Analytical modeling of hot gas clean up reactor

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Analytical modeling of hot gas clean up reactor

Y A Kagramanov, V G Tuponogov, A F Ryzhkov, P V Osipov
Ural Federal University, 620002, Russia, Yekaterinburg

E-mail: KagramanovYA@yandex.ru

Abstract. Thermal sustainability of zinc oxide was studied. Experiments were conducted in atmosphere of syngas components. Thermogravimetical analysis was used as the main method of investigation. Zinc oxide based sorbents were tested in methane, hydrogen, carbon and hydrogen sulphide atmospheres. Experimental data has shown intensification of reactions between zinc oxide and methane, hydrogen and carbon in temperature range from 650 to 800 °C and zinc evaporation and sorbent chemical destruction. Experiments did not reveal significant change of rate constant of reaction between zinc oxide and hydrogen sulphide. Ten probable reactions were numerically analysed. Equilibrium constants were calculated for all ten reactions. The temperature influence on equilibrium constants were calculated. Some elements of hot gas clean up desulfurization unit simulation model were also presented. Experimental rate constants for both four reactions were used in the model. Outlet gas composition and efficiency factor were calculated. Sorbent mass flow was determined. Recommended temperature range was identified.

1. Introduction
Desulfurization system is the main part of the syngas purification unit before the gas turbine combustor in the integrated gasification combined cycle (IGCC) [1-4]. Hot gas clean up is the most promising energy serving technology [5-7], because it does not contain syngas cooling and secondary heating [8]. Traditional hot gas desulfurization system works with zinc oxide based sorbent: Russian GIAP-10 (fixed bed) [9] or English Katalco-32-4 (fixed bed) or American RVS-1 (transport reactors) [10]. Zinc oxide based sorbents regeneration properties were investigated in [11], and have the highest sulfur capacity level among metal oxide sorbents. Recommended desulfurization temperatures are from 400 to 500 °C for petroleum gases. Higher temperatures cause sulfur capacity drop [12]. However, reasons of sorbent destruction were not considered in details in literature. Temperature range from 900 to 1100°C is the most effective according to the heat analysis. There is still no solution for hot gas clean-up in this range of temperatures. Nevertheless, there is information about high temperature stable sorbents based on titan dioxide and molybdenum oxide for transport systems [13-16]. Manganese ores are also used in cheap high temperature sorbent processing [18-19]. Though, incidental (side) reactions can occur at high temperatures [20-21]. This study investigates thermal sustainability of zinc oxide sorbent in the atmosphere of syngas components.

2. Research program. Materials and methods
Three types of balance were used in experiments: neutral (argon), reductive (hydrogen, hydrogen sulfide, methane, carbon) and oxidative (carbon dioxide). Temperature range was from 120 to
1000 °С. Kinetic constants of sorbent destruction processes were obtained. Tests were conducted in thermal gravimetrical analyzer. Experiments classification is shown in Table. 1.

|                  | Argon | Carbon | CO2 |
|------------------|-------|--------|-----|
|                  | powder| crushed| grain|
|                  | powder| crushed| grain|
| nonpreheated     | #4    | #3     | #2  |
| preheated        | #7    | #6     | #5  |
| without sorbent  | #1.1  | #1.2   | #1.3|
|                  | #1.4  | #1.5   |     |
|                  |       |        | #10 |
|                  |       |        | #11 |
|                  |       |        |     |

|                  | Methane | H2S | Hydrogen |
|------------------|---------|-----|----------|
|                  | powder  | crushed | grain |
|                  | powder  | crushed | grain |
| nonpreheated     | #12     |        |        |
| preheated        | #13     | #14   | #15    |
| without sorbent  | #1.7    | #1.8  | #1.9   |
|                  | #1.10   |       |        |

There were three types of materials: grain sorbent Katalco 32-4 (3 mm diameter), crushed sorbent Katalco 32-4 (50 - 80 µm diameter), and powder with 99% of zinc oxide (50 - 80 µm diameter).

3. Experiments

Several chemical reactions were considered by thermodynamic analysis:

\[ \text{ZnO} + \text{H2S} = \text{ZnS} + \text{H2O} \] (1)

\[ \text{ZnO} + \text{C} = \text{Zn} + \text{CO} \] (2)

\[ \text{ZnO} + \text{CH4} = \text{Zn} + \text{CO2} + \text{H2} \] (3)

\[ \text{ZnO} + \text{H2} = \text{Zn} + \text{H2O} \] (4)

\[ \text{ZnO} + \text{COS} = \text{ZnS} + \text{CO2} \] (5)

\[ \text{ZnO} + \text{SO2} = \text{Zn} + \text{SO3} \] (6)

\[ \text{ZnO} + \text{CO} = \text{Zn} + \text{CO2} \] (7)

\[ \text{ZnO} + \text{CO2} = \text{ZnCO3} \] (8)

\[ 2\text{ZnO} + 2\text{S} = 2\text{ZnS} + \text{O2} \] (9)

\[ \text{ZnO} + \text{CS2} = \text{ZnS} + \text{CO} + \text{S} \] (10)

Results for the first four reactions (1)-(4) are shown in Figure 1.
It can be seen that incidental reactions are very active at high temperatures, while the main reaction is relatively slow.

4. Analysis of experimental data
Temperature has a great impact on constant rates of side reactions, that is shown in Figure 2. It can be seen that the reaction with hydrogen sulfide is the slowest, while constant rates for incidental reactions are much higher. Side reactions occur only at temperatures higher than 650 °C.

Figure 1. Thermogravimetical curves for reactions (1)-(4)

Figure 2. Constant rates for ZnO reduction in a) carbon b) hydrogen c) methane d) hydrogen sulphide
In temperature range from 650 to 800 °C ZnO reduction in hydrogen is the fastest. At temperatures higher than 900 °C constant rates for methane and hydrogen ZnO reduction are approximately equal.

5. Discussion

Temperatures higher than 900 °C are the most desirable for syngas desulfurization from the technological point of view. It is not effective to cool the hot syngas on the gasifier outlet even down to temperatures at range from 500 to 650 °C, and then heat it again up to 1100 °C for better combustion inside the gas turbine chamber. But zinc oxide sorbents cannot be operated at temperatures higher than 650 °C, and it is not a problem of mechanical destruction. Experiments showed that chemical reduction of zinc oxide is the core of the problem.

Ten types of chemical reactions may occur during syngas desulfurization process. Reactions (1)-(4) are the main reactions, and these reactions were researched experimentally.

Mechanism (1) is positive: it describes how zinc oxide removes contaminant (H2S). At temperatures lower than 650 °C reaction (1) is the only reaction of the desulfurization process. Temperature increase makes H2S reduction (1) faster, but at higher temperatures negative (side) reactions (3)-(4) occur. It can be seen from reaction schemes, that reduction causes zinc evaporation and sorbent destruction. At temperatures higher than 650 °C the hydrogen reduction of zinc oxide starts. Next the carbon reduction of zinc oxide increases (800 °C), finally methane reduction of zinc oxide starts at 900 °C.

On the one hand according to experiment data the hydrogen reduction is the most dangerous for zinc oxide based sorbents, on the other hand concentration of hydrogen in syngas is high (approximately 13-20 % mass.). In addition, hydrogen reduction has the widest range of effect (Figure 2). The only positive reaction of the process is the slowest: according to experimental data constant rate for reaction (1) is much lower than constant rates for reactions (2)-(4) at temperatures higher than 650 °C (Figure 2).

6. Conclusion

Current study considered in detail the problem of zinc oxide-based sorbent destruction in the atmosphere of syngas components. Sorbent is stable at temperature lower than 650 °C with all types of balance gases except hydrogen sulfide. At temperatures higher than 650 °C the hydrogen reduction of zinc oxide starts. Next the carbon reduction of zinc oxide increases (800 °C), finally methane reduction of zinc oxide starts at 900 °C.

Incidental reactions were identified and researched experimentally. Constant rates, pre-exponential factors and energy activation were calculated.

The hydrogen reduction of zinc oxide is the fastest reaction, and its temperature range is the widest among incidental (side) reactions, while its equilibrium constant is the lowest.

According to simulation based on experimental data, regimes of hot gas clean-up were analyzed and preferable parameters were recommended.

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