$	Others/ $\%$	$\text{N}_2/\%$	$\text{O}_2/\%$	$\text{NO}_x/\text{mg}\cdot\text{l}^{-1}$
Li ₂ CO ₃ + K ₂ CO ₃ + Na ₂ SO ₄	CH ₄	1	copper oxides	88.1	124.5	6.2	93.1	6.1	17.2
		2	copper oxides	90.0	88.9	5.9	96.0	3.3	15.0
		3	composite	95.1	42.3	3.0	99.3	0.7	0
		4	copper oxides	79.0	264.5	8.7	93.0	6.1	19.4
		5	ferrous oxide	77.0	277.8	10.1	91.9	7.0	23.5

As indicated in Tab. 2, it is observed that there are quite a number of CO and CO_2 in the waste gas. According to this fact, we can presume that there are chemical reactions taking place between CH_4 and Na_2SO_4 or CuO , because this is the only reason to explain the fact that there are CO and CO_2 in the exhausted gas, and at the same time, Na_2S and Cu_2 are formed. Unexpectedly, however, there is lots of CO in the waste flow gas. This reveals that the

reaction process is much more complicated than we supposed. Maybe the whole reaction process can be divided into several stages rather than only one. Thus, the kinetics and mechanism of the reaction will be a key problem to be investigated. It is worth noting that the CH_4 remained in the waste gas is not detected owing to there is no CH_4 -sensor in the gas analyzer. According to our speculation, however, it is inevitable that there exists CH_4 in the exhausted gas.

in this stage if the reaction conditions are not controlled to reach an optimum point.

The experimental results of the section of producing oxide are also illustrated in Fig. 6. Fig. 6 displays that the exhausted gas of the section of producing oxide is relatively pure N₂, maybe 90.0% or more. This implies that the oxygen in air have interacted with Na₂S or Cu₂O which are formed in the first half combustion cycle. Unfortunately, the experiments show that the reaction rate is quite slow and far from what we anticipated. So we can conclude that the nonflame combustion process proceed as what it is expected but how it is expected. Regardless of how the process is going on, however the ultimate result of the two half combustion cycle is that CH₄ react with O₂ discharging thermal energy. Anyway, this technology was put forward and got researched very recently [9, 10]. There are some problems still to be resolved such as heat utilization reaction rates, kinetics, security of molten salts and how to utilize directly coal through this technology etc. In addition, the research methods on this technology need to be established.

It is difficult to detect the amount of heat discharged during the whole combustion process due to the scale of reactor is too small and the reactor is heated in a tube electric furnace. However, the quantity of heat can be broadly estimated through plus the enthalpy change($\Delta_r H$) of reaction (5) and (6). If reaction (5) adds (6), a reaction is got as following:

If the combustion reaction proceeds completely the whole thermal energy can be calculated from reaction (9). Based on the amount of CH₄ or O₂ consumed in experiments, we will compute the total of thermal energy during the whole redox reactions.

6 CONCLUSIONS

Thermodynamic calculations indicate that the nonflame combustion system using thermal cyclic carrier of molten salts is possible. In this work four types of typical nonflame combustion systems were analyzed. Results show that the two systems are thermodynamically favorable over a wide temperature range and it is not difficult to operate the

four systems in practical production. Owing to the O₂ and fuels interact respectively with the oxygen media in two different reactors, there are only two types of post-combustion gases, pure N₂ and CO₂, which can be easily recycled. Thus, CO₂, NO_x and SO₂ are fundamentally eliminated to discharge in the whole process. In brief, the NFCT is a type of clean, zero emission and environmental-friendly combustion technology.

It has an encouraging potential utilization in the heat and power production industry. The experimental results demonstrate that the combustion process may proceed as it is expected. However, the reaction rates are far from what we anticipated. Thus the kinetics and mechanism of reactions are still to be researched.

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