A PREDICTION OF COAL ASH SLAGGING UNDER THE GASIFICATION CONDITION FOR PREPRINTS OF THE AMERICAN CHEMICAL SOCIETY DIVISION OF FUEL CHEMISTRY

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ABSTRACT

Several candidate samples for coal gasification are experimented with proximate, ultimate and ash composition analysis and the fusion temperatures of coal ashes are determined with data from analysis. The effect of flux addition is also evaluated to find the optimum quantity for slagging condition, while considering negative effect of CaO addition on gasification reaction. In order to further expand the variety of candidate coals and the performance in an entrained-bed, the effect of ash fusion temperature drop is evaluated when blending coals. The results of the experiment suggested that optimum compositions of CaO flux are 10%, 20% with Alaska and Datong coal, respectively. However, the optimum value of blending ratio is not known when Posco coal is blended with candidate coals.

INTRODUCTION

As the need for electric power increases in Korea, large amounts of imported coal will be utilized in the future. One of the candidate technologies for producing electricity from coal in an environmentally sound manner and high efficiency is IGCC (integrated gasification combined cycle). In a slagging-type IGCC processes, ashes in the coal are cohered and formed slag which is discarded through the bottom of the gasifier. Slagging behavior of coal ash can be enhanced by adding a reduction agent such as limestone and dolomite.

The objective of this study is to predict the slagging and fluid behavior of various coal ashes for the optimum slag removal condition slagging-type IGCC power plants from the physical and chemical characteristics of original coals. The effect of flux addition is studied with candidate coal ash samples to evaluate optimum quantity of flux addition considering negative effect of CaO addition in the coal gasification reaction. The change of ash fusion temperature is also studied to find the optimum blending ratio of Posco coal with Datong coal and Alaska coal. The experimental values of ash fusion temperatures are compared with calculated values so that predictional methodology of ash slagging behavior will be verified within our experimental range. Another objective of the study is to prevent clogging of slag at the bottom of the gasifier which occurs due to solidation of melted slag. The result of this study will be used to determine optimum operation conditions of a 3 T/D slagging-type gasifier which is located in Ajou University, Korea.

SLAGGING BEHAVIOR IN COAL GASIFIER

Slag in the coal gasifier means the melt of coal ash which has constant viscosity and flow along the wall of gasifier. In order to remove ash by the slagging operation, the temperature of the gasifier should be maintained above the fusion temperature of the coal ash. Formed slag should easily flow down to the exit of the gasifier. To maintain this condition, viscosity of the slag should be maintained under the 100 poise [1]. Many empirical equations based on experimental data are proposed in order to explain relationship of chemical composition of coal ash and slag viscosity [-5]. In the present investigation, Urbain and Watt & Fereday equations are utilized in calculating slag viscosity which give reliable values under 100 poise.

(a) Prediction of slag viscosity

Ash slag viscosity can be predicted by Urbain or Watt & Fereday relation. The Urbain equation, in which composition of each slag component is expressed in mole fraction, is derived from $CaO-Al_2O_3-SiO_2$ three components system. The Urbain equation, as in Eqn (1), is mainly used to determine slag viscosity of low rank coal ash.

$$\ln \eta = \ln A + \ln T + 10^3 B/T - \Delta \quad (1)$$

in equation(1), T is the absolute temperature, A and B are functions of the chemical composition of the ash, and η is the viscosity in poise. Parameter "Δ" has different value with the quantity of silica in slag. If the quantity of silica is minimal, slag viscosity can be expanded from Eqns (2)-(13).

$$\Delta = mT + b \quad (2)$$
$$b = -1.8244(10^3 m) + 0.9416 \quad (3)$$
$$10^3 m = -55.3649F + 37.9186 \quad (4)$$

$$F = \frac{CaO}{CaO + MgO + Na_2O + K_2O} \quad (5)$$

$$\ln A = -(0.2693B + 11.6725) \quad (6)$$
$$B = B_0 + B_1(SiO_2) + B_2(SiO_2)^2 + B_3(SiO_2)^3 \quad (7)$$
$$B_0 = 13.8 + 39.9355\alpha - 44.049\alpha^2 \quad (8)$$
$$B_1 = 30.481 - 117.1505\alpha + 129.9987\alpha^2 \quad (9)$$
$$B_2 = -40.9429 + 234.0486\alpha - 300.04\alpha^2 \quad (10)$$
$$B_3 = 60.7619 - 153.9276\alpha + 211.1616\alpha^2 \quad (11)$$

$$\alpha = \frac{M}{M + Al_2O_3} \quad (12)$$

$$M = CaO + MgO + Na_2O + K_2O + FeO + 2TiO_2 + 3SO_3 \quad (13)$$

Meanwhile, in the case of medium silica quantity, Eqn(14)-(16) are used instead of Eqns. (3)-(5).

$$b = -2.0356(10^3 m) + 1.1094 \quad (14)$$
$$10^3 m = -1.3101F + 9.9279 \quad (15)$$
$$F = B(Al_2O_3 + FeO) \quad (16)$$

When the silica quantity is high in slag, similarly Eqns.(17)-(19) are used instead of Eqns(3)-(5).

$$b = -1.7737(10^3 m) + 0.0509 \quad (17)$$
$$10^3 m = -1.7264F + 8.4404 \quad (18)$$

$$F = \frac{SiO_2}{CaO + MgO + Na_2O + K_2O} \quad (19)$$

Using the Urbain equations in calculating slag viscosity of low rank coal, silica content should be cautiously determined. Silica content mostly affect the B value . In the case of a B value located in the boundary, the larger value is chosen. The experimental result of Watt and Fereday is accepted to determined a reliable relationship between the viscosity of slag and temperature. They proposed Eqn (20), which is derived from regression analysis of experimental data by Hoy et al [6].

$$Log_{10}\eta = \frac{10^7 m}{(T-150)^2} + C_2 \quad (20)$$

In Eqn. (20), m represents (0.00835 SiO2 + 0.00601 Al_2O_3 -1.09) where total percent of (SiO_2 +Al_2O_3 +Fe_2O_3+CaO+MgO) equals 100% and C_2 is (0.0415SiO2+0.0192 Al_2O_3 +0.0276 Fe_2O_3+ 0.0160CaO-3.92). η is viscosity in poise and T is in °C. This empirical equation is the best fit when the coal ash component is throughly melted so that no crystal exists. Prediction of slag viscosity is correct in the ash component range of Table 1.

The Urbain Watt and Fereday Equation utilized chemical composition of the ash derived by ASTM methods to predict ash fluidity behavior but not the exact behavior of ash fusion/slagging. Calculated viscosity data are represented for Alaska and Datong coal in Table 2 and 3.

(b) Prediction of critical viscosity temperature

Liquid phase slag behaves as a Newtonian fluid and, when decreasing temperature, it passes through the pseudo-plastic state before solidification. The separation from solid phase depends on the composition of slag. When the transition takes place from liquid state to the solid state, the temperature is call Critical Viscosity Temperature (Tcv). Watt [6] derived the equation which is related to chemical composition and Tcv in Eqn(21).

$$T_{cv} = 2990-1470(SiO_2/Al_2O_3) + 360(SiO_2/Al_2O_3)^2-14.7(Fe_2O_3+CaO+MgO)+ 0.15(Fe_2O_3+CaO+MgO)^2 \quad (21)$$

In Eqn (21), T_{cv} is in °C, and the total percent of ash component of SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO equals 100. Because of the limitation in using this equation, Tcv can be assigned as a hemispherical temperature determined by the ash fusion temperature plus 93°C [7].

EXPERIMENT OF ASH SLAGGING CHARACTERISTICS

Three different coal samples are utilized for ash fusion temperature and ash fluidity behavior. Proximate and ultimate analysis of coal samples are illustrated in Table 4.

From the experimental data of ash fusion determination, relationship fouling and slagging can be made from the coal combustion and gasification reactions. Determination of not only which coal is the best candidate for gasifier or combustor but also whether the dry or wet ash treatment method is appropriate for coal benification. It is well-known that the difference of fusion temperature are related to the degree of fouling and slagging. The greater the temperature difference between IDT and FT, the slower the fouling rate so that the intensity of fouling is decrease because more pores are generated in the fouling process.

The fusion temperature of samples has been measured by using the ash fusion determinator (LECO-600). The cones were manufactured to pyramidal shape, height 19mm, base 6.5mm. The temperature of 390°C, starting temperature of 538°C, final temperature of 1600°C and heating condition and air in oxidizing condition. Table 5 illustrates the measurement results of ash temperature of candidate coal while adding CaO as fluxing agent. Ash fusion temperature is decreased with CaO addition until a certain limit but it is increased after that limit because excess addition of CaO results in higher fusion temperature. Table 6 shows the change of the ash fusion temperature with mixing ratio and Table 7 shows fusion temperature change with the composition of surrounding gas.

Because ash viscosity measurement is performed in a nitrogen atmosphere, fusion temperature changes with the composition of the surrounding gas are evaluated as in Figure 1. Tcv measured in nitrogen is lower than the T_{cv} in air because Fe acted as strong fluxing agent in the high temperature range. Fusion temperature in a reducing atmosphere is lower than that in the oxidation atmosphere. The reason is that iron, which plays a significant role in ash slagging, exists as Fe_2O_3 in an oxidizing environment but FeO or Fe in reducing one. Actually, the fusion temperature of pure Fe_2O_3 is 1560°C, FeO is 1420°C and Fe is 1275°C. From Table 7, fusion temperature with N_2 as a surrounding gas is located in the midpoint between those in reduction and oxidation conditions. This result implies that Fe acts as fluxing agent in the inert environment. ΔT in Table 5, which is difference between fluidization temperature and initial deformation temperature is the index which estimates the degree of slagging. If ΔT is small, fusion takes place suddenly and thin layer of fusion slag is generated. Therefore, to carry out the optimal slagging in the gasifier, a candidate coal should be chosen that has an ash composition resulting in a lower ΔT value.

From figure 2 and 3, fusion temperature of Alaska, Datong and Posco coal are minimum when 10%, 20% and 30% CaO is added respectively. Also, ΔT value of Alaska, Datong, Posco coals is minimum when 20%, 20%, and 40% CaO is added respectively. Figure 4 shows the results if fusion temperature measurement when mixing Posco coal with Datong and Alaska coals from 10% to 50%, fusion temperatures increased with mixing ratio.

SUMMARY

The objectives of this study are minimization of the negative effects of CaO addition to maintain a slagging state and expanding the various candidate coals by use of the blending method. We considered the effect of degree of fusion by means of CaO addition and coal blending related with standard coals (Alaska, Datong) and a comparison coal (Posco). First, from the result of fusion temperature measurements when Posco coal with Datong and Alaska coals, fusion temperature is minimum when 10% of CaO is added to Alaska coal, 20% to Datong coal and 50% to Posco coal.

For Posco coal, we could estimate that fusion temperature is minimized by an increase of CaO content, because we varied the content of CaO from 10 to 50%. Also, when standard coal is blended with 10-50% of comparison coal, fusion temperature is minimized with blending of 10% comparison coal and increases with increasing blending ratio.

From the above experiments, we decided the optimal addition value. Fusion temperatures of Alaska, Datong and Posco coals are minimum when 10%, 20% and 30% CaO is added respectively. In the case of blending, there isn't a value which can satisfy viscosity less than 100 poise, because Alaska and Datong coals have viscosities greater than 100 poise at 1400°C. Therefore, we should determine a more suitable coal in using blending method. Also, we should measure viscosity using reduction gas in order to explain exactly the viscous flow and fusion of coal ash in the gasifier.

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Table 1. Range of ash component used in Watt and Fereday equation

Silica	SiO_2/Al_2O_3	Fe_2O_3	CaO	MgO
40~80 wt%	1.4~2.4 wt%	3~30 wt%	2~30 wt%	1~30wt%

Table 2: Calculated viscosity of Alaska ash

Temperature	Viscosity (poise)			
(°C)	Alaska	Alaska (10%)	Alaska (20%)	Alaska (30%)
1000	263634	35906	6877	1711
1100	14857	2826	714	224
1200	1829	443	137	51
1300	379	110	40	16
1400	113	38	15	7
1500	44	16	7	4
1600	20	8	4	2

Table 3: Calculated viscosity of Datong coal ash

Temperature	Viscosity (poise)			
(°C)	Datong	Datong (10%)	Datong (20%)	Datong (30%)
1000	8035920	785161	114268	22600
1100	248254	35913	7235	1881
1200	19737	3799	970	307
1300	2950	703	214	79
1400	683	192	67	28
1500	216	69	27	12
1600	86	31	13	7

Table 4 Proximate, ultimate analysis of sample coal

Coal	Proximate Analysis (wt%)				Ultimate Analysis (wt%)				
	M	V.M.	F.C.	Ash	C	H	O	N	S
Alaska	5.09	44.85	35.64	14.42	54.40	4.55	40.24	0.64	0.17
Datong	6.87	29.30	54.65	9.18	67.08	4.31	27.35	0.66	0.60
Posco	1.58	30.11	58.32	9.99	71.05	3.71	11.08	3.61	0.56

Table 5 Influence of CaO content on ash melting temperature

Coal	AFT(°C)	%CaO (reducing condition)					
		Raw	10%	20%	30%	40%	50%
Alaska	IDT	1165	1143	1187	1256	1406	1413
	ST	1176	1163	1200	1275	1471	1525
	HT	1212	1183	1211	1289	1527	1535
	FT	1287	1208	1218	1344	1529	1537
ΔT (FT-IDT)		123	65	31	88	123	124
Datong	IDT	1178	1139	1166	1256	1406	1413
	ST	1230	1182	1181	1275	1471	1525
	HT	1268	1222	1188	1289	1520	1535
	FT	1362	1282	1201	1344	1527	1537
ΔT (FT-IDT)		184	143	35	88	121	124
Posco	IDT	1369	1245	1193	1219	1257	1380
	ST	1420	1278	1215	1234	1268	1440
	HT	1460	1308	1243	1245	1275	1467
	FT	1519	1379	1317	1260	1286	1486
ΔT (FT-IDT)		150	134	124	41	29	106

Table 6 Influence of blending ratio on ash melting temperature

Coal	Datong			Alaska		
AFT(°C)	Reduction	N_2	Oxidation	Reduction	N_2	Oxidation
IDT	1176	1261	1279	1164	1191	1210
ST	1230	1279	1300	1176	1224	1231
HT	1268	1315	1327	1212	1269	1278
FT	1362	1376	1386	1287	1298	1307

Table 7 Influence of atmospheric condition on ash melting temperature

Coal	AFT (°C)	Reducing Condition				
		10:90	20:80	30:70	40:60	50:50
P:A	IDT	1167	1189	1193	1212	1224
	ST	1208	1215	1216	1249	1256
	HT	1234	1240	1253	1278	1287
	FT	1304	1327	1334	1343	1355
P:D	IDT	1197	1210	1220	1239	1285
	ST	1220	1250	1267	1279	1310
	HT	1290	1313	1320	1328	1388
	FT	1355	1379	1397	1414	1429

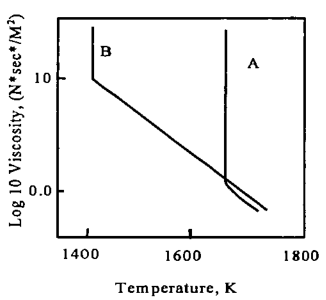

Fig. 1 Effect of atmospheric condition on slag viscosity (A: in air, B: in nitrogen).

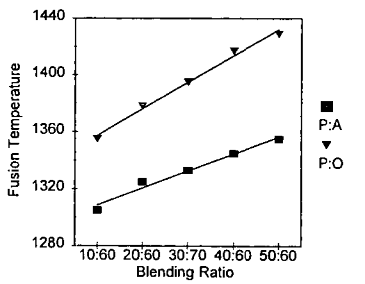

Fig. 2: Behavior of ash fusion drop due to blending coal.

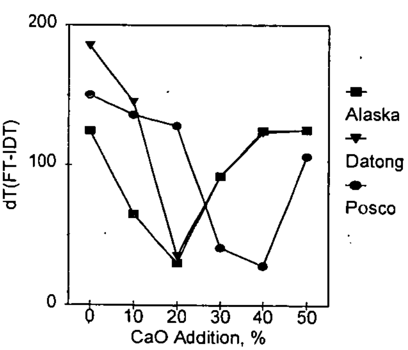

Fig. 3: Behavior of ash fusion temperature drop due to adding flux.

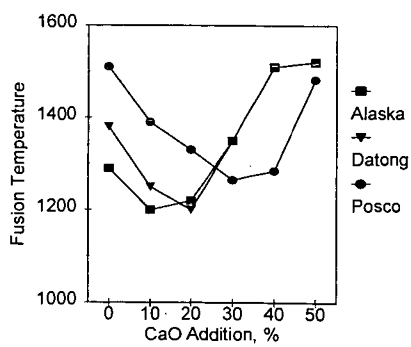

Fig. 4: Influence of CaO content on ash melting temperature.