Evaluation of A TGA Method to Predict the Ignition Temperature and Spontaneous Combustion Propensity of Coals of Different Rank

M. van Graan and J.R. Bunt

Abstract**—** Spontaneous combustion of coal is a global problem that plagues the industry. It not only poses a safety risk, which can be life threating in extreme cases, but also has a large environmental and economic impact. The tests commonly used to predict the spontaneous combustion of coal are either time consuming or not reliable enough to satisfy the industry's needs and thus research continues in this focus area. The low temperature oxidation of coal is commonly accepted as the main cause of spontaneous combustion. A method, based on low temperature oxidation, using a thermogravimetric analyzer (TGA) as a tool to predict the spontaneous combustion propensity of coal has recently been suggested. This method is a relatively simple and quick method, if proven repeatable enough. In this study the accuracy of this method was tested on five different coal samples of different rank, i.e. anthracite, bituminous, sub-bituminous, lignite and a blend of sub-bituminous and lignite coals. Small samples (< 30mg) of fine coal (<212µm) were reacted with air in a TGA/DSC at five different heating rates (3°C, 5°C, 7°C, 10°C and 20°C per minute). The TGA was used to measure the mass change of the coal as a function of temperature and time. The thermograms depicting mass as a function of temperature were used to predict the ignition temperature of each coal. The first derivative of mass as a function of time for the region where oxygen sorption takes place, prior to combustion, was used to calculate a spontaneous combustion index. This index was used to classify the coals according to their spontaneous combustion propensity. For comparison, a modification of the more conventional Smith-Glasser oxidation test was used to compare the oxygen sorption per mass of coal to the findings obtained from the TGA analysis. The TGA method showed excellent repeatability and there was no variation in results with initial weight. The TGA method has not been evaluated for known high risk coals and caution should be used for lower rank coals. The modified Smith –Glasser method showed a lower repeatability, but overall both of the tests followed the same trend. It is suggested that the TGA method can prudently be used to replace the current methods for higher rank coals.

Index Terms**—** Coal, Low temperature oxidation, Thermogravimetric analysis, Spontaneous combustion

I. Introduction

Globally coal is considered the most important non-renewable fossil energy source [1]. Even with the increasing emphasis on renewable energy, predictions still indicate that the use of coal will only increase and will remain the primary energy source for the foreseeable future [2]. The mining and storage of coal however poses a significant risk in the form of spontaneous combustion. Globally the industry is plagued by incidents of spontaneous combustion [3]. The spontaneous combustion of coal not only poses the obvious safety risk, but also has a negative impact on the environment, in the form of greenhouse gas emissions, and a negative economic impact due to loss of resources [4]. Spontaneous combustion is the result of a thermal runaway reaction in which the coal reacts with oxygen in air and produces heat. If this heat accumulates it can eventually result in the spontaneous ignition of coal [3] [5] [6]. There are several factors that influence the propensity of a coal to spontaneously combust. These factors can be represented by two main categories 1) intrinsic factors i.e. moisture content, mineral content, coal rank, porosity and density, volatile matter and particle size and; 2) extrinsic factors, i.e. temperature, oxygen concentration at particle surfaces and atmospheric moisture [7] [8] [9] [10] [11]. Although all of these factors contribute, it is widely accepted that the main cause of spontaneous combustion is the low temperature oxidation of coal [6] [7] [8] [10]. Smith and Glasser [12] proved this in their experiments aimed at determining the factor that has the largest influence on spontaneous combustion in development of a better method to determine spontaneous combustion propensity. The test developed by Smith and Glasser [12] is very accurate, but it is very lengthy and has no predictable endpoint. Many of the same intrinsic properties that influence the spontaneous combustion of coal also influence the ignition temperature [13] [14]. The ignition temperature is used in many of the other tests and thus contains useful information. There are various other tests available to determine the spontaneous combustion propensity of coal, these methods however all have major drawbacks amongst which complexity, lengthy experiments or methods not being comprehensive enough are the most common. The tests used in industry include, crossing point temperature, differential thermal analysis, Wits - EHAC index and the Olpinski index, to name a few [3] [15]. The industry has the need for a simple, quick and extensive test. Avila [16] developed a method using a thermogravimetric analyzer (TGA) to fill this void in industry. This method has however not been extensively tested and inaccurate testing can prove fatal. The focus of this study is to test the accuracy of this method against a modified version of the Smith-Glasser oxidation test.

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II. METHODOLOGY

A. Sample preparation and characterization

Five coal samples of different rank (labelled A-E) were procured from different parts of the world and the particle size was reduced to below 212µm. The samples were stored in an argon environment at a temperature below 8°C until use.

The coals were characterized by means of proximate (ACT-TPM-010, ACT-TPM-011, ACT-TPM-012, ACT-TPM-014) and ultimate analysis (based on ISO 12902) to obtain the intrinsic properties. Results on a moisture and mineral matter free basis were used to classify the coals samples according to rank.

B. TGA method

The TGA method was based on the method developed by [16]. Samples of 30 mg of each coal was reacted with air at a flow rate of 150ml/min in a TGA/DSC 1 STAR at five different heating rates i.e. 3, 5, 7, 10 and 20°C/min. Each sample was heated from the starting temperature of c.a. 30°C at the appropriate heating rate to 750°C, thereafter the temperature was kept constant for 10 min. The TGA was then water cooled to room temperature. This specific TGA is fully automated and can run 34 samples consecutively; one of the available carousels is used as a blank and the mass of the empty pan is automatically subtracted from each sample to minimize external effects. To ensure the quality of the results 60% of the experiments were repeated. Two additional samples of coal C of 10 and 50mg were also run at a heating rate of 7°C/min to prove that the experiment is independent of initial mass.

The mass loss as a function of both temperature and time was recorded. The normalized mass as a function of temperature was used to determine the ignition temperature [18]. The first derivative of the normalized mass as function of time was used to determine the spontaneous combustion index (TG_{spc}).

C. Modified Smith-Glasser oxidation test

The method used for the modified Smith-Glasser test was based on the test developed by [12] and further adapted by [17]. The adaption discards the use of expensive equipment and significantly reduces the experimental time. The setup used for the test can be seen in Fig. 1. 10mg of each coal sample was placed in an Erlenmeyer flask and the joins sealed with petroleum jelly to ensure that the coal is in an isolated environment. This setup along with a blank setup was placed in a water bath, with a closable lid, at a temperature of 40°C for 48hr. Oxygen sorption takes place and the volume change in oil is equal to the volume of oil absorbed by the coal. This value is then related back to the mole oxygen absorbed per gram of coal. The volume of oil change determined from the blank flask is subtracted from the volume change of oil of the sample to account for any atmospheric fluctuations.

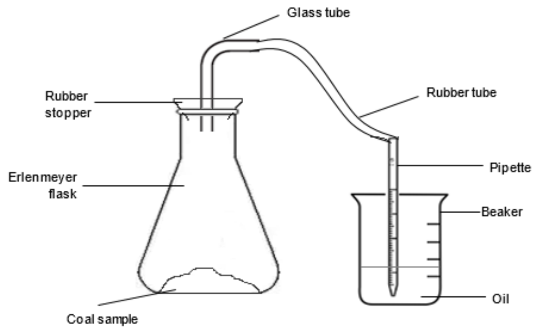

Fig. 1: Setup for the modified Smith-Glasser oxidation test

TABLE I
PROXIMATE AND ULTIMATE ANALYSIS RESULTS

Analysis	Basis	Coal A	Coal B	Coal C	Coal D	Coal E
Proximate analysis						
wt.% Inherent moisture content	ad	1.5	8.6	30.1	13.6	5.2
wt.% Ash yield	ad	11.2	15.4	6.6	12.3	27.9
wt.% Volatile Matter	ad	10.8	26.8	29.4	27.7	24.5
wt.% Fixed carbon (by difference)	ad	76.5	49.3	33.9	46.4	42.4
Gross Calorific value (MJ/kg)	ad	30.5	23.4	17.1	21.7	20.0
wt.% Volatile Matter	m.m.f.b	12.4	35.2	46.5	37.4	36.6
wt.% Fixed carbon (by difference)	m.m.f.b	87.6	64.8	53.6	62.6	63.4
Calorific value (MJ/kg)	m.m.f.b	34.0	27.9	18.3	25.0	28.2
Ultimate analyses (air dried)						
wt.% Carbon Content	ad	76.6	59.0	42.1	55.8	50.4
wt.% Hydrogen Content	ad	3.3	3.4	3.0	3.2	2.8
wt.% Nitrogen Content	ad	2.3	1.0	0.7	0.6	1.3
wt.% Oxygen Content (by difference)	ad	3.2	12.0	16.9	14.4	11.3
wt.% Total sulphur	ad	1.9	0.7	0.6	0.3	1.1

TABLE II
COAL RANK CLASSIFICATION

Coal sample	Rank
Coal A	Semi-anthracite
Coal B	High-volatile B bituminous
Coal C	Lignite A
Coal D	Blend (unknown mixture of bituminous and lignite) Acting as sub-bituminous A
Coal E	High-volatile B bituminous

I. RESULTS AND DISCUSSION

A. Characterization and classification

TABLE I shows the proximate and ultimate analysis results obtained for the 5 coals. The rank classification of the 5 coals is depicted in TABLE II.

B. TGA experiments

Fig. 2 shows a mass loss thermogram (as example) for Coal C at a temperature ramp of 7°C/min. It can be observed that the TGA experiments were highly repeatable, i.e. the starting mass has no effect on the normalized data from the TGA, and thus does not influence the experiment. The ignition temperatures of the coal samples were determined as depicted in Fig. 3 and the ignition temperatures determined for all of the coals are depicted in Fig. 4. It was found that the ignition temperatures had a maximum error of 7°C between repeat samples. The ignition temperature of the coal decreases with coal rank as expected. For the heating rate range of 3°C/min-10°C/min, the ignition temperature increases with an increase in heating rate. This increase in observed ignition temperature can possibly be attributed to a slight increase in heat transfer limitations at higher heating rates [14].

Spontaneous combustion index (TG_{spc}) in equation 1 is defined as the following by [16]:

$$TG_{spc} = \frac{\Delta weight\ loss\ rate}{\Delta Temperature}\ (wt\ \%\ °C^{-1}\ min^{-1}) \tag{1}$$

To calculate the TG_{spc} index, (using coal A as an example) the slopes of the initial increase in the first derivative mass with respect to time at the different heating rates are obtained as depicted in **Error! Reference source not found.**. These slopes are then plotted against the respective heating rates and a linear trend line is drawn (example shown in Fig. 5). The trend line's slope, Fig. 6, is then known as the TG_{spc} value. Even though coal samples C and D did not show an increase in mass due to oxygen absorption, the first derivative curve showed an increasing slope and the TG_{spc} value could still be calculated. The TG_{spc} results obtained together with their spontaneous combustion propensity categories as defined by [16] for all 5 coals are depicted in TABLE. The maximum error determined was 1%, so it shows extremely good repeatability.

None of the coal samples evaluated in this study are linked to spontaneous combustion incidents, so the classification of the coals' relative propensity to spontaneously combust at low temperature is considered to be low. The findings obtained from this work are thus in agreement with this postulate.

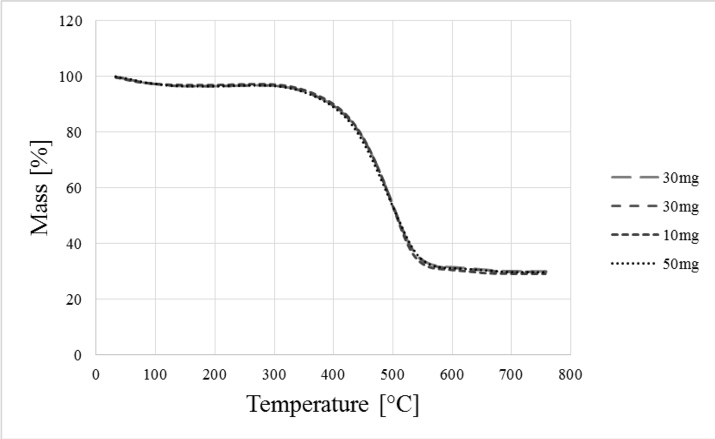

Fig. 2: Coal C at a temperature ramp of 7°C/min repeatability

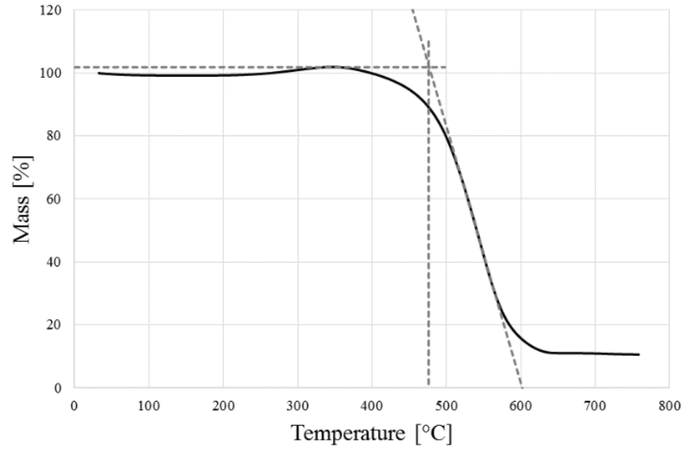

Fig. 3: Method used to determine the coal sample's ignition point

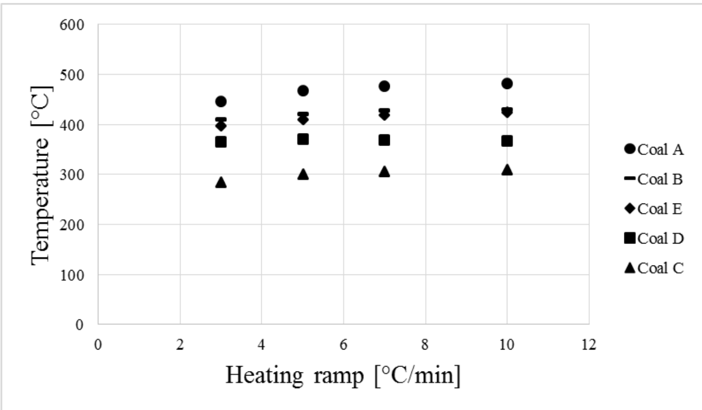

Fig. 4: Ignition temperatures at different heating rates

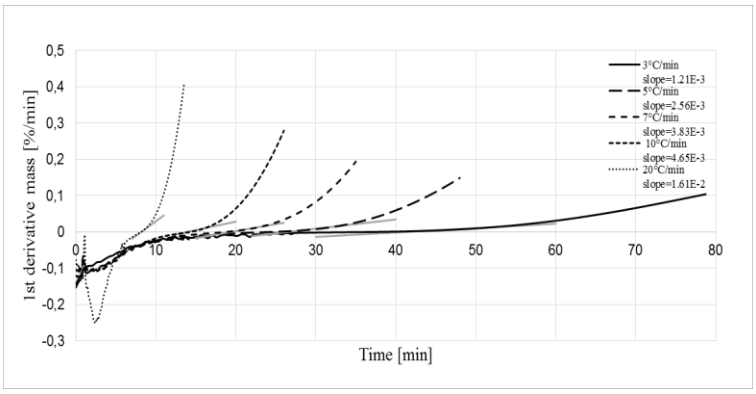

Fig. 5: Slopes from the first derivative mass as a function of time for coal A at different heating ramps

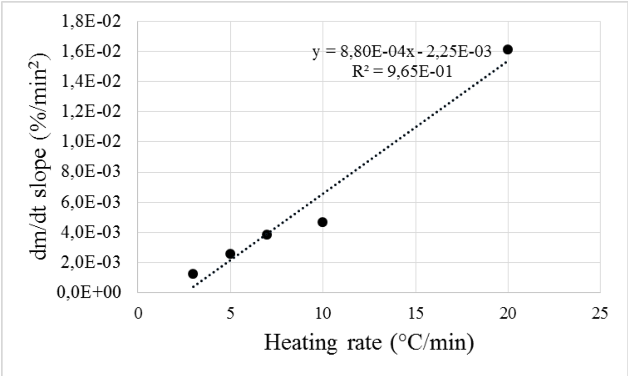

Fig. 6: Trend line to calculate the TG_{spc} index

TABLE III
TG_{SPC} VALUES FOR ALL OF THE COALS

Coal sample	TG_{spc} (wt.%./°C.min)	Category
Coal A	8.8E-4	TG_{spc} < 0.020 Unreactive at low temperature
Coal B	3.5E-3	TG_{spc} < 0.020 Unreactive at low temperature
Coal C	0.03	0.025 < TG_{spc} < 0.033 Less reactive at low temperature
Coal D	0.02	0.020 < TG_{spc} < 0.025 Non-reactive at low temperature
Coal E	2.0E-3	TG_{spc} < 0.020 Unreactive at low temperature

C. Modified Smith-Glassser oxidation tests

The results from the modified Smith-Glasser oxidation tests are given in TABLE . The maximum error was found to be 11.3% and the minimum error was 5%. The repeatability of this test is thus much lower than that of the TGA test. The observed volume change values obtained are however in the same order as those previously observed by [17]. Coal C shows a much higher absorption rate and thus higher reactivity than for the other samples, whereas coal A shows a much lower absorption rate. Coals B, D and E yielded results very similar in value. The TGA method grouped coals A, B and E together in the group with the lowest propensity to spontaneously combust (TG_{spc} <0.020), with coal D in the low range of the group (TG_{spc} >0.020 <0.025). Coal A had an extremely low value (TG_{spc} = 8.8E-4 wt.%/°C.min) compared to the other samples and coal C a much higher value (TG_{spc} = 0.03 wt.%/°C.min). The results from the modified Smith-Glasser tests thus follow the same trend as determined by the TGA method.

TABLE IV
RESULTS FROM THE MODIFIED SMITH-GLASSER OXIDATION TEST

Coal	mgO2/gCoal	molO2/gCoal
Coal A	0.029	1.97E-6
	0.025	1.59E-6
Coal B	0.040	2.51E-6
	0.037	2.32E-6
Coal C	0.223	1.40E-5
	0.212	1.33E-5
Coal D	0.054	3.38E-6
	0.060	3.76E-6
Coal E	0.050	3.12E-6
	0.045	2.79E-6

II. CONCLUSION

The results obtained from the spontaneous combustion propensity testing of both the TGA and Modified Smith-Glasser methods showed similar trends. The TGA tests are however a lot less time consuming and the repeatability is much better. The one drawback of the TGA method is that it requires more extensive data analysis. The Smith-Glasser test is a tested method and is known to be accurate. This test however requires more extensive equipment and takes a long time to complete with no predictable end point. On the other hand, the modified Smith-Glasser test requires very simple equipment and drastically reduces the time required to run a single experiment. This modified method however allows for significant error by the analyst when values are read off as well as by fluctuations in external conditions having an effect on the experiment, especially if an open water bath is used. Overall, because both methods produce results following the same trends, the TGA method can possibly prudently be used to replace the existing tests. For South Africa this test should be sufficient because of the high rank of South African bituminous coal. The lower ranks of coal did however not show an increase in mass due to oxygen absorption in the TGA experiments and can thus not directly be compared to the Smith-Glasser method. It is recommended that further and more extensive investigation using lower rank coals and coals linked to spontaneous combustion incidents be studied before the TGA method can be considered to replace current spontaneous combustion propensity tests used in industry.

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