

Low-temperature reactivity of coals for evaluation of spontaneous combustion propensity

Jungsoo Kim^{*,‡}, Yongwoon Lee^{*,‡}, Changkook Ryu^{*,†}, Ho Young Park^{**}, and Hyunsoo Lim^{**}

^{*}School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

^{**}Fuel and Combustion Group, KEPCO Research Institute, Daejeon 305-380, Korea

(Received 26 June 2014 • accepted 9 November 2014)

Abstract—Low rank coals are more reactive at low temperatures than high rank coals, which leads to spontaneous combustion if not controlled. Due to the increased use of low rank coals, preventing spontaneous combustion during storage and size reduction has become an important issue in power plants. The present study evaluates the low-temperature reactivity for various coals in terms of their rank and country of origin. The experimental method determined the temperature and its gradient for coals in a small fixed bed at the point surpassing that of input oxygen, which were defined as the crossing-point temperature (CPT) and slope (CPS), respectively. Combining the two parameters, a low-temperature reactivity index (LTR index) was proposed. The method tested 17 coals collected from a power plant that yielded CPTs ranging between 168–190 °C and CPSs between 0.862–1.228 °C/min. The LTR index for the coals was calculated to be 0.696 to 1.542. The LTR index was positively correlated with the moisture content and volatile matter/fixed carbon (VM/FC) ratio, and inversely correlated with the ash content. The ignition temperature, measured by thermogravimetric tests, also exhibited a positive relationship with the LTR index. However, no single property of coal was sufficiently correlated with the self-heating propensity for all the coals tested, illustrating the complex mechanisms involved.

Keywords: Cross Point Temperature, Ignition Temperature, Low Rank Coal, Low Temperature Reactivity, Self-heating, Spontaneous Combustion

INTRODUCTION

Despite the concerns surrounding greenhouse gas emissions, coal remains the dominant source of power generation, responsible for producing 40.6% of global power in 2010 [1]. In South Korea, it generated 39.9% of the country's electricity in 2010 [2]. Hard coals or high rank coals have formed the main fuel for power generation in South Korea. However, due to decreasing reserves and increasing mining costs, the use of low rank coals has recently increased [3]. South Korea imports 97% of its coal [2] from various countries, including Australia, Indonesia, and Russia. More than 48 types of coals were imported in 2010 by Korea South East Power alone, one of five major power supply companies in the country. Due to the large variation between coals, the rapid characterization of their fuel properties has become crucial for the stable operation of power plants. In terms of the boiler, important fuel properties include the combustion and ash slagging/fouling characteristics of individual coals and their blends [3,4].

For the handling and pre-processing of low rank coals, low-temperature reactions and self-heating phenomena are practically very important [5,6]. These characteristics contribute to spontaneous combustion during transport, storage, and pulverization of coal,

which may result in serious damage to the facility. In particular, coal stored in the yard of a power plant is highly susceptible to spontaneous combustion because the time and heat/mass transfer conditions are ideal for the self-heating of coals. It is common to see several plumes of smoke rising from the stockpiles of low rank coals in the yard, and water is often sprayed to prevent fire.

Self-heating of coal is caused mainly by the slow oxidation of coal at temperatures below 100 °C [7,8]. Some functional groups such as benzylic and aliphatic groups are known to react with oxygen at low temperatures to form carbonyl, carboxylic or aldehyde groups, which eventually produce CO₂, CO and H₂O by oxidation [9–12]. These exothermic reactions slowly release heat to increase the temperature of coal to above 100 °C from ambient temperature. Physical and chemical mechanisms also contribute to this self-heating, including the adsorption of moisture in dry coal and oxidation of pyrite (FeS₂) [6,10]. If the heat continues to accumulate without cooling, the reactions become rapid above 140 °C. This stage is sometimes referred to as thermal runaway. Once the temperature becomes 200 °C or higher, the rapid thermal decomposition and release of volatiles leads to self-sustained combustion.

A number of intrinsic properties of coal are associated with low temperature reactivity [9,10]. Low rank coals contain more reactive functional groups with higher O and H content, have larger porosity, and consequently, higher surface areas than higher ranked coals. In terms of coal macerals, liptinite is the most reactive, while inertinite is the least. The inert (ash) fraction in coal acts as a heat sink while reducing the combustible fraction, but the self-heating pro-

[†]To whom correspondence should be addressed.

E-mail: cryu@me.skku.ac.kr

[‡]Equal contribution as the first authors.

Copyright by The Korean Institute of Chemical Engineers.

density is not clear for coals with an ash content less than 20%, compared to the effect of coal seam type [13,14]. Smaller coal particles are more prone to self-heating due to the larger surface area to volume ratio. The exposure time to air is known to be very important, as coal gradually adsorbs oxygen to form oxygenated functional groups. Therefore, the rate of oxygen consumption at low temperatures exponentially decreases over time [9]. For this reason, the prevention of self-heating and combustion of coal has been a crucial issue in coal mining [15].

The self-heating of coal is also influenced by the heat and mass transfer conditions during storage. The shape, size, and porosity of a coal stockpile are known to determine the diffusion of oxygen and convective heat loss. The prediction by Akgun and Essenhigh [16] shows that hot spots are generated about 2 m in from the sides of a stockpile, leading to the ignition of coal piles greater than a minimum critical height. The porosity of a stockpile is changed by the degree of compaction and particle size distribution. Weather conditions such as the temperature, velocity, and humidity of air are other important factors. The addition of external moisture by water spraying also influences the degree of self-heating over time, which is the main control measure in a power plant. Controlling the heat and mass transfer conditions may significantly suppress the spontaneous ignition in coal stockpiles [17].

Due to the diversity of coal properties, evaluating the self-heating propensity has practical importance for storage and pre-processing in a power plant. As reviewed by Nalbandian [6] and by Sen et al. [18], a number of test methods have been developed to quantify self-heating. The most common include deriving the crossing point temperature (CPT), the self-ignition temperature (SIT), and the R_{70} test. The CPT test uses a wire-mesh basket of coal sample placed in an oven to which a controlled flow rate of air is supplied at a fixed heating rate [19]. SIT is defined as the minimum oven temperature leading to sustained self-ignition of the sample placed in an isothermal oven [20]. In contrast, the R_{70} method uses an adiabatic oven to monitor the time required for coal to reach 70 °C [13,21,22]. From a practical point of view for a power plant,

rapidly determining the self-heating propensity of a new coal upon arrival is essential to determine the precautions needed to prevent spontaneous combustion.

This study investigates the low temperature reactivity of coal with an experimental method based on a CPT test with oxygen. A total of 17 coals with different countries of origin sampled from a local power plant were tested to derive three critical parameters including a new index. The parameters were compared with key coal properties acquired from proximate analyses, ultimate analysis and ignition temperature. The results were discussed to understand important factors influencing the low temperature reactivity.

MATERIALS AND METHODS

1. Coal Samples

A total of 15 coal samples were collected from the yard at a local power plant in Korea among those that had been stored in the yard for less than 1 month. The samples were then crushed, dried in nitrogen and stored in sealed bags. In addition, one coal sample (coal Ko) was prepared by fry-drying of coal Ki, which is a method of effectively removing the moisture by immersing in a hot oil bath of approximately 130 °C [23]. Coal Y was collected from another power plant burning domestic anthracite or bituminous coal.

For characterization of the samples, proximate analysis was undertaken as per the standard method ASTM D3172. The ultimate analysis was conducted using an elemental analyzer (EA1108/NA2000, Fisons Instrument) for C, H, N, and S compositions. The higher heating value (HHV) was measured using a PARR bomb calorimeter. The ash composition was analyzed using an ICP-OES (CAP 6300 Duo, Thermo Scientific Co.) and ICP-MS (7700x, Agilent Technologies) for key elements and converted to the respective oxide composition.

Table 1 lists the summary of the fuel properties of the 17 coals tested (detailed data is presented in Table S1 of the Supplementary Info.). The coals were sub-bituminous and bituminous with a range of properties, and were imported from Australia, Indonesia,

Table 1. Summary of fuel properties of tested coals

Coal	Be	Bt	C	En	Ex	Fe	Fi	Fl	G	Kl	Ki	Ko	M	P	S	T	Y	
Country of origin	IND	US	AU	AU	AU	AU	IND	IND	AU	IND	IND	IND	AU	AU	RU	IND	KOR	
Proximate analysis (wt%ad)	IM	8.24	9.34	1.30	10.09	1.41	1.26	4.47	1.98	4.39	8.58	10.94	4.09	1.20	1.41	3.14	9.27	7.65
	Ash	10.69	12.44	18.28	5.08	16.12	20.53	14.85	17.30	10.27	14.25	10.74	7.18	15.97	14.83	15.40	11.36	18.29
	VM/FC	0.98	0.92	0.55	1.03	0.68	0.51	0.56	0.71	0.70	1.01	1.03	1.14	0.61	0.65	0.84	1.04	0.51
Ultimate analysis (wt%ad)	C	60.41	57.69	65.47	67.33	62.50	64.09	70.95	66.93	68.79	50.20	64.63	69.80	68.90	68.31	61.94	59.50	67.23
	H	4.08	3.16	3.92	4.32	3.94	3.94	4.69	4.40	5.06	4.09	3.10	4.79	3.91	4.34	4.02	3.84	2.49
	O	12.30	15.53	7.34	10.93	14.37	6.46	3.10	6.05	9.31	21.56	9.24	12.79	5.76	6.86	14.57	11.21	2.77
HHV (MJ/kg)		25.46	21.98	26.67	27.06	24.24	26.51	30.22	28.01	28.90	18.99	21.60	27.17	28.25	28.25	24.27	24.26	26.54
Ash composition (wt%)	SiO ₂	56.18	58.07	67.57	53.77	48.76	65.16	54.19	69.63	50.08	57.86	56.16	58.67	75.78	63.83	60.56	60.93	44.48
	Al ₂ O ₃	19.47	19.11	25.10	10.80	25.65	22.35	25.06	20.39	23.25	25.01	16.14	10.56	18.78	23.63	27.48	16.16	22.18
	CaO	3.03	1.81	0.35	11.59	11.44	0.71	6.08	0.96	10.99	2.30	5.31	7.15	0.20	1.74	3.18	4.00	9.19
	Fe ₂ O ₃	9.02	15.99	2.02	10.15	7.77	6.11	7.81	3.51	6.61	9.67	15.10	16.14	1.72	4.64	3.47	10.41	18.73

IM: inherent moisture, VM: volatile matter, FC: fixed carbon, AU: Australia, IND: Indonesia, RU: Russia, US: United States, KOR: South Korea (Detailed data available in Table S1 of the Supporting Information)

the United States, and Russia except for coal Y. The inherent moisture content was between 1.20% (coal M) and 10.09% (coal Ki). The ratio of volatile matter and fixed carbon (VM/FC) ranged from 0.51 (coal Y) to 1.14 (coal Ko). The ash content was the lowest in coal En (5.08%) and the highest in coal Ki (10.94%). SiO₂ was the dominant oxide form in ash, ranging between 48.8% (coal Ex) and 69.6% (Coal Fl), which is typical for coal. Other major compounds in ash were Al₂O₃, CaO, and Fe₂O₃, but individual weight fractions widely varied between coals.

2. Determination of Ignition Temperature Using Thermogravimetric Analysis

The ignition temperature of coal is an indicator of its low temperature reactivity [6]. For 7-10 mg of each coal sample, the test was performed by thermogravimetric analysis (TGA) (Scinco TGA N-1000) under 50 ml/min of oxygen heated at 20 °C/min from room temperature. The ignition temperature is defined as the value showing a rapid rate of mass loss (>2%/°C). Note that the temperature used is for the input O₂, while the actual temperature of the coal sample becomes higher due to the oxidation of volatiles released followed by combustion of char.

3. Experimental Method for Self-heating Propensity

The experimental setup for the self-heating propensity of coals consisted of a coal sample cage (diameter 36 mm and height 30 mm), with an insulating tube (ceramic fiber, height 250 mm and thickness 10 mm) holding the cage, and an electrically heated reactor (SUS304, diameter 150 mm and height 300 mm) (see Fig. 1). It was designed to control the mass transfer of oxygen by passing all the gas through the sample. The heat released from the coal at the top of the cage can be also accumulated within the sample by the gas flow. The heat loss from the sample was minimized by the flow of the preheated gas surrounding the insulating tube. To perform the test, a coal sample was sieved for a fixed size range, added to the cage, which was then placed within the insulating tube. The cage was made of 100 mesh sieve to hold the sample particles while allowing the gas to flow through. It typically required 15 g of sample to fill the cage. Once the cage was placed inside the alumina tube, nitro-

gen was initially supplied into the reactor at a flow rate of 500 ml/min for 30 minutes to remove the air. The gas pressure at the mass flow controller was maintained at 2 bar to purge the gas flow through the bed of fine particles in the cage. Then, the gas was switched to pure oxygen at the same pressure with a fixed flow rate. Next, the electric heater surrounding the reactor was turned on, which raised the gas temperature before it entered the inner cylinder to pass through the coal cage. The temperature was monitored by two K-type thermocouples, one placed 20 mm above the cage top for input gas (T1), and one at the middle of the cage (T2). Due to the very low flow rate of gas, the gas temperature at T1 and its heating rate monitored above the cage was accurately coupled to the temperature controller of the electric heater. After testing different values, the heating rate was fixed to 0.5±0.025 °C/min, which was found appropriate considering the test duration and the response of coals. Note that the heating rate of 0.5 °C/min required about six hours if the final temperature was 200 °C.

The effect of O₂ flow rates between 50-200 ml/min was evaluated for selected coals. The ranges of particle size tested were 0.1-0.5 mm, 0.5-1.0 mm, 0.1-1.0 mm, 1.0-2.8 mm, and 2.8-5.0 mm for the selected coals. These ranges represented the finer fraction of raw coals after crushing, prior to pulverization. After pulverization, the average particle size becomes 50-55 μm with a mass fraction for <75 μm of 80%. Despite the small particle size, self-heating is rarely a concern for pulverized coal, since convective cooling by transport air (typically about 80 °C) becomes dominant. After examining the effect of particle size, the final size range of 0.1-1.0 mm was selected for comparison between coals. The repeatability of the results was also assessed for key test conditions and coals. It was found to be satisfactory with deviations of ±0.2 °C for CPT and ±0.02 °C/min for the slope at CPT, when repeated for identical samples (prepared together) and tested within a day.

Fig. 2 shows an example of the temperatures measured at T1

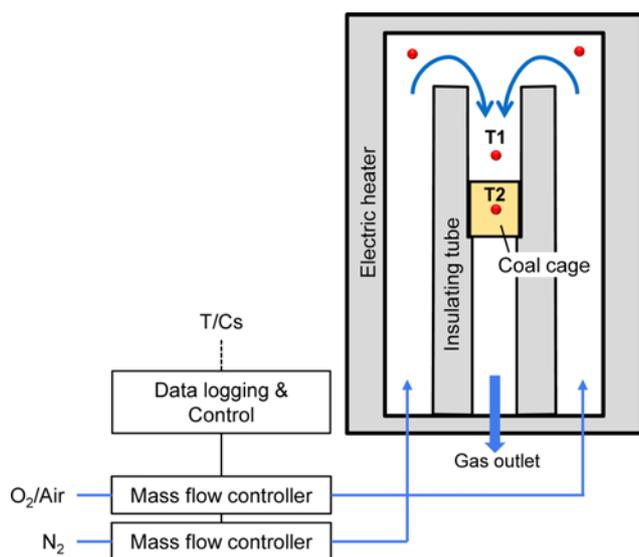


Fig. 1. Schematic of the reactor for coal self-heating test.

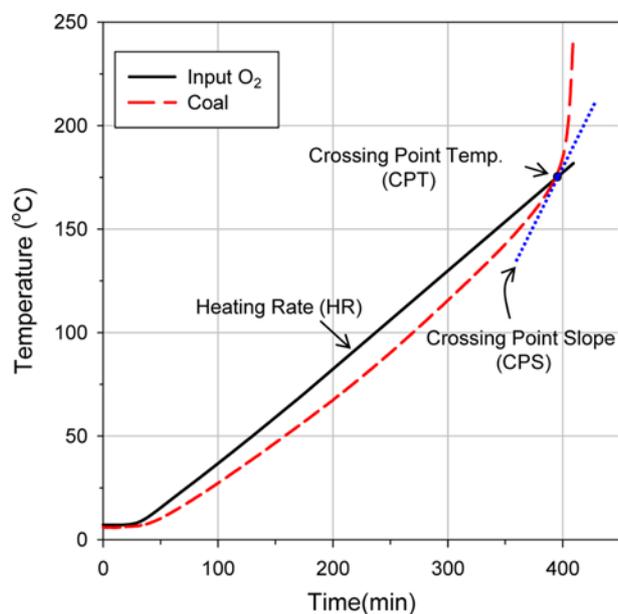


Fig. 2. Profiles of temperature increase for coal M at an O₂ flow rate of 100 ml/min.

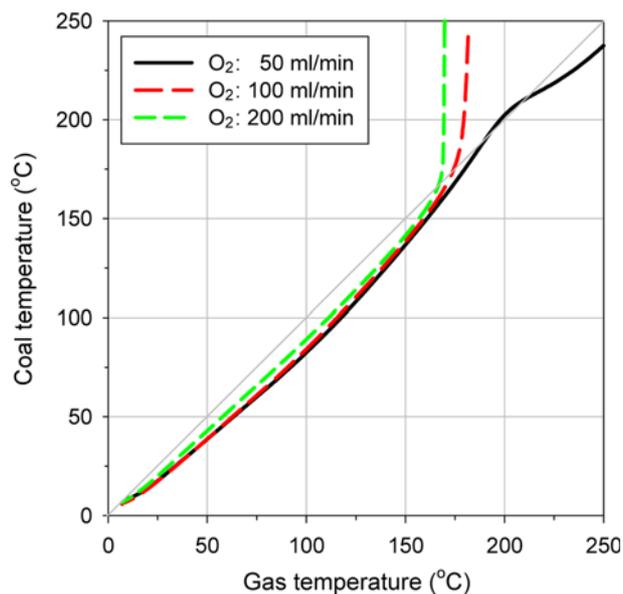


Fig. 3. Coal temperature vs. input gas temperature at various O_2 flow rates.

and T2 for coal M. While the O_2 temperature increased at the controlled gas heating rate (GHR) of $0.5\text{ }^\circ\text{C}/\text{min}$, the increase in coal temperature at the early stage was delayed by the thermal mass of the sample. As the coal temperature became above $100\text{ }^\circ\text{C}$, it started to accelerate by endothermic reactions and eventually surpassed the input gas temperature. This value was defined as the CPT, which is a direct indicator for low temperature reactivity. In addition, the slope at the CPT (crossing point slope, CPS) had an important meaning as the rate of temperature increased, influenced by the reactivity around the CPT, the heating value of reactive compounds, and the specific heat of coal.

RESULTS AND DISCUSSION

1. Effect of Test Parameters

Fig. 3 shows the comparison of coal temperatures measured for different O_2 flow rates for coal M. For a flow rate of $50\text{ ml}/\text{min}$, the trend of temperature above the gas temperature around the CPT was not clear, especially for low reactivity coals. This was due to an insufficient amount of oxygen available for reaction, compared to the continuous increase of the gas temperature. When the O_2 flow rate was increased to $200\text{ ml}/\text{min}$, the reactions became rapid with differences in CPT between coals of $12\text{ }^\circ\text{C}$. For better differentiation of the CPT between coals, the O_2 flow rate was fixed to $100\text{ ml}/\text{min}$. The results also imply that the convective heat loss was minor within the flow rates.

Table 2 shows the effect of particle size for two selected coals. For both coals, larger particle sizes led to higher CPT and lower CPS. For example, coal FI had a CPS of $1.055\text{ }^\circ\text{C}/\text{min}$ at a CPT of $172.1\text{ }^\circ\text{C}$ for $0.1\text{--}0.5\text{ mm}$ particles, while the CPS decreased to $0.784\text{ }^\circ\text{C}/\text{min}$ at a CPT of $202.5\text{ }^\circ\text{C}$ for $2.8\text{--}5.0\text{ mm}$ particles. This was due to the reduced surface area per mass of coal particles. While the convective heat loss was not significant at this low gas flow rate, the increased surface area contributed to accelerating the oxida-

Table 2. CPT and CPS measured for different particle sizes of selected coals

Particle size (mm)	Coal FI		Coal Ki	
	CPT ($^\circ\text{C}$)	CPS ($^\circ\text{C}/\text{min}$)	CPT ($^\circ\text{C}$)	CPS ($^\circ\text{C}/\text{min}$)
0.1-0.5	172.1	1.055	174.4	1.305
0.5-1.0	176.9	0.929	184.9	1.024
1.0-2.8	193.0	0.828	187.3	0.901
2.8-5.0	202.5	0.784	190.4	0.715
0.1-1.0	173.8	0.975	182.8	1.228

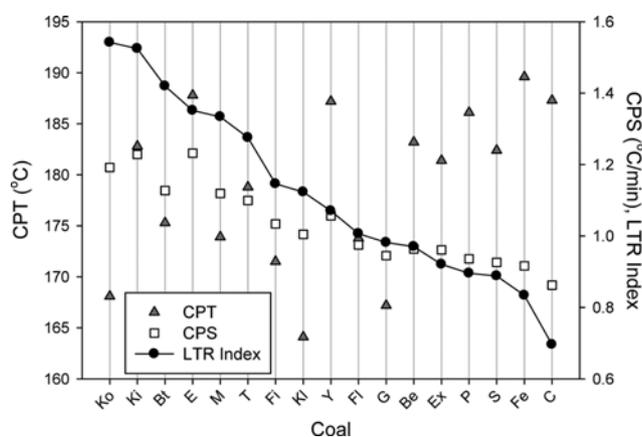


Fig. 4. CPT, CPS, and LTR index acquired for tested coals.

tion reactions. The particles with a size range of $0.1\text{--}1.0\text{ mm}$ had both CPT and CPS values between those of $0.1\text{--}0.5\text{ mm}$ and $0.5\text{--}1.0\text{ mm}$ particles, which was used for comparison between coals.

2. Self-heating Propensity of Coals

Fig. 4 shows the measured data of CPT, CPS, and the LTR index derived for all coal samples. CPT ranged between $168\text{--}190\text{ }^\circ\text{C}$ while CPS was $0.862\text{--}1.228\text{ }^\circ\text{C}/\text{min}$. Lower values of CPT and higher values of CPS imply higher reactivity of coal at low temperatures. However, the two parameters are not directly inter-related between coals. For example, coal E had a CPT of $187.8\text{ }^\circ\text{C}$ (the second highest) with a CPS of $1.232\text{ }^\circ\text{C}/\text{min}$ (the highest). In contrast, coal KI had the lowest CPT while its CPS was not particularly high ($1.005\text{ }^\circ\text{C}/\text{min}$). Consequently, a review of how the parameters are correctly interpreted was required. CPT represents the integrated effect of the starting temperature of early oxidation reactions and the accumulated heat up to the point (in time) where the input gas temperature is surpassed. Comparing the values of CPT with the coal properties, however, no clear relationship was identified as shown in Fig. 5 for the moisture content. One of the reasons could be that the history of the coals during mining, transport, and storage was not known, and these factors contribute to the time exposed to oxygen and the loss of reactivity, especially in very reactive functional groups. The diverse sources of origin for the coal samples could be another reason. As shown in Table 2, however, a clear relationship was identified for CPT with the particle size for a single coal. For the coals from the same seams, the self-heating propensity was well correlated with coal properties in the literature [13,14].

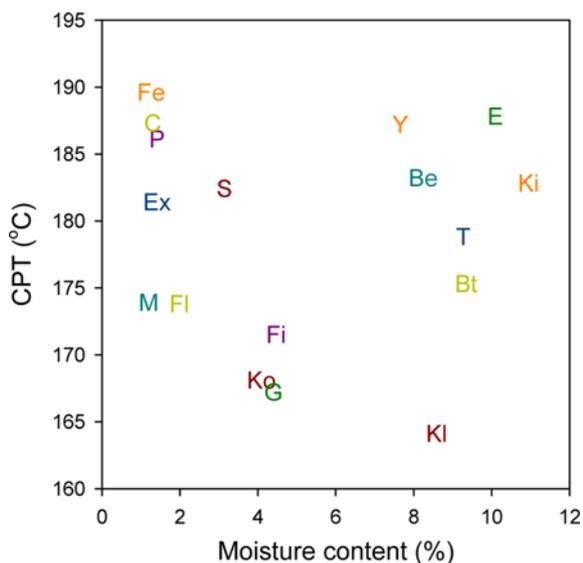


Fig. 5. Comparison of moisture content and CPT.

In contrast, CPS can be considered more meaningful since it reflects the key properties of coal that influence the oxidation rate

and temperature increase. As shown in the mass balance equation below, CPS (dT/dt , $^{\circ}C/min$) can be considered as the product of the reaction rate (\dot{m}_r , kg/min), the enthalpy of reaction (Δh_r , J/kg) divided by the specific heat of coal (C_p , $J/kg/^{\circ}C$) and the mass of coal (m_{coal} , kg) when the oxygen temperature becomes identical to that of coal.

$$m_{coal}C_p \frac{dT}{dt} = \Delta h_r \dot{m}_r$$

Therefore, a new parameter, the low temperature reactivity (LTR) index, was introduced to incorporate both indicators, as follows:

$$LTR\ Index = 2 \frac{(CPS - GHR)}{CPT/180}$$

Here, (CPS - GHR) represents the net rate of temperature increase ($^{\circ}C/min$) by reactions of coal. In this way, the effect of experimental error in the control of GHR can be also minimized. This rate was divided by the relative temperature of CPT ($^{\circ}C$), normalized by the typical value of $180^{\circ}C$. Therefore, the LTR index may represent a relative time leading to spontaneous combustion for easy comparison between coals. It was finally multiplied by 2, which was only intended to adjust the LTR index values to around 1.0

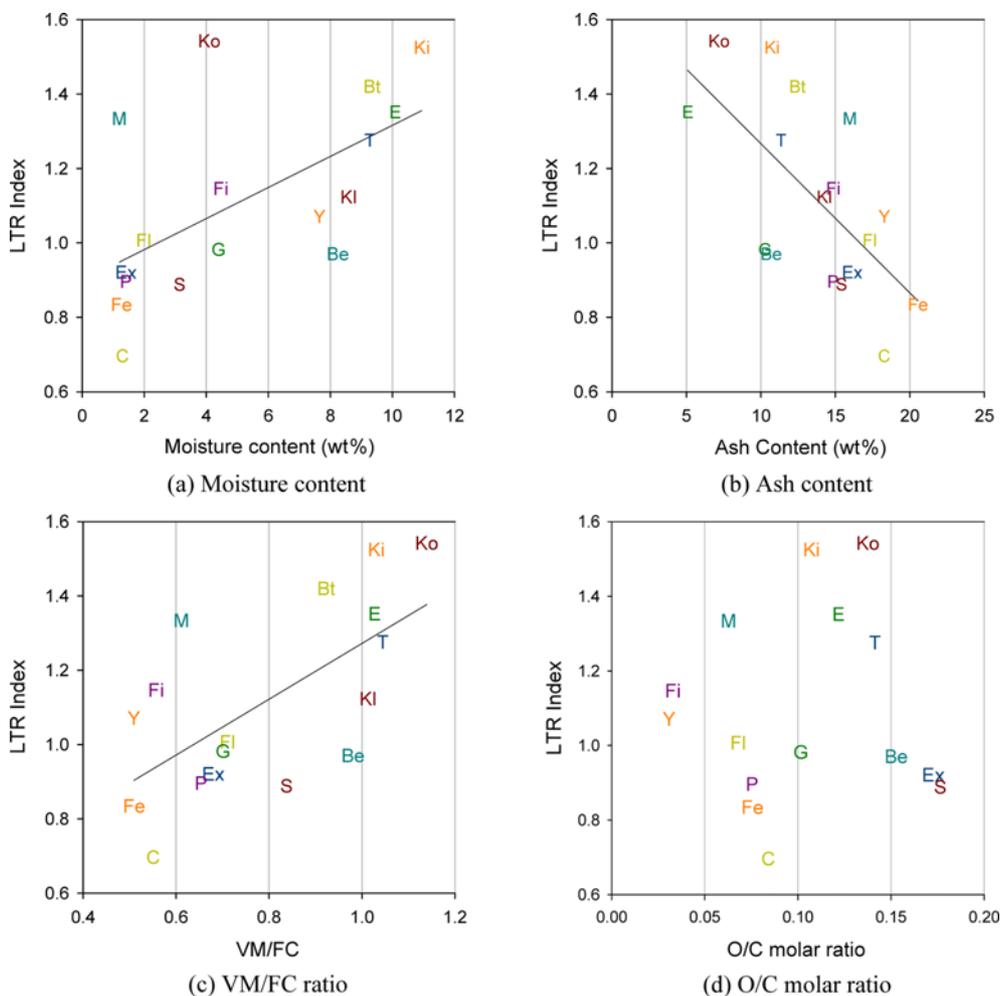


Fig. 6. Comparison of the LTR index with fuel properties from the proximate analyses and O/C ratio.

for easy comparison. Note that the resultant values ranged from 0.7 to 1.5. The higher values of the LTR index indicate reactive coals, and vice versa. The index can be used for power plant operators to identify particular coals that may require a higher level of caution and frequent monitoring during the storage and size-reduction processes.

When converted into the LTR index, CPS has more influence than CPT as shown in Fig. 4. Note that the coals are arranged in order of the LTR index in the Figure, which was more correlated to CPS. This is because the relative differences of CPS between coals were larger than those of CPT.

As a result, the coals had LTR index values ranging from 1.542 (coal Ko) to 0.696 (coal C). The diverse values of the LTR index between coals indicate that the proposed test method could be helpful in evaluating the self-heating propensity for various coals with about six hours of test duration. Unlike other coals, coal Ko is a special sample of coal prepared by fry-drying (immersed in oil at $\sim 150^\circ\text{C}$) coal Ki. Since the original coal also had the second largest value (1.525) for the LTR index, the result may mean that fry-drying would not lower the self-heating propensity. However, the result was not conclusive. Further investigations on the effect of fry-drying are required with various samples.

3. Relationship with Coal Properties

Fig. 6 shows the relationship of the LTR index with coal properties acquired from the following proximate analyses: moisture content, ash content, and the VM/FC ratio. The inherent moisture content was overall proportional to the LTR index (Fig. 6(a)). The inherent moisture content indicates the degree of microscopic surface area adsorbing the water molecule, and then oxygen, after evaporation [24]. Although a high moisture content may require more heat for evaporation, the effect of increased surface area was dominant on the overall result. Two coals, Ko and M, had large deviations from the trend. As mentioned earlier, coal Ko was an exceptional sample. Fry-drying is known to effectively reduce the moisture content of coal. Its original coal (Ki) had the highest moisture content and the second largest LTR index value. Coal M was well known at the power plant to have a high propensity of spontaneous combustion, even though it was not a low rank coal. This means that other mechanisms became important for some coals.

As shown in Fig. 6(b), the LTR index was inversely proportional to the ash content. In general, higher ash content results in a reduced amount of combustible compounds and a larger capacity to consume the heat release from oxidation. However, the variation in the LTR index for the same ash content was as large as 0.55. Therefore, the ash content could not be related with the LTR index for all coals.

As shown in Fig. 6(c), the LTR index was overall proportional to the VM/FC ratio, which is considered as the main indicator for the rank of coal. VM represents the fraction of combustible matter released into vapor by thermal decomposition of weak chemical bonds. The coalification process slowly removes such fractions, leaving behind more carbon-rich fractions that often consist of the least reactive aromatic carbon chains. Consequently, a coal with a higher VM content is likely to contain more reactive functional groups such as aliphatic groups. However, individual coals in the present study had significant deviations from the trend line, as large as 0.4 (coal M). Since the three properties are largely independent

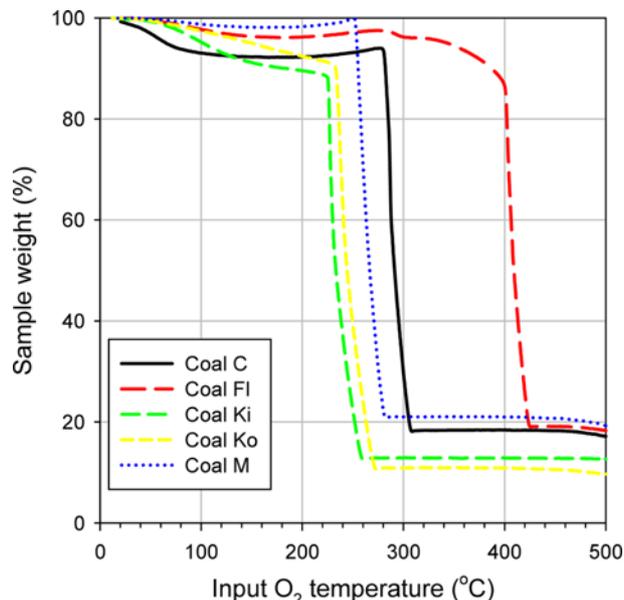


Fig. 7. Profiles of sample weight from TGA tests of selected coals.

of each other, their relationship with the LTR index illustrates the complex nature of self-heating. The same analysis was performed for O/C and H/C ratios, but no relationship was identifiable, as shown in Fig. 6(d).

Fig. 7 illustrates the changes in the sample weight during TGA tests for the selected coals. In terms of the reaction condition, the TGA test and the self-heating test had a common feature: supply of O_2 with temperature controlled by a fixed heating rate. Therefore, the low temperature reactions of coal observed in the self-heating test also took place in TGA. This can be identified in the TGA curves. For example, the sample weight slightly increased by adsorption of O_2 before ignition for coal Fi by 2 wt% at about 260°C . Such increases were observed in nine coals, with peaks mostly ranging between $254\text{--}286^\circ\text{C}$. In addition, a slow decrease in the weight by ongoing reactions was observed in most coals before the rapid decrease by ignition. The weight loss before ignition was up to 10.9 wt% (coal Fi), whereas some coals such as coals C and M did not have a noticeable loss.

However, the TGA revealed a huge difference in terms of heat accumulation and diffusion, compared to the self-heating test. The sample in TGA was about 7 mg and, therefore, did not have enough thermal mass to accumulate the heat. Instead, the heat released by exothermic reactions was transferred to the metal crucible holding the sample and then to the ambient gas. The high thermal conductivity of the material (typically platinum) was one of the essential requirements of TGA to quickly reach a thermal equilibrium with the gas. This thermal equilibrium lasted until the temperature of the sample became high enough for rapid release of the volatiles (tar, CO , CO_2 , H_2 , H_2O and hydrocarbons) and their ignition. Due to the ignition, the actual temperature of the coal sample would be much higher than the input gas above T_{igr} . In contrast, the self-heating test was intended to accumulate the heat released from low temperature reactions within the sample since the gas flows through the cage. The heat loss to the insulating tube was also minimized

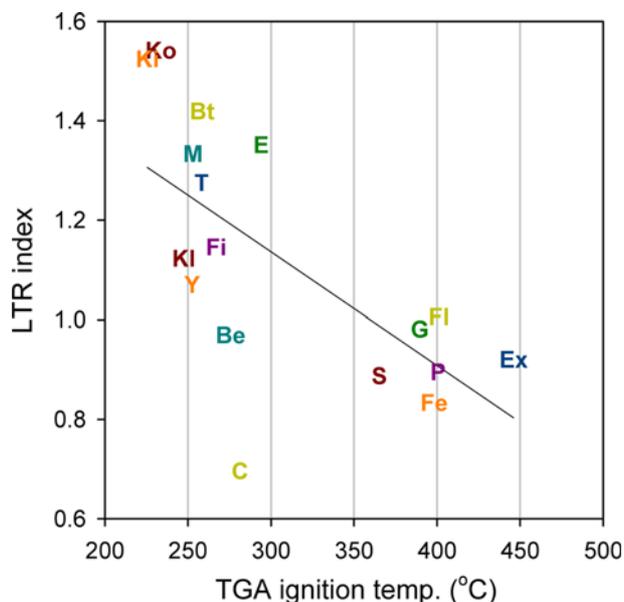


Fig. 8. LTR index vs. ignition temperature measured by TGA.

by the reduced surface area to volume ratio of the sample. In this way, the test could capture the low temperature reactivity of coal as can be found from the values of CPT ranging from 164 °C to 190 °C.

Fig. 8 compares the LTR index with T_{igi} measured from the TGA test. The LTR index was inversely proportional to the ignition temperature for most coals. This confirms that a coal with a low T_{igi} is more prone to spontaneous combustion. For example, coals Ki and Ko both scored high on the LTR index and exhibited the lowest T_{igi} of 225.5 and 233.6 °C, respectively. Interestingly, Coal M (T_{igi} of 253.0 °C) lay well within this trend, but not with the proximate analyses in Fig. 6. This suggests that coal M contained more reactive functional groups, which cannot be predicted by the results of proximate analyses. Conversely, coal C had a relatively low T_{igi} (281.3 °C) although the LTR index was the lowest, which deviated the most from the overall trend.

CONCLUSIONS

The low temperature reactivities of coals with various sources of origin were evaluated for their susceptibility to spontaneous combustion. They were quantified using a fixed bed of coal particles ranging between 0.1-1.0 mm exposed to an oxygen flow of 100 ml/min with temperature increasing linearly at 0.5 °C/min. The CPT of the test coals ranged between 168-190 °C, but did not have a meaningful relationship with basic coal properties. Based on CPT and CPS, a new index for self-heating propensity, the LTR index, was proposed. When tested against 17 coals collected from a power plant, meaningful relationships were observed between the LTR index and coal properties. Overall, the LTR index was proportional to the moisture content and VM/FC ratio, and inversely proportional to the ash content and ignition temperature. T_{ig} measured by thermogravimetric tests, also exhibited a positive relationship with the LTR index. However, no single property of coal was directly correlated with the low temperature reactivity for all coals tested, illus-

trating the complex mechanisms involved. The experimental method and the LTR index derived would be helpful in promptly evaluating and identifying particular coals that require careful monitoring during the storage and size-reduction processes in a power plant. Further investigations are required to link the index to the propensity of differently ranked coals for spontaneous combustion.

ACKNOWLEDGEMENTS

This work was supported by the Power Generation & Electricity Delivery Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant, funded by the Korea Government Ministry of Trade, Industry, and Energy (No. 2011101010004B). Thanks are also due to Mr. Sanghyun Park, Mr. Minsoo Kim, Mr. Jinje Park and Mr. Gyuseon Song (Sungkyunkwan University) for their technical assistance.

REFERENCES

1. International Energy Agency (IEA), *Key world energy statistics* (2012).
2. Korea Energy Economics Institute, *Yearbook of energy statistics 2012*. Ministry of Knowledge Economy, Uiwang, Korea (2012).
3. N. S. Dong, *Utilisation of low rank coals*, CCC/182, IEA Clean Coal Center (2011).
4. C. Moon, Y. Sung, S. Ahn, T. Kim, G. Choi and D. Kim, *Appl. Thermal Eng.*, **54**, 111 (2013).
5. A. M. Carpenter, *Coal quality assessment - the validity of empirical tests*, IEA CCC/63. IEA Clean Coal Centre (2002).
6. H. Nalbandian, *Propensity of coal to self-heat*, CCC/172, IEA Clean Coal Center (2010).
7. J. N. Carras and B. C. Young, *Prog. Energy Combust. Sci.*, **20**, 1 (1994).
8. Q. Xuyao, D. Wang, X. Zhong, J. Gu and X. Tao, *Mining Sci. Technol.*, **20**, 0372 (2010).
9. H. Wang, B. Z. Dlugogorski and E. M. Kennedy, *Prog. Energy Combust. Sci.*, **29**, 487 (2003).
10. J. D. Mao, A. Schimmelmann, M. Mastalerz, P. G. Hatcher and Y. Li, *Energy Fuel*, **24**, 2536 (2010).
11. W. Jo, H. Choi, S. Kim, J. Yoo, D. Chun, Y. Rhim, J. Lim and S. Lee, *Korean J. Chem. Eng.*, **30**, 1034 (2013).
12. G. Dou, H. Xin, D. Wang, B. Qin and X. Zhong, *Korean J. Chem. Eng.*, **31**, 801 (2014).
13. B. B. Beamish, *Int. J. Coal. Geology*, **64**, 139 (2005).
14. B. B. Beamish and A. Arisoy, *Effect of intrinsic coal properties on self-heating rates*, 12th U.S./North American Mine Ventilation Symposium, 149-153 (2008).
15. G. B. Stracher, *Geology of Coal Fires: Case Studies from Around the World*, The Geological Society of America, 2007, Boulder, Colorado, USA.
16. F. Arkun and R. H. Essenhigh, *Fuel*, **80**, 409 (2001).
17. C. J. Kim and C. H. Sohn, *Fuel Process. Technol.*, **100**, 73 (2012).
18. R. Sen, S. K. Srivastava and M. M. Singh, *Indian J. Chem. Technol.*, **16**, 103 (2009).
19. Q. Xuyao, D. Wang, J. A. Milke and X. Zhong, *Mining Sci. Technol.*, **21**, 255 (2011).

20. J. García-Torrent, Á. Ramírez-Gómez, E. Querol-Aragón, C. Grima-Olmedo and L. Medic-Pejic, *J. Hazard. Mater.*, **213-214**, 230 (2012).
21. B. B. Beamish, M. A. Barakat and J. D. St George, *Thermochim. Acta*, **362**, 1 (2000).
22. B. B. Beamish, *Int. J. Coal. Geology*, **64**, 139 (2005).
23. T.-I. Ohm, J.-S. Chae, J.-H. Lim and S.-H. Moon, *J. Mech. Sci. Technol.*, **26**, 1299 (2012).
24. A. H. Clemens and T. W. Matheson, *Fuel*, **75**, 891 (1996).

Supporting Information

Low-temperature reactivity of coals for evaluation of spontaneous combustion propensity

Jungsoo Kim^{*,‡}, Yongwoon Lee^{*,‡}, Changkook Ryu^{*,†}, Ho Young Park^{**}, and Hyunsoo Lim^{**}

^{*}School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

^{**}Fuel and Combustion Group, KEPSCO Research Institute, Daejeon 305-380, Korea

(Received 26 June 2014 • accepted 9 November 2014)

Table S1. Fuel properties of tested coals

Coal	Be	Bt	C	En	Ex	Fe	Fi	Fl	G	Kl	Ki	Ko	M	P	S	T	Y	
Country of origin	IND	US	AU	AU	AU	AU	IND	IND	AU	IND	IND	IND	AU	AU	RU	IND	KOR	
Proximate analysis (wt%ad)	IM ^a	8.24	9.34	1.30	10.09	1.41	1.26	4.47	1.98	4.39	8.58	10.94	4.09	1.20	1.41	3.14	9.27	7.65
	VM ^b	40.14	37.53	28.55	42.98	33.37	26.41	28.86	33.52	35.16	38.82	39.77	47.25	31.43	33.10	37.13	40.55	25.00
	FC [*]	40.93	40.69	51.87	41.85	49.11	51.80	51.82	47.20	50.17	38.35	38.59	41.48	51.40	50.66	44.33	38.82	49.06
	Ash	10.69	12.44	18.28	5.08	16.12	20.53	14.85	17.30	10.27	14.25	10.74	7.18	15.97	14.83	15.40	11.36	18.29
	VM/FC	0.98	0.92	0.55	1.03	0.68	0.51	0.56	0.71	0.70	1.01	1.03	1.14	0.61	0.65	0.84	1.04	0.51
Ultimate analysis (wt%ad)	C	60.41	57.69	65.47	67.33	62.50	64.09	70.95	66.93	68.79	50.20	64.63	69.80	68.90	68.31	61.94	59.50	67.23
	H	4.08	3.16	3.92	4.32	3.94	3.94	4.69	4.40	5.06	4.09	3.10	4.79	3.91	4.34	4.02	3.84	2.49
	O [*]	12.30	15.53	7.34	10.93	14.37	6.46	3.10	6.05	9.31	21.56	9.24	12.79	5.76	6.86	14.57	11.21	2.77
	N	2.84	1.09	3.49	2.23	1.66	3.39	1.94	3.22	2.17	1.32	1.04	0.98	3.90	4.13	0.78	4.17	0.83
	S	1.44	0.75	0.20	0.02	0.00	0.33	0.00	0.12	0.00	0.00	0.35	0.37	0.36	0.12	0.15	0.65	0.74
HHV (MJ/kg)	25.46	21.98	26.67	27.06	24.24	26.51	30.22	28.01	28.90	18.99	21.60	27.17	28.25	28.25	24.27	24.26	26.54	
Ash composition (wt%)	SiO ₂	56.18	58.07	67.57	53.77	48.76	65.16	54.19	69.63	50.08	57.86	56.16	58.67	75.78	63.83	60.56	60.93	44.48
	Al ₂ O ₃	19.47	19.11	25.10	10.80	25.65	22.35	25.06	20.39	23.25	25.01	16.14	10.56	18.78	23.63	27.48	16.16	22.18
	CaO	3.03	1.81	0.35	11.59	11.44	0.71	6.08	0.96	10.99	2.30	5.31	7.15	0.20	1.74	3.18	4.00	9.19
	Fe ₂ O ₃	9.02	15.99	2.02	10.15	7.77	6.11	7.81	3.51	6.61	9.67	15.10	16.74	1.72	4.64	3.47	10.41	18.73
	K ₂ O	2.10	1.42	2.35	1.17	2.00	2.10	1.67	2.06	1.52	2.02	2.32	1.72	0.37	1.55	0.93	1.27	2.60
	MgO	1.82	1.10	0.29	3.33	1.04	1.16	1.64	0.60	3.83	2.17	3.22	3.73	0.11	0.97	0.72	1.94	1.05
	Na ₂ O	6.20	0.62	0.84	6.36	0.72	0.40	1.58	1.20	0.98	0.50	0.54	0.49	1.29	1.99	1.41	3.64	0.60
	MnO	0.03	0.10	0.03	0.05	0.12	0.07	0.20	0.02	0.10	0.07	0.16	0.22	0.01	0.04	0.02	0.11	0.16
	P ₂ O ₅	1.12	0.89	0.53	1.30	1.01	0.96	0.39	0.57	0.92	0.21	0.20	0.20	0.84	0.57	0.94	0.75	0.26
	BaO	0.10	0.06	0.05	0.26	0.09	0.18	0.07	0.05	0.21	0.09	0.20	0.08	0.01	0.04	0.13	0.11	0.14
	SrO	0.11	0.05	0.07	0.28	0.08	0.09	0.08	0.04	0.20	0.07	0.06	0.04	0.01	0.07	0.17	0.07	0.09
	TiO ₂	0.82	0.77	0.80	0.93	1.33	0.70	1.23	0.98	1.30	0.05	0.59	0.40	0.86	0.94	0.99	0.60	0.51