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Prediction of chlorine behavior in coal gasifier by process simulation

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Abstract

Coal gasifier simulation using CEMCAD7 carried out. Comparing the results of the actual synthetic gas with the simulation, there was a difference of about 5% between them. A study which aim is to identify behavior of chlorine in gasifier also was performed. More temperature in gasifier higher, more HCl generated while calcium chloride gradually decreases. At a heat exchanger section, the number of potassium chloride was the highest. However, at a char recovery flow which is a flow start from char cyclone return to gasifier, the number of Hydrochloric acids is higher than Potassium chloride. Chlorine in slug exit where slugs come out from the gasifier was almost released as the form of potassium chloride. With a number of chemical reactions taking place in the coal-fired power plant, the behavior of chlorine seems to be dynamic depending on each section. However, in areas where only temperature changes exist like heat exchange zone, there was not much change in it.

1 Introduction

Coal has been avoided as an energy source since it has relatively more pollutants such as carbon dioxide and sulfur oxides than oil and natural gas. However, due to the abundance of reserves, relatively equal distribution of coal deposits in the world, the low price and excellent supply stability, Japan relies on coal for a large portion of its power generation fuel. As demand for coal continues to be used in the future, way to alleviate the pollution problem caused by coal is seriously being considered. In the meantime, IGCC (Integrated Gasification Combined Cycle) is being recognized as a way that can contribute greatly to alleviating the environmental problem of coal. IGCC is a complex power system that reacts coal with oxygen to produce synthetic gas under high temperatures and operates gas and steam turbines. It is considered an eco-friendly clean power technology for its new concept that combines coal-fired power plant, chemical plant and combined power plant. It also has a higher efficiency than the existing coal-fired power plant and has a lower pollution output [1]. However, to test-run a lot of coal in real power plant is very costly. Therefore, simulation tool was used in this paper for get Synthetic gas data.

In the middle 1940's, Crossley (1946), based on all the methods of that time, provided the most detailed concept of chlorine in coal. He concluded that Cl may occur in coal in at least four or five forms. 1) Mineral chlorine, mostly as NaCl (70-80% of the total chlorine). 2) Oxychloride form (not present in all coals), 3) Sorbed chlorine (5-10% of the total chlorine) 4) Organic chlorine (0.5-25% of the total chlorine) [2]. This paper tried to identify the behavior of chlorine at each part of gasifier and factors that would affect it. Chlorine is one of the factors affecting the operation of the coal-fired power plant and reduces the efficiency of the power generation. One of the impacts is this; some chlorines are attached to coal, causing the heat exchanger to be blocked. Therefore, it is important to find out chlorine's behavior and build mechanisms that predict its movement with high probability. In this paper, we focused on behavior of mineral chlorine.

There are two main purposes of this paper.

1) To predict the ratio of synthetic gas by type of coal by using simulation program
2) To identify behavior of chlorine in each reactors and the factors that affect chlorine movement.

2 Process simulation procedure

CHEMCAD7 is chemical process simulation software made by Chemstation. It is highly customizable, flexible and affordable. the operation of this program is also relatively simple compared to other simulation programs.

Fig.1 shows process flow of a coal gasification process. The left hand part is the hottest part of the gasifier, which is most chemical reactions taking place in the reactor. Since the reactions within gasification are very diverse and complex, four reactors replaced the gasifier's role. After the chemical reaction, the gas comes out from the outlet of the reactor (D) and enters the heat exchanger area. After finishing the heat exchange, the synthetic gas passes through both the char cyclone and the char filter, where the fine chars fall and return to the gasifier. In this study, it is assumed that char is not re-circulated. Table 1 shows the chemical reactions applied to Carbon conversion(C) and Chemical reactions(D) reactor. Combustion(A) and Devolatilization(B) reactor is Gibbs energy reactor.

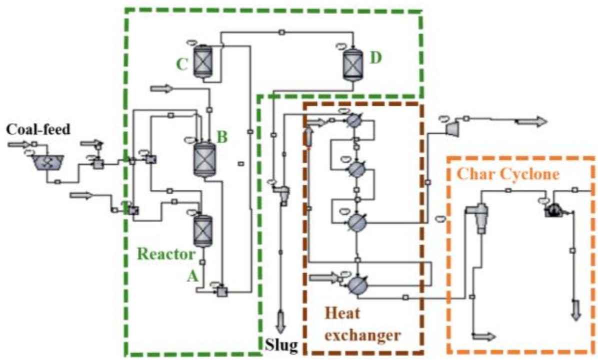

Fig 1 IGCC gasifier Simulation using chemcad7

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Reactor Name	Reaction	Description
(A)	Combustion	Chemical reactions with a relatively rich oxygen
(B)	Devolatilization	Chemical reactions that produce carbon monoxide and hydrogen with little oxygen
(C)	Carbon conversion	Chemical reaction in which the char is converted to another chemicals
(D)	Chemical reactions	Additional chemical reactions to increase the rate of generation of the Carbon monoxide

Table 1: Reactors' role in simulation

Reactor	Chemical reaction
Carbon conversion	$C_{(s)} + 0.5O_2 \rightarrow CO$
	$C_{(s)} + CO_2 \rightarrow 2CO$
	$C_{(s)} + H_2O \rightarrow CO + H_2$
Chemical reactions	$H_2 + 0.5O_2 \rightarrow H_2O$
	$CO + 0.5O_2 \rightarrow CO_2$
	$CH_4 + 2O_2 \rightarrow CO + 2H_2O$
	$CO + H_2O \rightarrow CO_2 + H_2$
	$CH_4 + H_2O \rightarrow CO + 3H_2$

Table 2: Chemical reactions in reactors

Adaro	Carbon	Hydrogen	Sulfur	Nitrogen	Oxygen	Ash
(%)	71.50	4.79	0.14	0.96	19.24	2.63

Table 3: Chemical composition

Table 3 lists ultimate analysis for subbituminous coal using this study. The fuel ratio (=Fixed carbon/Volatile matter) was about 0.9.

3 Results and discussion

3.1 Chemical composition change by temperature in devolatilization reactor(B)

The result of the synthetic gas obtained from the simulation was compared to the results of the actual synthetic gas. This comparison of results can be used as a reference to how much error the actual plant operation and simulation. In other words, the reliability of the simulation would be assessed. The simulation results showed a difference of approximately 5% from the actual value in case of CO shown in Table 4.

Composition	Simulation result (%)	Actual result (%)
H_2	**23.1**	**24.9**
CO	**55.1**	**52.6**
CO_2	**3.4**	**5.7**
N_2	**16.9**	**11.8**
CH_4	**1.2**	**1.8**

Table 4 results of synthetic gas in simulation and in reality

Changes in the proportion of the main components were observed according to the temperature inside reactor(B). Carbon dioxide and hydrogen have steadily increased from 500 degrees Celsius, with little change being observed from about 1050 degrees Celsius or higher.

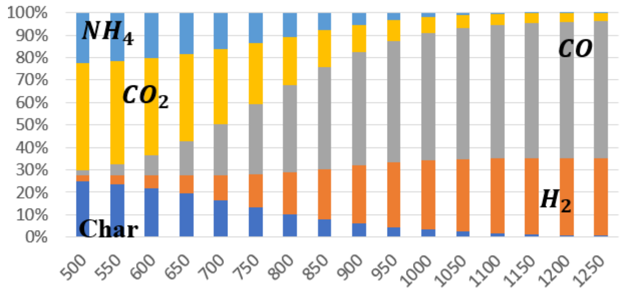

Fig 2 The graph of the proportion of the main components by temperature in devolatilization reactor(B)

3.2 Behavior of chlorine by temperature in each reactors.

The change of chlorinated compounds was observed in each of the reactors' temperature.

1) Combustion reactor(A)

Calcium chloride decreases rapidly from low temperatures and was no longer observed in the range of about 750 degrees. Sodium chloride rapidly decreased from about 1050 degrees Celsius and was not observed in the range of 1150 degrees or higher. A proportional increase in hydrogen chloride was observed, meaning that the chlorine in calcium chloride and sodium chloride reacted with hydrogen.

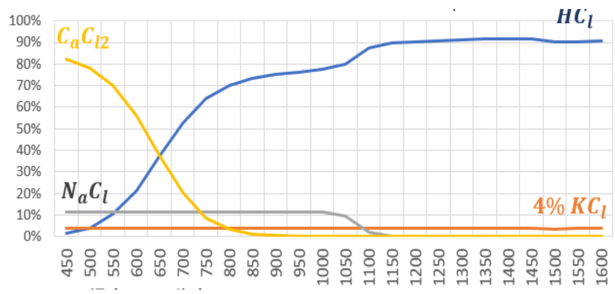

Fig 3 The graph of the proportion of the main components by temperature in devolatilization reactor(A)

2) Devolatilization reactor(B)

Compared to the reactor(A), the temperature at which potassium chloride and sodium chloride were not completely observed was higher. Calcium chloride was not found in excess of 1,000 degrees and sodium chloride in excess of 1250 degrees.

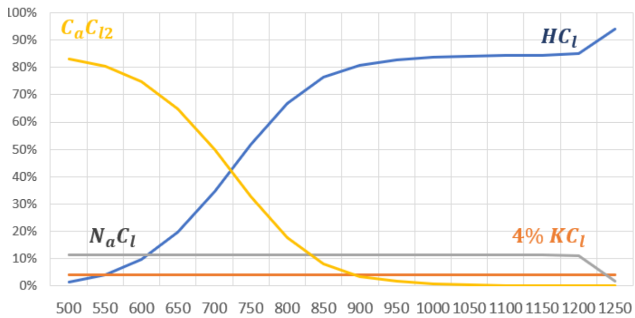

Fig 4 The graph of the proportion of the main components by temperature in devolatilization reactor(B)

3) Chlorine at the gasifier outlet

This graph shows the trend changes in the chemical form of chlorine at the gasifier outlet depending on gasification temperature changes. Calcium chloride decreases continuously, while hydrochloric acid increases proportionally to the reduction of calcium chloride. This would mean that chlorine in calcium chloride becomes chlorine in the form of hydrochloric acid as the temperature rises. The proportion of sodium chloride decreased sharply from about 1250 Celsius degrees and was not observed in temperatures above 1300 Celsius degrees. (In case of Calcium chloride, chlorine content in the graph is twice the actual rate.)

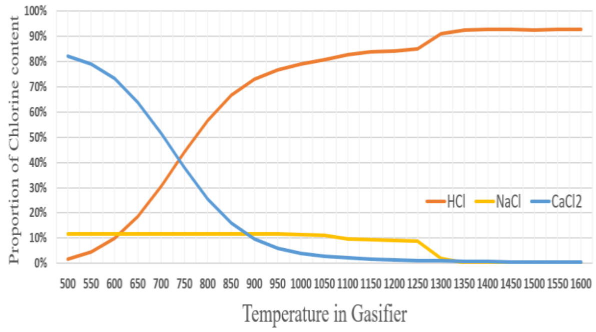

Fig 5 The graph of behavior in chlorine by temperature in gasifier

3.3 Behavior in chlorine at heat exchanger area

Heat exchanger section consists of ECO, Eva1, Eva2, and Eva3. As it passes through the heat exchanger in turn, the water eventually turns into steam and enters the steam turbine. In this paper, ECO is defined as the zone between where the chemical reaction is almost complete and heat exchanger section. A heat exchange with water exists. After passing through the ECO, the synthetic gas passes through Eva1, Eva2, and Eva3 to keep conducting heat exchange. Unlike synthetic gas, slugs are released into the slug outlet.

Figure 6 shows the changing behavior of chlorine in the heat exchanger area. Through simulation, hydrochloric acid and potassium chloride occupy the bulk of the chlorine compounds in synthetic gas, we focused on the ratio of these two substances. As a result, no change in behavior of chlorine compounds was observed in Eva1, Eva2 and Eva3 where there are only temperature differences. At slug exit, Chlorine exists as a form of potassium chloride.

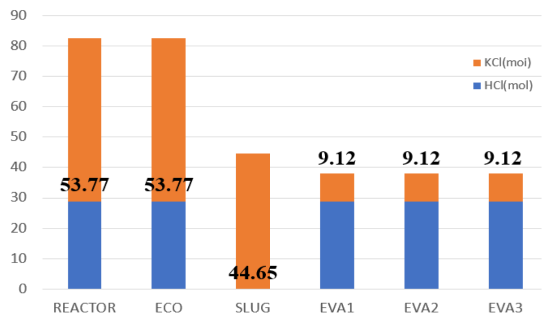

Fig 6 Variation of Chlorine Behavior in Synthetic Gas

3.4 Behavior in chlorine in char recovery flow

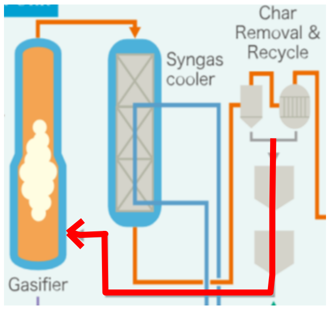

Fig 7 Char recovery flow from char cyclone to gasifier [3].

The char cyclone and char filter pick up char which couldn't respond and returns it to the gasifier. Figure 7 shows the behavior in chlorine between char cyclone and gasifier. There was a very large proportion of hydrochloric acid in Figure 8.

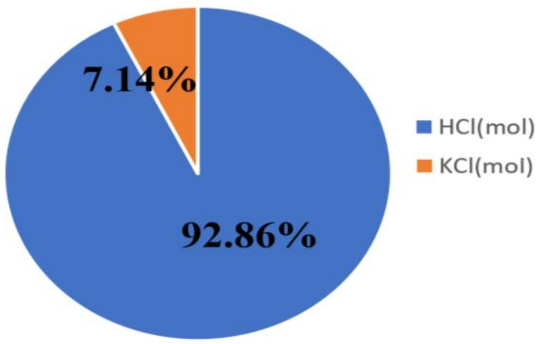

Fig 8 Ratio of chlorine compounds in char recovery flow

3.4 The relationship between temperature difference in heat exchanger and behavior of chlorine

With four heat exchangers, the average temperature difference between the heat exchangers is about 200 Celsius degrees. Figure 9 shows the graph shows the behavior of chlorine when there is no EVA1 which means that the temperature drops considerably when synthetic gas pass through from ECO to EVA2. However, it shows that behavior of chlorine is not significantly affected by temperature changes.

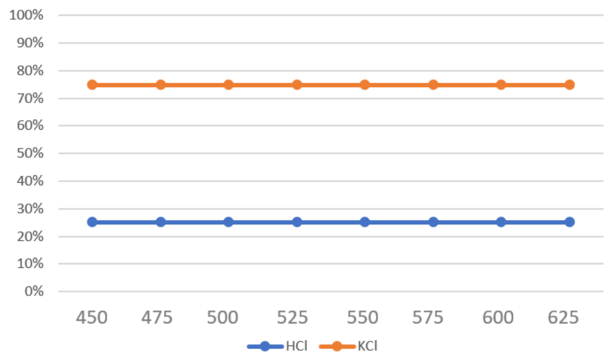

Fig 9 The Change of the Ratio of Chloride Compounds by Temperature difference between ECO and EVA2

4 Conclusions

(a) Though gasifier was designed with multiple reactors, the simulation results of the synthetic gas did not differ significantly from the actual results.

(b) Depending on the temperature of the reactor, the component proportions of the synthetic gas vary greatly.

Chlorine behavior at some areas of the gasifier have been specified.

(c) As the temperature increases, the chlorine in potassium chloride and sodium chloride reacts with hydrogen, producing hydrogen chloride. If a large amount of oxygen is contained, the temperature at which calcium chloride and sodium chloride are completely replaced by hydrogen chloride is higher than it is not.

(d) At a slug exit, Chlorine exists as a form of potassium chloride.

(e) At EVA1, EVA2 and EVA3, there is no change in behavior of chlorine.

(f) At char recovery flow, Hydrochloric acid accounted for a high percentage.

(g) Temperature differences between heat exchangers do not significantly affect changes in behavior of chlorine.

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