Combustion and Physicochemical Properties of Raw and Thermally treated Bamboos

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DECLARATION

I declare that this dissertation is my own unaided work, unless otherwise stated and acknowledged. It is being submitted for the degree of Master of Science in Engineering to the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other university.

Signed: …….. on this ……. Day of ……., year ……..

ABSTRACT

South Africa is economically vulnerable to climate change because its economy is powered by electricity generated from coal fired power stations. There is a need to reduce the reliance on fossil fuel energy not only because of greenhouse gas emissions but also energy security. Bamboo is touted as a renewable energy source, however, like other woody biomass material, it has poor physicochemical properties and low energy densities. Therefore, the bamboo samples utilized in this study were subjected to thermal pre-treatment methods to improve on their combustion and physicochemical properties. Bamboo samples of 1, 3 and 4+ years old were subjected to torrefaction at 250°C and 280°C as well as low temperature carbonisation at 350°C and 400°C. A standard HGI method was modified during the course of this research for studying the grindability of the raw and treated bamboo material. The fuel properties and combustibility of these raw and thermally treated bamboo materials were then studied using thermogravimetric analysis.

The raw bamboo samples exhibited a CV ranging from 17 MJ/kg to 18 MJ/kg, whereas the torrefied samples and the carbonised samples had a CV ranging from 25 MJ/kg to 28 MJ/kg and 28 MJ/kg to 30 MJ/kg, respectively. The 4 year old bamboo carbonised at 400°C had the highest CV of 30.24 MJ/kg. The CV improvement occurred as a result of molecular modification observed through an increase in fixed carbon content from 16 to 74%. The energy yields ranging from 48 to 74% were achieved for the torrefied samples and 44 to 54% for the low temperature carbonised samples, depending on the age of the bamboo sample. At torrefaction temperatures tested, the 4 year old bamboo had the highest mass and energy yield, whereas at carbonisation temperatures, 3 year old bamboo had the highest. The number of differential thermogravimetric peaks was observed to decrease from 2 to 1 as the thermal treatment temperature increased to a carbonisation range (350-400) °C. This can be attributed to the less VM content in the carbonised samples.

The raw bamboo and thermally treated bamboo had higher reactivity, lower ignition and burnout temperatures compared to that for coal. Blending of coal with bamboo (raw and thermally treated) appeared to increase the reactivity and lower the ignition temperature during co-firing.

The activation energies of the individual fuels ranged from 56 to 289 kJ/mol, using the Ozawa model. Bamboo samples carbonised at 400°C had the highest activation energy, irrespective of age. The activation energy was also the highest when co-firing a blend with the highest proportion of coal.

Based on the co-firing tests undertaken in the TG analyser in which a percentage of coal is blended with various proportions of raw and thermally treated bamboo, the results showed that as the percentage of coal in the blend increases there is less interaction or influence of biomass. The role of biomass is to aid with ignition of devolatilization in the coal at lower temperatures. At the carbonisation stage, biomass behave more like coal in principle.

It was confirmed in this study that in terms of combustibility, the torrefied bamboo samples had a greater capacity to provide lower ignition and burnout temperatures over the low carbonised bamboo samples utilized, and this might support its application as a source of fuel in an industrial burning combustor. The carbonised 4 year old bamboo appears to be the preferred alternative source fuel to be fired solely in an existing pulverised boiler in South Africa or co-fired with coal due to the carbonised bamboo samples exhibiting the higher CV and more coal-like combustion profile.

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CHAPTER 1: INTRODUCTION

1.1. Background and motivation

Climate change is happening and it is caused by human activities (WWF-SA, 2011). Among the human activities is the emission of greenhouse gases into the atmosphere through the combustion of fossil fuel (e.g. coal, natural gas, etc.) to generate thermal energy. Many countries, including South Africa are investigating ways to curb the emission of greenhouse gases into the atmosphere. South Africa is economically vulnerable to climate change because its economy is powered by electricity generated from coal fired power stations (WWF-SA, 2011). There is a need to reduce the reliance on fossil fuel energy not only because of greenhouse gas emissions, but also for energy security since fossil fuel is not a renewable energy (Sarfo, 2008). Hartnady (2010) has shown in his study that South Africa's coal reserves are also being depleted and may eventually run out.

Biomass has received great attention from researchers in recent years as the main potential alternative renewable energy source for electricity production because of its low ash content and its ability to be carbon neutral as a renewable resource among other fuel characteristics (Bridgeman *et al*, 2010; Rousset *et al*, 2011; and Teixeira *et al*, 2012). Biomass do not contribute to the accumulation of CO_2 gas in the atmosphere because it absorbs CO_2 for photosynthesis during growth period, thereby cancelling out the CO_2 gas produced during combustion of these materials (Gil *et al*, 2010; and Ibrahim *et al*, 2013). Studies have shown that biomass can be converted into energy either by combustion, liquefaction or through gasification (Gil *et al*, 2010; and Fang and Jia, 2012). In addition, recent investigations have also shown that biomass can be co-fired with coal in existing power plant with very little modifications (Gil *et al*, 2010 and Ohliger *et al*, 2013). Many power stations in the United Kingdom generate electricity by solely firing of biomass or co-firing with coal (Jones *et al*, 2012). Co-firing biomass with coal shows a potential for reducing CO_2 and NO_x emission among other benefits. An investigation conducted by Li *et al* (2012) combusting biomass and coal at a ratio of 1:1 in the co-fired boiler, reduces the net CO_2 emission from 915 kg/MWh to 403 kg/MWh, which was half the emissions obtained from pure coal.

The challenge with using biomass for energy conversion is (i) the difficulty in reducing it to an acceptable particle size for transportation, handling, bio-degradation and homogenization; and (ii) increasing its energy yield (Kargo *et al*, 2010; Phanphanich and Mani, 2011; Park *et al*, 2012 and Jones *et al*, 2012). Literature has shown that these challenges can be addressed by thermal pre-treatment of the biomass by a mild pyrolysis process, i.e. "torrefaction and low temperature carbonization" (Bergman *et al*, 2005; Kargo *et al*, 2010; Phanphanich and Mani, 2011; Rousset *et al*, 2011; Park *et al*, 2012; Ohliger *et al*, 2013; and Ibrahim *et al*, 2013). The application of these techniques has a major influence on the chemical and physical properties of raw biomass. During this pre-treatment process, biomass molecules are restructured and this leads to losses in hydrogen and oxygen content of biomass with the decomposition of the cellulose and lignin of woody biomass and, ultimately, the conversion of biomass into a densified solid with improved grindability and non-polar unsaturated products (Uslu *et al*, 2008; Bridgeman *et al*, 2010; and Park *et al*, 2012). Bergman *et al* (2005) also supported the fact that pre-treated biomass has energy densities similar to that of coal, which could render it more suitable for co-firing.

The main key factors under investigation in this research were the grindability, fuel properties and combustibility of biomass in the form of bamboo. Bamboo was utilized as an alternative sole source of fuel and as a co-fired product with South African coal. The biomass "bamboo" was thermally treated with a view to establishing whether the physical and combustion characteristics as listed earlier could be improved. The species of bamboo utilized in this investigation is *Bambusa balcooa*, which was sourced from the Western Cape region, South Africa.

1.2. Study aim and objectives

A need for this project emanated from the country's drive to fight climate change and energy security by switching to renewable energy. The aim of this research is to study the physical properties of raw, torrefied and low temperature carbonised bamboo to establish the potential of these materials as suitable biomass sources for firing alone or co-firing with coal. The aim was achieved through the following objectives:

- To investigate the impact of torrefaction and carbonization/pyrolysis on the physical (grindability) and combustion characteristics of the biofuel and Hardgrove Grindability Index.
- To compare the physical and combustion characteristics of different ages of *Bambusa balcooa* plants (1, 3 and 4 years old).
- To determine the combustion profiles using TGA for torrefied and carbonized bamboos, and also biomass/coal blends at different ratios.
- To identify suitable reaction kinetic models for biomass and biomass-coal blends during combustion and thereby to evaluate their activation energies.

1.3. Key questions to be addressed

1. Will the pre-treatment of bamboo by torrefaction and low temperature carbonization improve the Hardgrove Grindability Index of the products?
2. Which of the two techniques (torrefaction and low temperature carbonization) would have more impact in regard to the increase in the energy and mass yield in the bamboo products?
3 Does torrefaction and carbonisation improve the combustion characteristics of raw bamboo?
4 What are the combustion characteristics of raw, torrefied and carbonised bamboo as identified in thermogravimetric analyses (TGA)?
5 What are the combustion characteristics of coal and biomass (in raw, torrefied and carbonised conditions) when co-fired together in different proportions in the TGA analysis?

1.4. Hypothesis

The thermal heat treatment of bamboo will improve its grindability through the molecular modification to its hemicellulose group and the breaking down of its OH functional groups. This will also improve its combustion properties in terms of ignition and burnout temperatures and aid in its burning compatibility with coal as a co-fired fuel.

1.5. Structure of the Dissertation

The dissertation comprises of 5 chapters, each chapter covering a different aspect of the work. Chapter 1 is the introduction, followed by a literature study presented in chapter 2, covering the current energy profile in South Africa as well the biomass energy conversion used worldwide and its potential use in South Africa. The full experimental approach used in this work is reported in chapter 3. The results obtained are reported and discussed in chapter 4. Lastly, conclusions drawn from results in chapter 5 and recommendations on future work are reported in chapter 6.

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction

This section gives an overview of the previously published work related to the proposed research. In addition, the theoretical principles relevant to this research are also presented. Previous studies on grindability, thermal treatment, co-firing and the kinetic model to be applied are discussed. The literature presented in this section is essential for discussion and interpretation of the results.

2.2. Electrical energy in South Africa

South Africa has an electricity generating capacity of a little more than 40 000 MW, with approximately 88% of this capacity emanating from coal fired power stations. The remaining 12% is generated from nuclear power, hydro power and fossil fuel "diesel" (Government Gazette, 2008). Of the total capacity, only 17.2% is consumed domestically and the rest consumed in various sectors of the economy, i.e. agriculture (2.6%), mining (15%), industrial (37.7%), commercial (12.6%), transport (2.6%) and general (12.3%). The capacity reserve margin has fallen due to the growing economy and population leading to recent load shedding, which puts a strain on the economy of the country.

Eskom is the primary producer of electricity in South Africa, predominantly from coal fired power stations. On average, Eskom consumed about 121.5 million tonnes of coal per annum in the past 10 years, emitting about 223 million tonnes of CO_2 per annum in the same period (Eskom, 2015). Most of the power plants are built with electrostatic precipitators to reduce emissions of particulates. However, none of the old existing power plants have flue-gas desulphurizers (FGD) installed. The new supercritical power stations under construction, i.e. Medupi and Kusile power plants, will have a flue-gas desulphurisation systems installed (Eskom, 2014).

Since of the awareness of climate change, the world in general has been forced to take extreme measures to reduce the carbon footprint. For a developing country like South Africa, where the economy is powered by coal generated electricity, the devastating impacts of climate change

leave the economy vulnerable. Global markets will hurt South Africa's economy by imposing penalties on goods and services with a high carbon footprint. Foreign investment is also at risk for carbon intensive technology projects and this will slow down the economic growth (WWF-SA, 2011). In addition to the climate change problems, South Africa's over reliance on coal as the main source of energy is a threat to its energy security. From 2009, the South African government has since pledged to undertake mitigating actions to transform to a cleaner economy which will result in carbon emissions cutbacks of 34% by 2020 and 42% by 2025 (WWF-SA, 2011). The mitigating actions could include the exploration of using alternative renewable energy sources such as biomass for electricity production. Eskom's short term plans also include co-firing with biomass to reduce the organisation's carbon footprint (Eskom, 2010). An investigation conducted by Li *et al* (2012) combusting biomass and coal at a ratio of 1:1 in the co-fired boiler, reduces the net CO_2 emission by 50%.

Bamboo plants have received significant attention with a positive prospect as a future energy source due to its fast growth rate, considerable strength and mass, and high quality fuel physiochemical properties (Yao *et al*, 2008; Rousset *et al*, 2011; Bada *et al*, 2014 and Basu *et al*, 2014). For these reasons, South Africa has been investigating the prospects of establishing a bamboo industry (NBASA, 2012). This is because bamboo offers the potential for more value adding opportunities in addition to being an energy source, i.e. it is a source for furniture, textiles, construction, carpets, blinds and other manufactured goods as well a potential source for paper making and liquid fuel production (NBASA, 2012). There are currently no natural forests in South Africa, only a few clumps of bamboo that grow naturally in various environments, predominantly "*Bambusa balcooa*". However, there are pilot projects throughout the country looking to harvest bamboo with a view to grow them to a commercial scale (NBASA, 2012).

2.3. Coal in South Africa

South Africa has large reserves of recoverable coal, estimated to be between 15 and 55 billion tonnes (Eberhard, 2011). Therefore, it is no surprise that coal accounts for 73% of South Africa's primary energy, 93% of electricity generation and 30% for liquid fuels (Jeffrey, 2005; SACR, 2011; and Eberhard, 2011). In addition to local consumption, South Africa is also the

sixth leading exporter of hard coal (steam coal) globally, with a reported export figure of 72 and 76 million tonnes for the year 2013 and 2014, respectively (WCA, 2014 and IEA, 2015). Locally, the main consumer of coal is Eskom (70%) for electricity generation, followed by Sasol with 20%. Figure 1, presents the extent of coal use in South Africa.

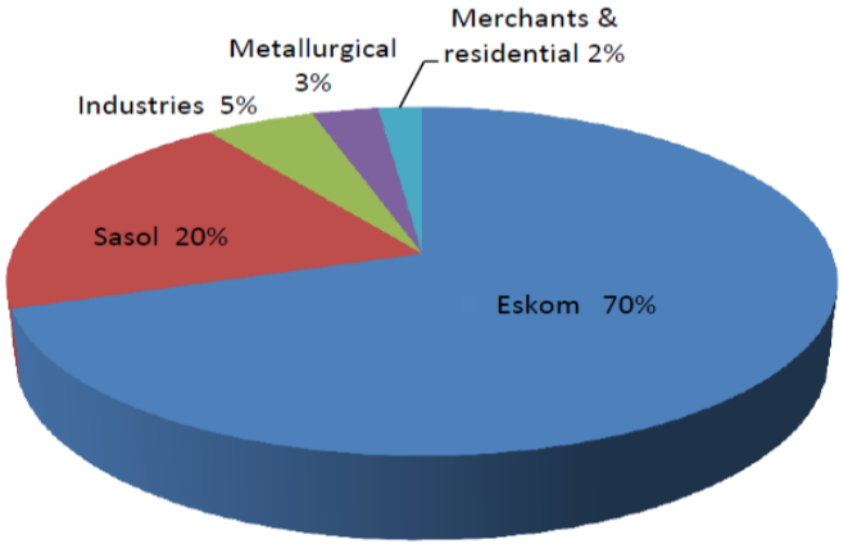

Figure 1: Coal use in South Africa (Eberhard, 2011)

Coal mined in South Africa generally has a high ash content (up to 65% in the Waterberg field) and therefore it requires further beneficiation to improve its quality in order to meet export standards (max 15%) (Eberhard, 2011). The by-products of this beneficiation process are two grades of coal with poorer qualities (high ash and sulphur contents), namely, middlings and discards, some of which are consumed by Eskom for electricity generation (Eskom, 2010 and Eberhard, 2011).

2.4. Bioenergy

Biomass is material made up of vegetation (plants) and consequently formed as a product of photosynthesis. Photosynthesis is a process where light energy is captured and used to convert carbon dioxide (CO_2) absorbed from the atmosphere and water (H_2O) into chemical energy which can later be released to fuel plant growth. As the energy that is stored in the plant is from the sun (solar energy), and as plants continue to grow and regenerate themselves, biomass is said

to be a renewable resource. The simplest technique for extracting this energy from biomass is by direct combustion (Carter, 2012). A typical large scale electric generating power plant using direct combustion of fuel (biomass or coal) in a boiler to produce steam for a turbine is shown in Figure 2. Moreover, many studies have been conducted on the co-combustion/co-firing of biomass with coal for electric power generation (Bergman *et al*, 2005; Kastanaki and Vamvuka, 2006; Gil *et al*, 2010; and Li *et al*, 2012).

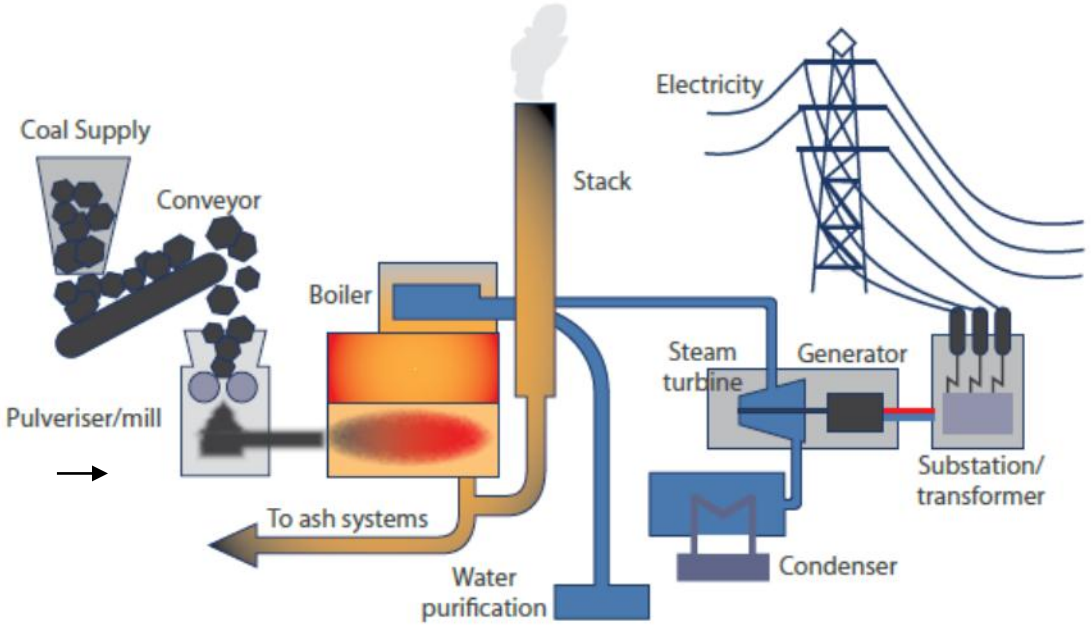

Figure 2: Schematic of a coal fired steam turbine for electric production schematic (SACR, 2011)

Co-firing is the combustion of two or more different fuel components blended together simultaneously in the same combustion unit. The NETBIOCOF project (2005-2007), co-financed by the European Commission, provided a road map on the co-firing activities in Europe with more than 100 co-firing units in place (Al-Mansour and Zuwala, 2010). An impression of the extent of co-firing plants worldwide is shown in Figure 3. Many of these plants are in Europe with Finland having 78 co-firing plants. Most of these co-firing plants employ direct combustion configuration and have generating capacity ranging from 20 to 310 MW. The United State of America (USA) is the second highest with 40 co-firing plants operating on a commercial basis (Al-Mansour and Zuwala, 2010).

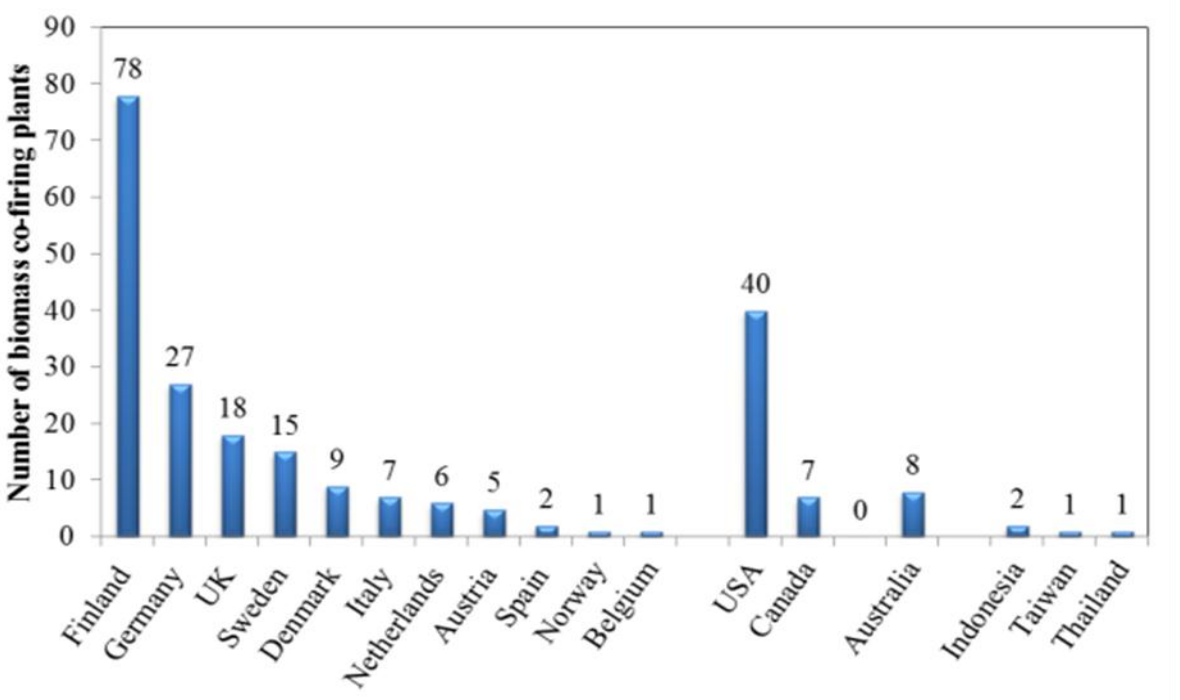

Figure 3: Distribution of co-firing plants worldwide (Al-Mansour and Zuwala, 2010)

The co-firing of biomass with coal has many advantages and also some disadvantages. Co-firing biomass with coal promises environmental, technical and economic benefits (Kastanaki and Vamvuka, 2006). These benefits include reduction of fossil fuel usage, reductions in greenhouse-gas emissions (sulphur oxide, nitrogen oxide and CO_2), and it also provides a stable flame in the boiler among other benefits (Gil *et al*, 2010; Li *et al*., 2012; Momeni, 2013; and Basu *et al*, 2014). However, co-firing can also result in slagging and fouling problems (Kargbo *et al*, 2010; and Teixeira *et al*, 2012).

The herbaceous nature of biomass is believed to be the cause for slagging and fouling due to its higher inorganic matter content such as, the presence of the alkalis, sodium and potassium, sulphates, chlorides and carbonates in the ash (Li *et al*, 2012; and Fang and Jia, 2012). Slagging and fouling problems affect heat transfer efficiencies and may also result in unplanned frequent plant shut down for maintenance of the affected equipment. Teixeira *et al* (2012) studied the slagging and fouling tendencies of straw pellets, olive cake and wood pellets during combustion and co-combustion with coal using an ash fusibility index (AFI). It was found that the AFI values were in close agreement to the behaviour of ash during combustion in a pilot fluidized

bed. Furthermore, it was found that the biomass exhibited different tendencies for fouling and slagging with fruit biomass presenting higher tendency due to the KCl and K_2SO_4 contents in the ash.

As aforementioned, biomass is a very promising renewable energy source. But the inherent fuel characteristics of biomass compared to that of fossil fuels such as coal renders them unfavourable for energy production. Biomass has high moisture content, low heating value and low bulk densities, and the hydrophilic attributes of raw biomass make it difficult to store, handle and transport efficiently (Kargbo *et al*, 2010; and Phanphanich and Mani, 2011). Moreover, biomass is fibrous in nature and this makes it difficult to grind. This is a major constraint for the combustion or co-combustion of biomass either alone or with coal (Ibrahim *et al*, 2013; Jones *et al*, 2012). Some authors suggest that these challenges can be addressed by a mild thermal pre-treatment step, i.e. Torrefaction and Carbonization (Bergman *et al*, 2005; Rousset *et al*, 2011; Li *et al*, 2012; and Park *et al*, 2012).

2.5. Bamboo

2.5.1. Occurrence

Bamboo refers to as a group of large woody grasses with relatively fast growth rates, some reaching maturity within five years (Scurlock *et al*, 2000; and Rousset *et al*, 2011). There are about 1400 different species of bamboo distributed worldwide, most of which are found in China and India (Yeasmin *et al*, 2015). In South Africa, there are no natural bamboo forests, only countless clumps of bamboo growing naturally and predominantly in the coastal regions of the country. The species are mostly *Bambusa balcooa* (NBASA, 2012). However, South Africa has commissioned projects with the intention of setting up significant commercial bamboo plantations within the coming years (NBASA, 2012).

2.5.2. Uses of Bamboo

Bamboo is commonly utilized for food, furniture, construction ("scaffolding"), as fibre, textiles and for many other applications by over 2.5 billion people worldwide. In Asia, bamboo is commonly utilized for bridges, scaffolding and housing, predominantly as a temporary structure (Scurlock *et al*, 2000; and NBASA, 2012). It has since found commercial application in the

production of paper, textile, board, furniture and many other home products. Moreover, bamboo can also be used as an alternative energy source (Scurlock *et al*, 2000; Rousset *et al*, 2011; and NBASA, 2012). As such, it has potential as a biomass energy fuel in various forms, i.e. charcoal, bio-coal, bio-pellets. As an energy source, it is used alone or as a co-fired product, and it is also a source of liquid and gaseous fuels (Scurlock *et al*, 2000; and NBASA, 2012).

Because of the aforementioned applications, having a bamboo industry in South Africa would have positive effects on the economy of the country, improving such issues as job creation and poverty alleviation and it would also present an alternative renewable energy source. The latter effect will further help the country move towards greener energy in the country's future energy plan.

2.5.3. Fuel Characteristics

Bamboo like other woody biomass material, has a low ash content, high volatile matter and low fixed carbon content. The moisture content of bamboo ranges from 8 to 23% (Scurlock *et al*, 2000). A positive characteristic of the bamboo, from a combustion viewpoint, is the very low nitrogen and sulphur contents (as can be seen in Table 1 below for some bamboo species), which would be beneficial for co-firing in power plants thereby minimising greenhouse gas emission. Fuel characteristics of some bamboo species are presented in Table 1 below. There it is shown that the bamboo species listed have low ash contents, very high volatile matter and low fixed carbon.

Table 1: Fuel characteristics of selected bamboo species (Scurlock *et al*, 2000).

	Phyllostachys nigra			*Phyllostachys bambusoides*			*Phyllostachys bissetti*		
	1 year	2 year	4.5 year	1 year	2 year	4.5 year	1 year	2 year	4.5 year
Proximate Analysis (% as received)									
Moisture	8.42	8.79	13.62	22.61	12.92	9.54	8.52	10.66	21.97
Ash	0.86	0.87	0.41	0.66	0.84	0.53	1.14	0.78	0.9
Volatiles	73.94	73.66	72.27	62.93	70.51	75.55	73.18	72.24	64.99
Fixed Carbon	16.78	16.68	13.7	13.8	15.73	14.38	17.16	16.32	12.14
Higher Heating Value (GJ/t dry basis)									
	19.57	19.48	19.27	19.49	19.53	19.09	19.42	19.50	19.51
Ultimate Analysis (% dry matter)									
C	51.89	51.19	51.39	52.28	51.84	50.85	51.22	51.7	51.07
H	5.21	5.29	5.25	5.09	5.18	5.40	4.90	5.00	4.51
N	0.4	0.29	0.21	0.59	0.6	0.38	0.55	0.3	0.32
S	0.04	0.03	0.03	0.05	0.05	0.04	0.05	0.03	0.05
Cl	0.19	0.14	0.05	0.06	0.06	0.04	0.07	0.03	0.06
O*	41.52	42.12	42.61	41.10	41.33	42.75	41.98	42.11	42.91

C: Total carbon; H: Hydrogen; N: Nitrogen; S Total sulphur; Cl: Chlorine; and O: Oxygen

2.5.4. Estimated bamboo production potential in South Africa

The results of the desktop study conducted by the Agricultural Research Council-Institute for Soil, Climate and Water (ARC-ISCW) on the potential bamboo production areas in South Africa are presented in Table 2 below.

Table 2: Potential bamboo production regions in South Africa (NBASA, 2012)

	Province area	Sustainability class				Total	Total
Province	(ha)	(ha)				(ha)	(%)
		High	Moderate	Low	Marginal		
Eastern Cape	16 896 598	42 839	315 078	489 468	465 860	1 313 245	8%
Free State	12 982 516	-	26 655	219 964	659 589	906 208	7%
Gauteng	1 817 830	-	-	2 264	666 768	669 032	37%
KwaZulu-Natal	9 436 133	188 023	916 221	914 117	684 986	2 703 347	29%
Mpumalanga	7 649 471	147 902	271 680	650 061	992 269	2 061 912	27%
Limpopo	12 575 396	36 737	49 263	82 463	722 506	890 969	7%
North West	10 488 168	-	-	-	364 025	364 025	3%
Western Cape	14 010 998	6 214	11 179	16 630	48 468	82 491	1%
Total SA	85 857 110	421 715	1 590 076	2 374 967	4 604 471	8 991 229	10%
% Sustainability class		0.5%	2%	3%	5%	10%	

Table 2 shows that South Africa has about 421 715 hectares that has high potential to be utilized for sustainable bamboo production, which is equivalent to 0.5% of the total South Africa's surface area. Kwazulu-Natal has the highest potential, followed by Mpumalanga. The high potential in Mpumalanga province presents an opportunity for bamboo to be utilized for co-firing, since most of the coal-fired power stations are located in the same province.

2.6. Thermal treatment

Thermal treatment of biomass at the pre-treatment stage has been studied by researchers over the years. It has since been categorized into two processing methods, namely torrefaction and carbonization. Torrefaction is defined as thermal treatment of biomass in the temperature range 200-300^{o}C with residence times typically ranging from 15 min to 3 hours. Meanwhile, carbonization is the thermal treatment of biomass in the temperature range 300-500^{o}C with residence time ranges similar to torrefaction. (Park *et al*, 2012; and Carter, 2012). Both processes are carried out under atmospheric conditions in an inert carrier gas to prevent combustion. During these thermal treatment processes, moisture and reactive volatiles are removed from the biomass, leaving a biomass char as a product. More often, depending on the type of biomass utilized, 70% of the starting mass is retained as biomass char, containing 90% of the original energy content after torrefaction (Bergman *et al*, 2005). A study conducted by Rousset *et al* (2011) found that at torrefaction temperatures between 250°C and 280°C, hemicellulose and cellulose decomposes, yielding a biomass char that possess a higher lignin content. Thermal treatment removes oxygen and volatiles, resulting in a char product with improved fuel quality. Uslu *et al* (2008) also shows that the O-H bonds of the biomass are broken during thermal treatment, resulting in the formation of a fragile non-polar solid structure, i.e. an easy to grind biomass, which required reduced energy in grinding.

Torrefaction and carbonization of woody biomass followed by fuel characterization of the products were conducted by Park *et al* (2012). Energy yields of 80-90% were reported for torrefied and 46-63% for carbonized material, respectively. It was also indicated that the combustion properties of biomass can be further improved to render them similar to that of coal by the same thermal pre-treatment process. Phanphanich and Mani (2011) investigated the impact of torrefaction on the grindability and fuel characteristics of pine chips and logging

residues. Torrefaction temperatures ranging from 225-300^{o}C were investigated at a residence time of 30 min. The specific grinding energy consumption for pine chips was reduced from 237 kWh/t to 23.9 kWh/t by torrefaction. The same trend was observed for logging residues. Also, the high heating value of pine chips was increased from 18.46 MJ/kg to 25.38 MJ/kg, with the logging residue following the same trend.

2.7. Grindability

Size reduction is of paramount importance not only for fuel combustion in boilers, but also for biomass transportation and handling and also for mill design (Mani *et al*, 2004; Bridgeman *et al*, 2012; and Ibrahim *et al*., 2013). The particle size distribution has significant consequences on combustion parameters such as combustion efficiency, residual carbon in the ash and the stability of the flame during combustion (Bridgeman *et al*, 2010). The fibrous nature of biomass makes it difficult to grind and results in a high amount of energy needed to grind to acceptable sizes (Ibrahim *et al*, 2013). The most common test method for determining the grindability of coal is the Hardgrove Grindability Index (HGI), which gives information in regard to the energy required for milling different samples, the design capacity of the mill and its performance (Bridgeman *et al*, 2010). The standard method for HGI uses a fixed mass of 50g of coal sample, however Tichanek (2008), Bridgeman *et al* (2010) and Ibrahim *et al* (2013), suggested using the fixed volume approach for heterogeneous coal and biomass. The scholars argued that using a fixed mass approach gives unsatisfactory results because of significant differences in volume between coal and biomass. Ohliger *et al* (2013) also studied the impact of torrefaction on the grindability of beechwood by the Hardgrove Grindability Index (HGI) method. It was demonstrated that the grindability of beechwood improved and increases with the mass loss of the solid during torrefaction. An HGI value of 122 (easy to grind) was achieved at a mass loss of 50%. These findings are in agreement with those found by Bridgeman *et al* (2010) on willow and miscanthus.

2.8. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is the most common method used to investigate the thermal behaviour and the reaction kinetics during combustion, gasification and pyrolysis of solid

materials (Kastanaki and Vamvuka, 2006; Gil *et al*, 2010; Mani *et al*, 2011; and El may *et al*, 2011). The TGA gives mass change profiles of a sample as a function of temperature and time and can also be used to distinguish between competing models (El may *et al*, 2011). Mass loss with a change in temperature is an indication of the conversion of products emanating from gas given off at different stages of thermal decomposition. This technique can also be used to predict different components of biomass, i.e. moisture, hemicellulose, cellulose and lignin content (Carter, 2012). A typical weight loss profile of a biomass sample obtained from a TGA is presented in Figure 4. The thermal behaviour can be interpreted using two methods, i.e. (i) The TGA curve which gives a weight loss profile and (ii) the derivative thermogravimetric (DTG) curve which gives a differential profile of the weight loss. The weight loss in biomass can be divided into 3 stages, i.e. moisture loss which occurs around 100°C, followed by devolatilization, mainly hemicellulose at around 200^{o}C and then char degradation at 400^{o}C, composed of cellulose and lignin (Gil *et al*, 2010; Loo *et al*, n.d; Yanfen and Xiaoqian, 2010; and El may *et al*, 2011).

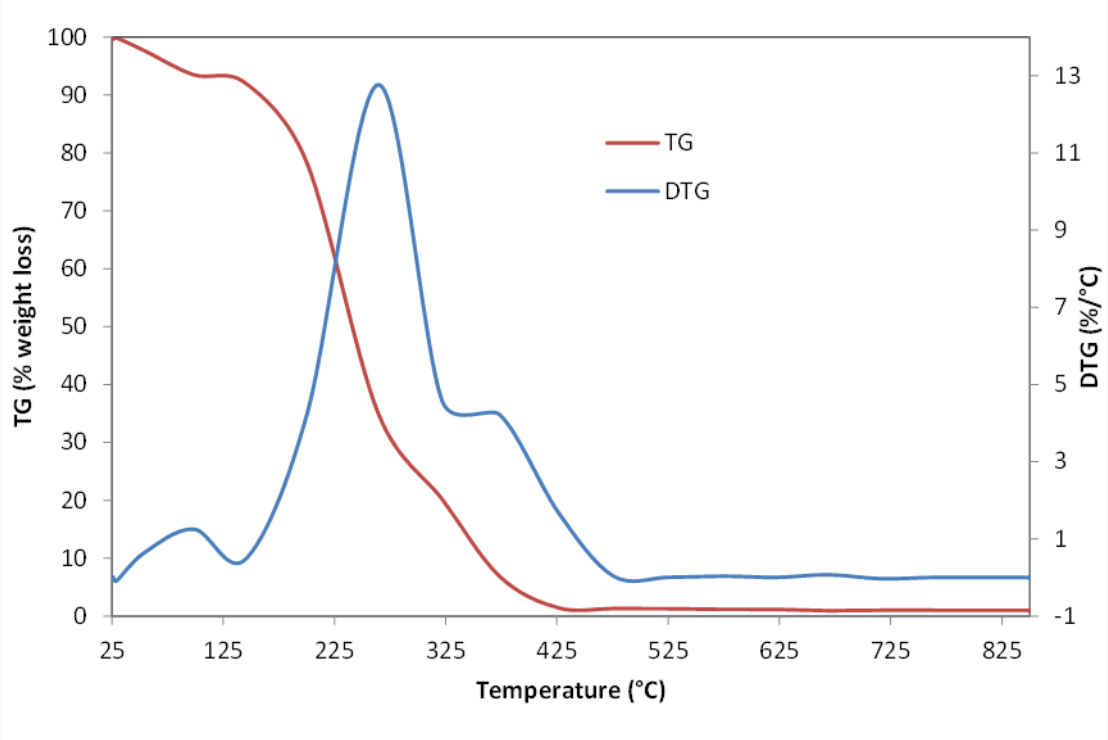

Figure 4: Thermal degradation profile of untreated bamboo

Combustion processes have been studied by many researchers using thermogravimetric analysis (Yanfen and Xiaoqian, 2010; and Sahu *et al*, 2013). Thermal behaviour and kinetics of biomass and biomass/coal blends during the combustion reaction is of paramount importance for the design and operation of co-combustion process units (Sadhukhan *et al*, 2008; and Idris *et al*, 2012). The influence of physical properties of char such as porosity, surface area, and particle shape and size on char reactivity cannot be ignored (Momeni, 2013). The char-oxygen reaction mostly occurs on the external surface of the char particle and is controlled by ash layer diffusion (Irfan *et al*, 2011). The reaction tends to progress towards the gas film diffusion controlled regime when the temperature and particle size increases. However, if temperature and/or particle size substantially decreases, the reaction proceeds towards the chemically controlled regime and takes place evenly throughout the internal pore surfaces of the particles (Irfan *et al*, 2011). A study by Irfan *et al* (2011) reported that for particle sizes below 50 μm, combustion is chemical reaction controlled in pulverized fuel combustors. However, for particle sizes above 100 μm, the reaction is diffusion dominated.

Kinetic analysis of combustion reaction is usually defined by a single step kinetic "Equation 1"

$$\frac{dx}{dt} = k(T)f(x) \qquad (1)$$

Where, *t* is the time, *T* is the temperature, *x* is the extent of conversion and *f(x)* is the reaction model. A suitable/applicable reaction model must be applied to the TGA data/profiles to determine the kinetic parameters of the thermal decomposition process (Ozawa, 1965; Gil *et al*, 2010; and El may *et al*, 2011). The temperature dependency of the rate constant *K(T)* can be explicitly expressed by introducing Arrhenius equation, resulting in Equation 2

$$\frac{dx}{dt} = f(x)Ae^{-(E/RT)} \qquad (2)$$

Where *R* is the gas constant (8.314 J/(mol K). Parameters *A* and *E* is the pre-exponential factor and reaction activation energy, respectively, and together with reaction model *f(x)* are known as the kinetic triplet. These parameters are used to define the characteristics of combustion. A lot of

work has been done on determining these kinetic parameters. There are two methods for determining the kinetics that stand out from literature, namely; model-free/iso-conversion kinetic methods and model-fitting/model dependent kinetic methods (Vyazovkin and Wight, 1999; and Wang *et al*, 2005).

Model-free methods evaluate the activation energy *E* for the reaction independent of the reaction model *f(x)* (Yao *et al*, 2008). Meanwhile, model-fitting evaluate *E* by for fitting non-isothermal TGA data to the hypothetical reaction model. Vyazovkin and Wight (1999) compared the two approaches to kinetic analysis of isothermal and non-isothermal data. The authors noted that model-fitting approaches give excellent fits for both isothermal and non-isothermal data, but Arrhenius parameters yielded by this approach is extremely ambiguous when applied to non-isothermal data. Reason being that *x* and *T* vary simultaneously during non-isothermal experiment and model-fitting fails to attain clean separation between the temperature dependency of *K(x)* and reaction model *f(x)*. According to Vyazovkin and Wight (1999), model-free approaches avoid these shortcomings and can be used to obtain reliable and consistent kinetic information for both isothermal and non-isothermal data.

Model free/iso-conversional approaches are applied using two methods, namely; differential methods and integral methods. Differential methods are said to be the worst of the model-free methods, even though they do not assume any approximations (Friedman, 1965). A study conducted by Starink (2003) found that, when there is doubt over baseline of the thermal analysis data, or the accuracy of the conversation rate determination is limited, integral methods will prevail over differential methods. For differential iso-conversion method, Equation 2 is linearized by taking logarithms, resulting with Equation 3

$$\ln\left(\frac{dx}{dt}\right) = -\frac{E}{RT} - \ln\big(f(x)\big) \tag{3}$$

Which can be further rearranged into Equation 4 for constant heating rate (β)

$$\ln\left(\frac{dx}{dT}\beta\right) = -\frac{E}{RT} - \ln\big(f(x)\big) \tag{4}$$

E can be evaluated in Equation 4 which is a straight line plot of $\ln\left(\frac{dx}{dT}\beta\right)$ vs $\frac{1}{T}$ with a slope *E/R*. An example of this differential iso-conversional method is the Friedman method (Wang *et al*, 2005; and Bai *et al*, 2015). The integral method is derived by rearranging Equation 2 for constant heating rate, the integrating leading to Equation 5 below.

$$\int_0^x \left(\frac{dx}{f(x)}\right) = \frac{A}{\beta}\int_{T_0}^{T} EXP(-\frac{E}{RT})\, dT \qquad (5)$$

Subsequent to this, integral methods like the Coats-Redfern method (Coats and Redfern, 1964) or Flynn-Wall-Ozawa method could be applied to integrate the expression and determine the *E* (Yao *et al*, 2008). Meanwhile the iso-conversional methods only determine *E* for the reaction independent of the reaction model, numerous techniques must be applied to evaluate the remainder of the kinetic triplet. The techniques involve assuming a reaction model, then evaluating the corresponding pre-exponential factor *A*. Thereafter, efforts are made to verify if the kinetic triplet is real. This is done by inverting the overall model equation and using the obtained kinetic triplet to compute the mass fraction reacting. Several reaction mechanisms have been proposed for the modelling of biomass and biomass-coal blends in literature, many proposing first order reactions (Nassar, 1999; Zhou *et al*, 2006; and Gil *et al*, 2010).

The kinetic reactions of biomass and biomass-coal blends are heterogeneous. As a result Nassar (1999) identified two thermal events, which could be represented by first order reactions on his pyrolysis investigation of rice straw and bagasse. Zhou *et al* (2006) also identified more than one thermal event when he studied the pyrolysis of various biomasses. Sutcu (2007) also successfully studied the pyrolysis kinetics of peat, reed, lignite and bituminous coal applying the description of separate events and single first order reaction. The same approach was used by Gil *et al* (2010) identifying 2 thermal events. The authors demonstrated that chemical first order reaction is the most effective mechanism for the devolatilization stage, however, diffusion was found to be responsible for the biomass char reaction. Ozawa (1992) also found that the conversion at the maximum rate of conversion is constant and autonomous of the heating rate and in the case where heating is linear the rate constant follows the Arrhenius law. Following this, it is assumed

that the dominating reaction is at a conversion conforming to the maximum rate of decomposition for a single first order reaction when the material is heated up at a constant rate.

Therefore, the combustion reaction kinetics in this work were studied using the Kissinger and Ozawa methods.

2.9. Kissinger and Ozawa methods

2.9.1. Kissinger method

The Kissinger method is a model-free non-isothermal method which allows for kinetic parameters to be determined without assuming the reaction mechanism. This method eliminates the need to evaluate the kinetic parameters by means of evaluating the activation energy for each conversion. Kissinger (1956) derived Equation 6 to evaluate the kinetics from Equation 2;

$$\ln\left(\frac{\beta}{T_P^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_P} \qquad (6)$$

For different heating rates β and corresponding peak temperature T_P, Equation 6 gives a linear relationship when plotting $\ln\left(\frac{\beta}{T_P^2}\right)$ against $\frac{1}{T_P}$. The peak temperature is the temperature at the maximum rate of conversion (obtained from DTG curve) as presented in Figure 5. The activation energy *E*, is calculated from the slope of the Kissinger plot, *E/R*.

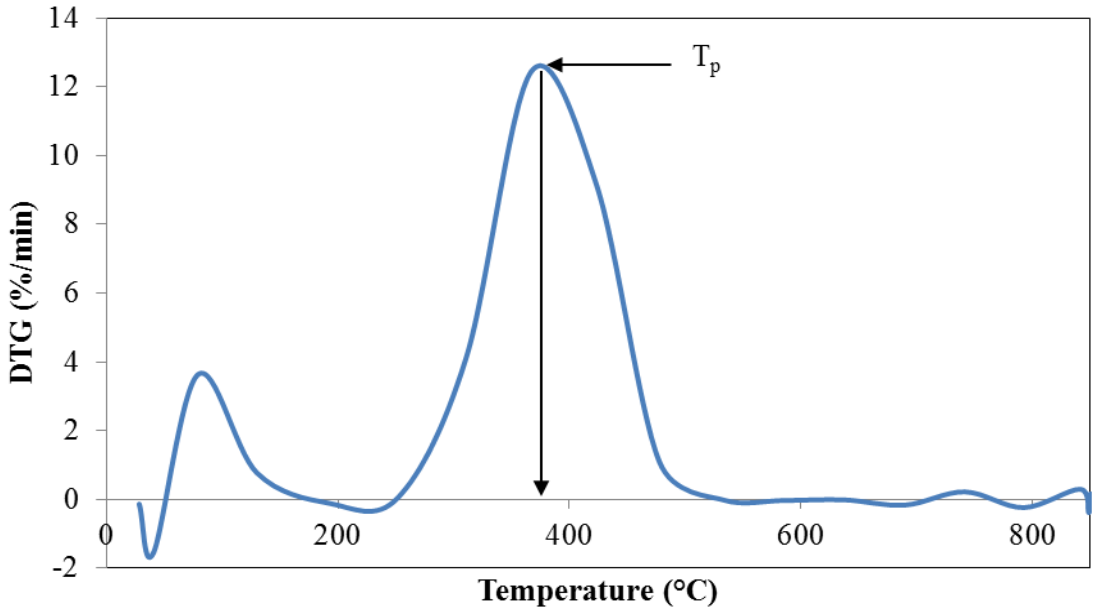

Figure 5: DTG curve of a combusting species

2.9.2. Ozawa method

The Ozawa method is also a model-free non-isothermal method of evaluating kinetic parameters derived by Ozawa (1965). The author also derived Equation 7 to evaluate the reaction kinetics on the basis that the degree of conversion is a constant value autonomous of the heating rate when the DTG curve reaches a maximum. The peak temperature is obtained the same way as that of the Kissinger method outlined earlier in Figure 5 above.

$$\ln(\beta) = constant - 1.052\frac{E}{RT_P} \qquad (7)$$

The Ozawa plot is also gives a linear relationship curve when plotting $\ln(\beta)$ against $(1/T_p)$. The activation is calculated from the slope given by $1.052E/R$.

The above methods are important to this study because the activation energy can be evaluated from the thermogravimetric data without knowing the reaction model. The footprint of application of these methods to study the kinetics of biomass combustion and co-combustion with coal is well documented in literature (Ozawa, 1965; Yao *et al*, 2008 and Slopiecka, *et al*, 2012).

CHAPTER 3: RESEARCH METHODOLOGY

3.1. Materials

3.1.1. Bamboo

Mature bamboo plants "*Bambusa balcooa*" of different age, sourced from the Western Cape were utilized as the raw biomass material. The *Bambusa balcooa* was of three different age groups (1 year, 3 years and 4 years old). The stem known as culm was blended from the top, the middle part, the bottom, and the underground root also known as rhizomes. The bamboo was further cut into blocks of approximately 25 X 25 X 10 mm in size (see Figure 6).

Figure 6: *Bambusa balcooa* blocks

A sub-sample of these blocks was reduced using Retsch SM 200 size reduction equipment and further pulverised to -212 µm, and used for characterization and combustion investigations. Bamboo was further blended with high ash coal to form biomass/coal blend with biomass content by weight ranging from 25 to 75% for co-firing combustion investigations. The rest of

the bamboo blocks were used for thermal pre-treatment and grindability investigations discussed in section 3.4 and 3.5, respectively.

3.1.2. Coal

Four coal samples of different HGI values sourced from the Limpopo and Free State Province were utilized to develop a calibration curve for HGI Vs. mass percent passing 75 µm (see section 3.5.1). Meanwhile, a high ash coal sourced from the Free State was used as fuel for co-firing with the raw bamboo and the thermally treated bamboo samples in this investigation. The sample was pulverized to -212 µm in a pulveriser.

3.1.3. Gases

High purity N_2 gas, O_2 gas and technical standard air were used for the thermo-gravimetric analyses. N_2 gas was also used for thermal pre-treatment investigations.

3.2. Equipment

The following pieces of equipment were used to carry out experimental procedures:

- Glass tube reactor for torrefaction and carbonization testwork.
- Muffle furnace as a heating source for thermal pre-treatment processes.
- A TGA instrument (TGA 701 Leco) for combustion tests and proximate analysis.
- A Leco AC500 calorimeter for calorific value determination.
- A ball mill equipment, Retsch PM 100 for HGI investigations.
- Size reduction equipment, Retsch SM 200 for particle size reduction.
- Particle size analyser, namely a Mastersizer (2000) of Malvern Instruments Ltd.

3.3. Fuel characterization

All samples except biomass/coal blend were characterized for their physical and chemical properties based on the analytical techniques described in this section.

3.3.1. Proximate Analysis

The proximate analyses involve determining the inherent moisture, ash content and volatile matter present in the sample, with fixed carbon calculated by difference. The analysis was conducted in accordance with the ASTM D-5142. Approximately 1 g of each sample (coal and bamboo sample) was utilized in a TGA 701 Leco instrument for this analysis. The ASTM D-5142 method involved the drying and devolatization in N_2 atmosphere, subsequently, combustion in an O_2 atmosphere. The drying step measures the moisture content by mass loss within the room temperature to 110^0C points in time. The devolatization is measured as the mass loss within a temperature range of 110^0C to 700^0C, whereas the combustion step that follows, evaluates the mass loss between the 700^0C and the 900^0C.The residual mass is considered to be the total ash in the sample.

3.3.2. Ultimate analysis

The ultimate analyses were conducted in accordance with the ASTM D3176-89, standard test method for coal and coke. The elemental constituents Carbon (C), Hydrogen (H), Nitrogen (N), and Sulphur (S) are determined, meanwhile Oxygen (O) is estimated by difference.

3.3.3. Calorific value determination

The calorific value known as the measure of the heat content was determined for both coal and bamboo biomass using a Leco AC500 bomb calorimeter in accordance with ASTM D5865-04. Bomb calorimetry determines the total amount of heat produced from completely burning one unit mass of fuel under high pressure oxygen atmosphere. The system uses an electronic thermometer with an accuracy of 0.0001 ^{0}C to measure the temperature every six seconds, with the results obtained within 4.5 to 7.5 minutes. For each test, approximately 0.96 g of sample was loaded into a crucible and placed on a sample holder in the bomb. Oxygen gas was charged to a pressure of 3000 kPa using a valve pin. The bomb was then lowered into the calorimeter to commence the analysis. Water from a thermostatically controlled tank circulated the calorimeter's walls using a jacket circulation system. This provided a controlled temperature

environment around the bomb during the determination. The calorimeter measured the heat energy produced per unit mass in burning.

3.3.4. Particle size

The particle size of the samples was measured using a laser based particle size analyzer, namely a Mastersizer (2000) of Malvern Instruments Ltd. The instrument uses wet sample dispersion unit as an integral part of the measurement process.

The sample was slowly added into the dispersion unit containing distilled water (dispersant). The unit is built-in with a stirrer that maintains a homogenized suspension of the sample in the mixture. A laser light is then passed through the suspended particles and measures the laser diffraction which is then translated into particle sizes using the Mastersizer 2000 software. Only the samples with a particle size of -1mm were analysed using this instrument. Samples with a +1mm particle size fraction were characterized using sieves (1000, 850, 600, 425, 300, 212, 150, 106, 75 and 53 μm).

3.4. Thermal treatment Experiment

3.4.1. Torrefaction and Carbonization

The torrefaction and carbonization of the bamboo were conducted in a laboratory scale heated electric muffle furnace embedded with a glass tube reactor, in an inert atmosphere (N_2 gas) to avoid combustion. A schematic representation of the experimental setup is shown in Figure 7 below. Approximately 600g of raw bamboo biomass blocks was charged into the glass tube reactor at room temperature and heated at a constant heating rate of 3^0C/min to the set temperature, and allowed to remain at this temperature for 40 min and thereafter cool down naturally. Nitrogen gas was charged into the furnace at a rate of 0.5 standard litres per minute to create an inert atmosphere. Torrefaction was carried out at 250 and 280^{o}C, meanwhile low temperature carbonization was conducted at slightly higher temperatures, i.e. 350 and 400^{o}C. Table 3 presents a summary of the thermal treatment test conditions.

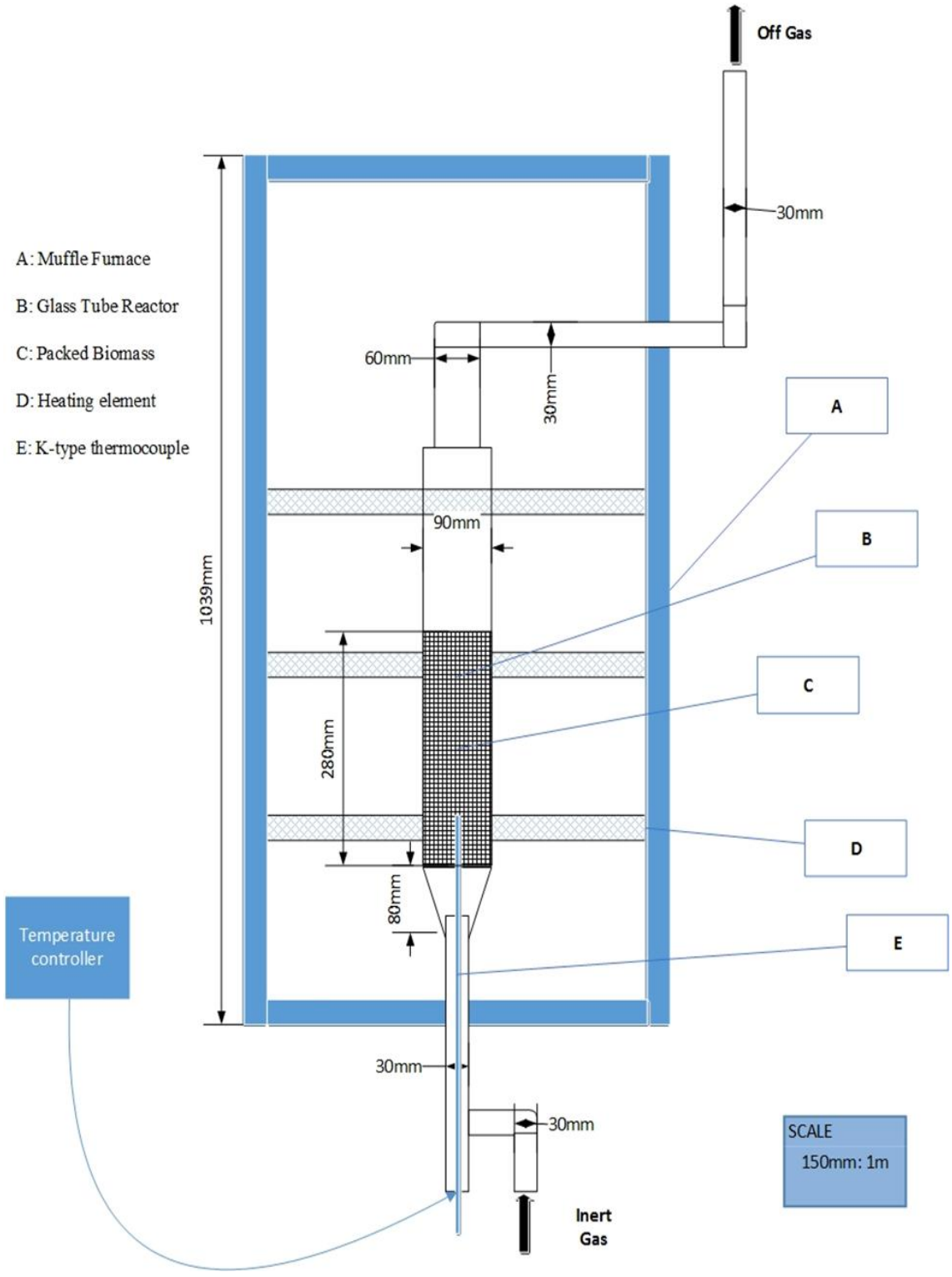

Figure 7: Thermal treatment experimental setup

Table 3: Thermal treatment conditions

Sample ID	Temperature (°C)	Heating rate(°C/min)	New Sample ID	Test type
1 year old bamboo	250	3	1 year T250	Torrefaction
	280		1 year T280	
	350		1 year C350	Carbonization
	400		1 year C400	
3 year old bamboo	250	3	3 year T250	Torrefaction
	280		3 year T280	
	350		3 year C350	Carbonization
	400		3 year C400	
4 year old bamboo	250	3	4 year T250	Torrefaction
	280		4 year T280	
	350		4 year C350	Carbonization
	400		4 year C400	

T250: Torrefied at 250°C; T280: Torrefied at 280°C: C350; Carbonized at 350°C; and C400; Carbonized at 400°C

3.4.2. Energy and Mass yield

The mass yield (n_M) and energy yield (n_E) obtained at different pre-treatment temperature were calculated using Equations 8 and 9

$$n_M = \left({}^{W_t}/_{W_o} \right) \ dry\ basis \tag{8}$$

$$n_E = n_M \left({}^{GCV_t}/_{GCV_o} \right) \ dry\ basis \tag{9}$$

Where W_0 and W_t are the initial biomass mass and final mass of the biomass after thermal treatment, respectively. GCV_t and GCV_o are the initial biomass gross calorific value and final biomass gross calorific value after pyrolysis, respectively.

3.5. Grindability Test

A modified version of the HGI method was used to determine the grindability of raw bamboo and pre-treated bamboos. Four standard coal samples with known different HGI values were used to determine the calibration curve of the mill. In this approach, a fixed volume (50 cm^3) of each coal with a grain size of 0.6 to 1.18 mm was milled and after 60 revolutions, the size passing 75 µm is recorded. A calibration curve showing HGI and the amount of sample passing 75 µm was established. The same approach was used by Bridgeman *et al* (2010) studying the grindability of two torrefied energy crops. The detailed approach is presented below:

3.5.1. Calibration of the mill

- About 0.5 kg of a standard reference coal with known HGI was crushed using a Retsch cutting mill SM 100, using a 4 mm screen.
- The sample was then sieved using 1.18 mm and 600 µm size sieves.
- A measuring cylinder with an accuracy of ±0.1 cm^3 and a balance accurate to ±0.01g were then used to sample and weigh 50 cm^3 of each sample.
- The 50 cm^3 sample was then transferred into a 500 ml capacity stainless steel milling cup with 25 × 20mm stainless steel balls and ground for 2 minutes at 165 rpm using the Retsch PM 100 ball mill equipment.
- Following this, the sample was removed from the grinding cup and separated using a 75 µm sieve and a sieve shaker (5 mins). The two separate fractions are weighed to the nearest 0.01 g. If there is a loss of sample greater than 0.5 g the test is aborted and repeated.
- The percentage of mass passing through the 75 µm sieve was calculated and recorded
- The process was repeated three more times and an average value calculated from the four results was used.
- The process was repeated for the three other coal samples.
- The results are used to plot a calibration curve for the mill of HGI versus mass percentage passing 75 µm.

Note: Coal samples used were of HGI values of 53, 57, 62 and 78.

3.5.2. Testing of biomass fuel

The same steps as in section 3.5.1 were repeated for all raw bamboo biomass, torrefied, and carbonised fuels, although the results were repeated 3 times. The average of the 3 results for each sample was used to determine the equivalent HGI value using the calibration curve.

3.6. Thermal analysis

3.6.1. Thermo-gravimetric analysis

As aforementioned, this is the common technique for studying the thermal decomposition behaviour of materials. The technique monitors the mass change of a sample as a function of temperature and /or time as the sample is subjected to a defined heating and atmosphere conditions. The combustion behaviour of bamboo biomass and bamboo/coal blends was studied using this technique for non-isothermal heating. The combustion tests were conducted in an oxidative atmosphere using air as a source of oxygen. The thermo-gravimetric analyser (TGA 701 Leco) instrument was used to produce thermal degradation profile. Approximately 100 mg of each sample (particle size of -212 µm) of raw bamboo biomass, coal, pre-treated bamboo and all the different bamboo/coal blends were charged to the TGA. The combustion profiles were obtained by heating the TGA furnace at a rate of 5, 10 and 15 ^{o}C/min to a combustion temperature of 850^{o}C. DTG curves indicating the rate of weight loss (%/min) with increasing temperature were used to determine the combustion properties. Table 4 shows the combustion and co-combustion test matrix of bamboo and high ash coal.

Table 4: Combustion experimental test matrix

Sample ID	Condition 1 (100% Biomass)	Condition 2 (25% Biomass)	Condition 3 (50% Biomass)	Condition 4 (75% Biomass)
1 year Raw	5°C/min	5°C/min	5°C/min	5°C/min
1 year T250				
1 year T280	10°C/min	10°C/min	10°C/min	10°C/min
1 year C350				
1 year C400	15°C/min	15°C/min	15°C/min	15°C/min
3 year Raw	5°C/min	5°C/min	5°C/min	5°C/min
3 year T250				
3 year T280	10°C/min	10°C/min	10°C/min	10°C/min
3 year C350				
3 year C400	15°C/min	15°C/min	15°C/min	15°C/min
4 year Raw	5°C/min	5°C/min	5°C/min	5°C/min
4 year T250				
4 year T280	10°C/min	10°C/min	10°C/min	10°C/min
4 year C350				
4 year C400	15°C/min	15°C/min	15°C/min	15°C/min

T250: Torrefied at 250^{o}C; T280: Torrefied at 280^{o}C: C350; Carbonized at 350^{o}C; and C400; Carbonized at 400^{o}C

High ash coal also underwent combustion tests at the 3 set heating rates. Combustion experiments were conducted at 3 different heating rates to satisfy the requirements of the kinetic methods used for interpreting and solving the kinetic parameters of the reactions taking place.

3.6.2. Kinetic analysis

Ozawa and Kissinger methods were used to evaluate the kinetic parameters of the combustion reaction. For studying the interaction of two fuels during co-combustion, a calculated DTG curve was compared to the actual experimental DTG curve of the blend obtained from TGA. A calculated DTG curve was based on a weighted average model (Equation 10), and the calculated DTG curve for the individual component in the blends (bamboo/coal) at different % volume ratio was determined as shown in Equation 10.

$$\left(\frac{dm}{dt}\right)_{sum} = y_1\left(\frac{dm}{dt}\right)_{biomass} + y_2\left(\frac{dm}{dt}\right)_{coal} \quad (10)$$

Where $(dm/dt)_{biomass}$ and $(dm/dt)_{coal}$ are the normalized rates of mass loss of biomass and coal, respectively, obtained from individual experiments. y_1 and y_2 are mass fraction of biomass and coal in the blend, respectively. The reactivity (R_m) of the combusting material was quantified using the same expression as that used by Bada *et al* (2014) and is presented in Equation 11:

$$R_m = \frac{100 \times \mathrm{DTG_{max}}}{\mathrm{PT}} \tag{11}$$

Where $\mathrm{DTG_{max}}$ is the maximum weight loss rate (%/min) and PT is the corresponding peak temperature.

CHAPTER 4: RESULTS AND DISCUSSIONS

This Chapter presents the results of the tests and analyses outlined in Chapter 3.

4.1.Fuel Characterisation

The results of the proximate analysis of the raw and thermally treated bamboo are depicted in Table 5, along with their calorific values. The results of the ultimate analyses for raw samples (1, 3 and 4 year old bamboo) are presented in Table 6.

Table 5: Fuel properties of raw and thermally treated bamboo

Sample ID	*As received proximate*				*Dry proximate*			
	M	FC	VM	Ash	FC	VM	Ash	CV
	wb.%	wb.%	wb.%	wb.%	db.%	db.%	db.%	MJ/kg
Raw 1 year	7.97	16.59	74.58	0.86	18.03	81.04	0.93	18.53
1 year T250	1.26	45.58	50.72	2.44	46.16	51.36	2.47	25.94
1 year T280	0.92	50.21	46.41	2.47	50.67	46.84	2.49	27.78
1 year C350	2.52	66.91	27.02	3.56	68.64	27.72	3.65	28.51
1 year C400	1.99	68.55	26.88	2.58	69.94	27.43	2.63	28.54
Raw 3 year	7.01	16.97	73.64	2.37	18.25	79.20	2.55	17.10
3 year T250	3.05	52.32	38.33	6.30	53.97	39.54	6.50	27.34
3 year T280	3.18	64.60	25.10	7.13	66.71	25.92	7.36	28.39
3 year C350	3.30	66.34	22.13	8.25	68.60	22.88	8.53	29.76
3 year C400	4.14	68.46	18.90	8.50	71.42	19.72	8.87	30.17
Raw 4 year	8.09	17.69	72.81	1.41	19.25	79.22	1.53	17.63
4 year T250	1.41	57.76	37.25	3.59	58.58	37.78	3.64	25.46
4 year T280	1.62	62.61	31.63	4.15	63.64	32.15	4.21	26.38
4 year C350	2.07	71.62	21.62	4.69	73.14	22.08	4.78	29.16
4 year C400	2.62	74.59	17.75	5.04	76.60	18.23	5.18	30.24
Coal	6.28	29.64	19.36	44.72	31.63	20.66	47.72	12.70

M: Moisture; FC: Fixed carbon; VM: Volatile matter; CV: Calorific value; wb: Wet basis and db: Dry basis

Table 6: Ultimate analyses of untreated bamboo

Sample ID	*Ultimate, wt % as received or air dried*				
	N	C	H	S	O
1 year old bamboo	0.88	44.91	6.17	0.07	47.97
3 year old bamboo	0.41	46.76	6.22	0.02	46.60
4 years old bamboo	0.32	46.52	6.26	0.03	46.87

N: Nitrogen; C: Total carbon; H: Hydrogen; S Total sulphur; and O: Oxygen

The proximate and ultimate analysis of raw bamboo samples showed that the raw fuel has low ash contents (see Table 5) and an insignificant amount of sulphur (Table 6). The nitrogen content is also low, suggesting that NO_x emissions might be minimised during combustion. These characteristics are essential for clean coal combustion conditions (Gil *et al*, 2010). There was little difference observed from the proximate results of the three raw bamboo samples in terms of moisture content, fixed carbon and volatile matter, these ranged from 7.01 to 8.09%, 18.03 to 19.25% (db) and 79.20 to81.04% (db), respectively. The calorific value was found to be between 17.10 and 18.53 MJ/kg. Rousset *et al* (2011) also found comparable proximate results on raw *Bambusa vulgaris*. *Bamusa multiplex* studied by Bada *et al* (2014) gave completely different proximate results. However, the calorific value reported by Bada *et al* (2014) on raw *Bambusa multiplex* was comparable to that of raw bamboo samples tested in this work.

Torrefaction and low temperature carbonisation treatments were successfully applied to improve the fuel properties of the raw bamboo samples. Fixed carbon and calorific value were both observed to increase with the increase in treatment temperature. Consequently, moisture and volatile matter content were reduced by thermal treatment. This is as a result of the free moisture driven off followed by devolatilisation, resulting in a product with less volatile matter and moisture.

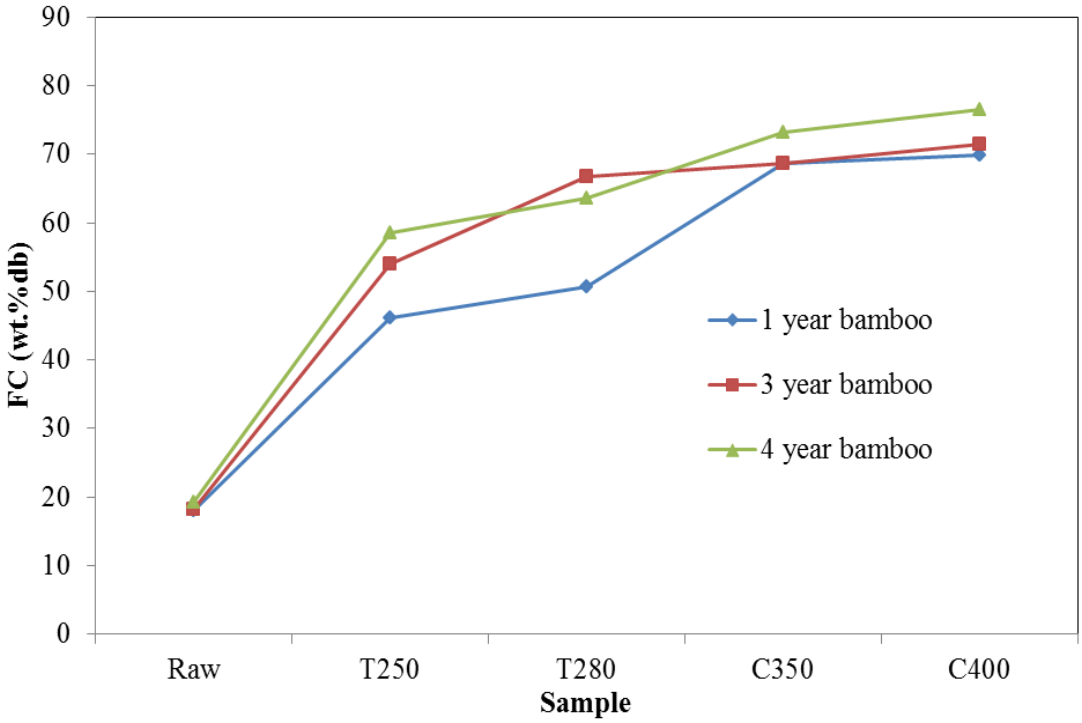

Figure 8: Fixed carbon content after thermal treatment

The plot of the fixed carbon (FC) obtained from all the thermally treated samples against thermal temperature was depicted in Figure 8. It can be seen that the fixed carbon for the 4 year old bamboo was more than tripled from 19.25% to 63.64% by torrefaction at 280°C and increased to 76.6% by low temperature carbonisation at 400°C. Similarly, a study by Park *et al* (2012) found that the FC content of woody biomass was more than tripled after torrefaction at 275°C. Carter (2012) also reported a FC content of 55.43%, 52.65% and 57.94% for pine, sweetgum and switchgrass, respectively, torrefied at 275°C for 45 min. The older bamboo is observed to have a higher FC content at all treatment temperatures with the exception of torrefaction at 280°C, where a slightly higher FC content was observed for a 3 year old bamboo sample. Also worth noting is that 1 year old and 3 year old bamboo show similar FC contents at the carbonisation temperatures tested. In conclusion, it has been shown that the 4 year old bamboo carbonised at 400°C has the highest FC content.

The effect of thermal treatment on volatile matter content was studied and the results are presented in Figure 9 below.

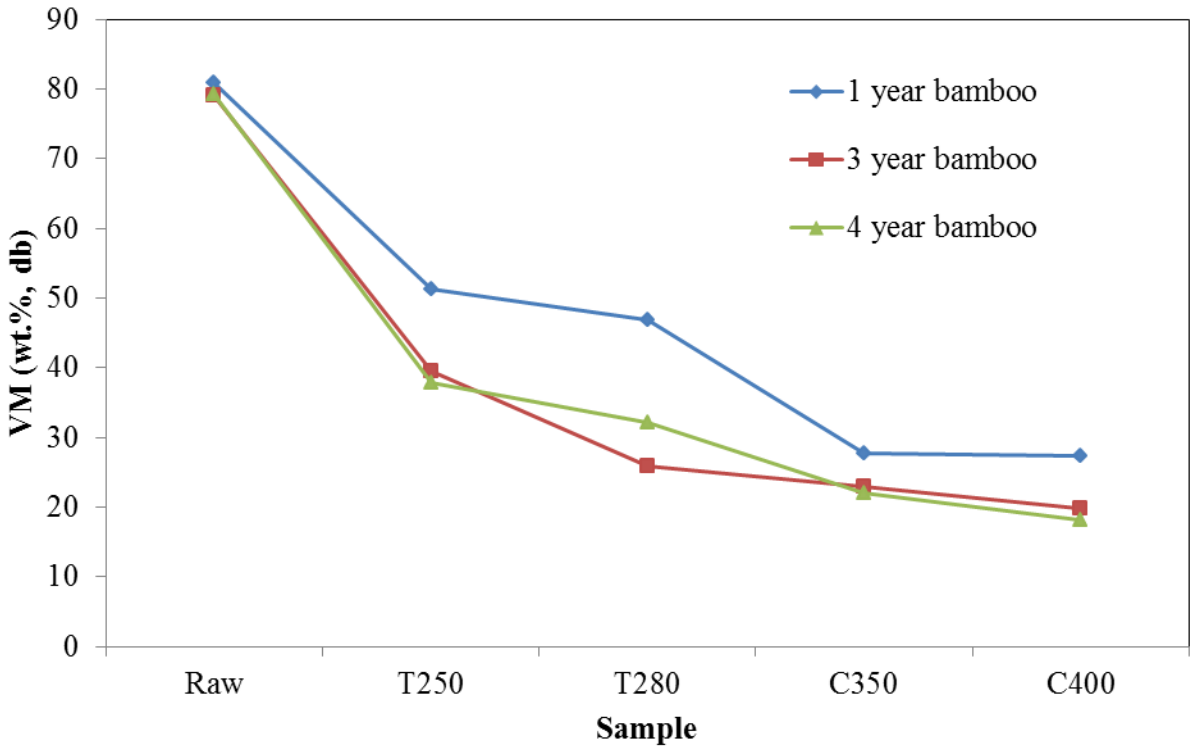

Figure 9: Effect of thermal treatment on volatile matter content

Thermal treatment involves the decomposition of the active volatiles in the biomass and consequently reduces the volatile content in the final treatment material. As expected, Figure 9 shows that the VM content decreases with an increase in harsh treatment conditions irrespective of the age of the bamboo. The VM content of 3 year and 4 year old bamboo samples was decreased by about half from 79% to 37% and 39% by torrefaction at 250°C. Moreover, VM content of 3 year and 4 year old bamboo samples torrefied at 280°C was further reduced to 25.92% and 32.15%, respectively. Volatiles remaining at 350^{o}C and 400^{o}C was just slightly less for both samples than the 280°C value. The degree at which the bamboo samples tested in this study devolatilized was found to be more pronounced than samples reported by other authors, such as *Bambusa vulgaris*, pine chips, logging residue chips, willow, eucalyptus and woody biomass (Rousset *et al*, 2011; Phanphanich and Mani, 2011; Park *et al*, 2012; and Ibrahim *et al*, 2013). Biagini *et al* (2002) further reported that for co-combustion process, a VM content of

about 35% is desirable to provide stable flame in the boiler. In this investigation, volatile matter after carbonisation was well below 35% for all bamboo samples. Therefore, 1 year old bamboo torrefied at 280°C is expected to perform very well in power station based on this fact. Also, raw bamboo samples (1, 3 and 4 year old) are expected to ignite easily (have low ignition temperature) during combustion because of their high VM content. Figure 10 below represents the volatile matter/fixed carbon (VM/FC) ratio of the coal, the raw and the thermally treated bamboo. Untreated biomass typically has a ratio greater than 4, meanwhile, coal is found with a ratio below 1 (Gil *et al*, 2010). Raw bamboo samples showed ratios that are in agreement with the aforementioned findings by Gil *et al* (2010). It was further shown in Figure 10 below that the VM/FC ratios of the thermally treated bamboo samples are below 1 at all treatment levels except for 1 year old bamboo torrefied at 250°C, suggesting similar fuel properties as coal used in this study.

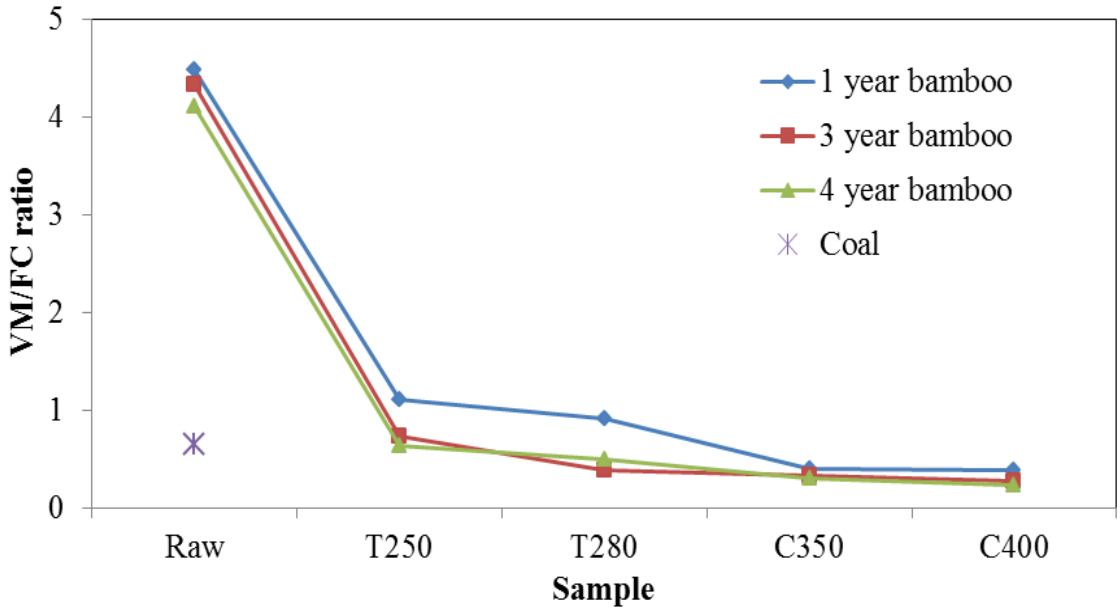

Figure 10: Volatile matter/fixed carbon ratio of raw and thermally treated bamboo.

The plot of the ash content obtained from each sample against the thermally treatment temperature is presented in Figure 11 below. The ash content was seen to increase as the treatment temperature increases. This can be expected because of the loss of volatiles and moisture and therefore a higher proportion of minerals in the body of the biomass materials. During this time, a re-arrangement or transformation of mineral contents occurs in the bamboo

samples during thermal treatment thereby forming further inorganic materials and oxides. When grouped together, these materials are referred to as ash (Sadaka *et al*, 2014; and Bada *et al*, 2015). Furthermore, the increase in ash was rapid at torrefaction temperature of 250°C, however slow at higher treatment temperatures for all bamboo samples, due mainly because all volatiles and moisture had been released by that time. The 1 year old bamboo had the lowest ash content (0.93-3.65%) at all treatment temperatures as can be seen Figure 11 below. Meanwhile, at all treatment temperatures the ash content for the 3 year old bamboo was at least 1.5 and 2 times more than that of the 4 year old bamboo and 1 year old bamboo, respectively.

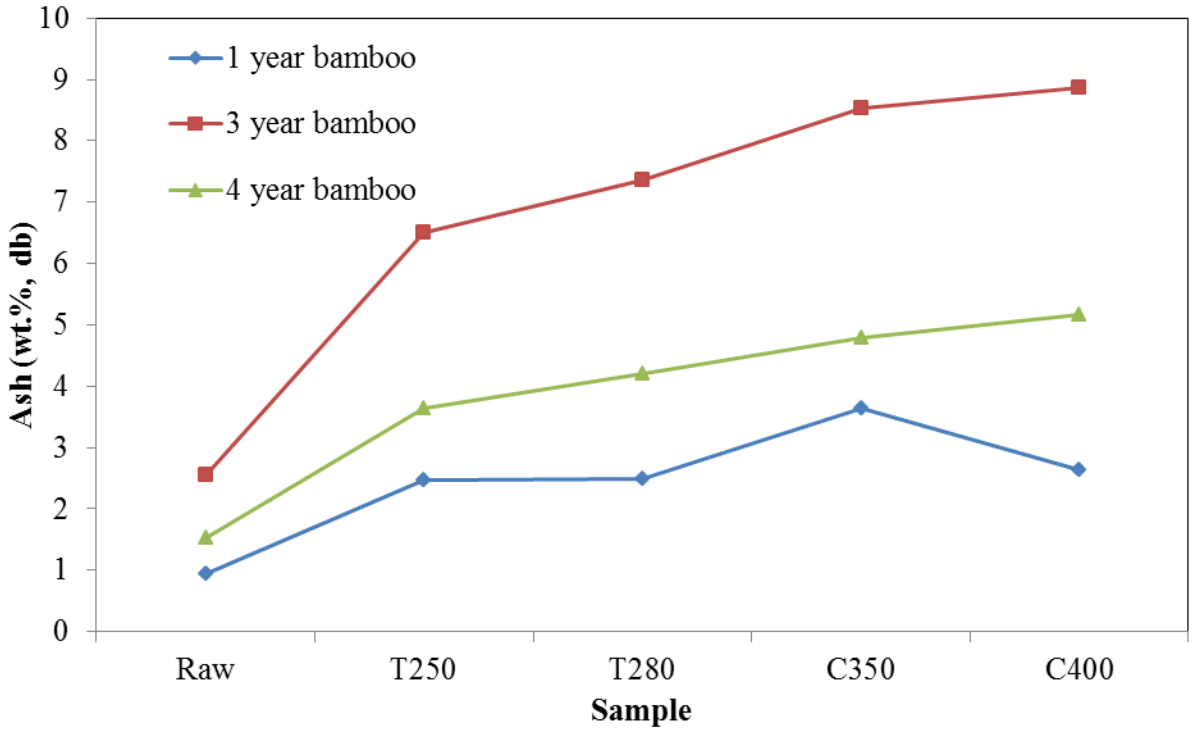

Figure 11: Effect of temperature on the ash content

The effect of treatment temperature on calorific value (CV) is shown in Figure 12 below. The CV of all raw bamboo samples (1, 3 and 4 year old) was increased by at least 40% after torrefaction at 250°C while the increase was other temperatures was at most 10.5%. This is because more of the active pyrolysis occurs in this temperature range (decomposition of both hemicellulose and partly cellulose). The CV value of the 4 year old bamboo was increased from 17.63 MJ/kg to 26.38 MJ/kg and 30.24 MJ/kg after torrefaction at 280°C and carbonisation at 400°C, respectively. Phanphanich and Mani (2011) found similar results for logging residue

chips torrefied at 275°C. Ibrahim *et al* (2013) and Bada *et al* (2014) also found similar results for eucalyptus and *Bambusa multiplex*, respectively. In conclusion, 4 year old bamboo sample carbonised at 400°C is preferred because it has the highest energy density, indicated by highest CV of 30.24 MJ/kg in Figure 12 below. However, the difference in CV value between 3 year old bamboo and 4 year old bamboo carbonised at 400°C is marginal.

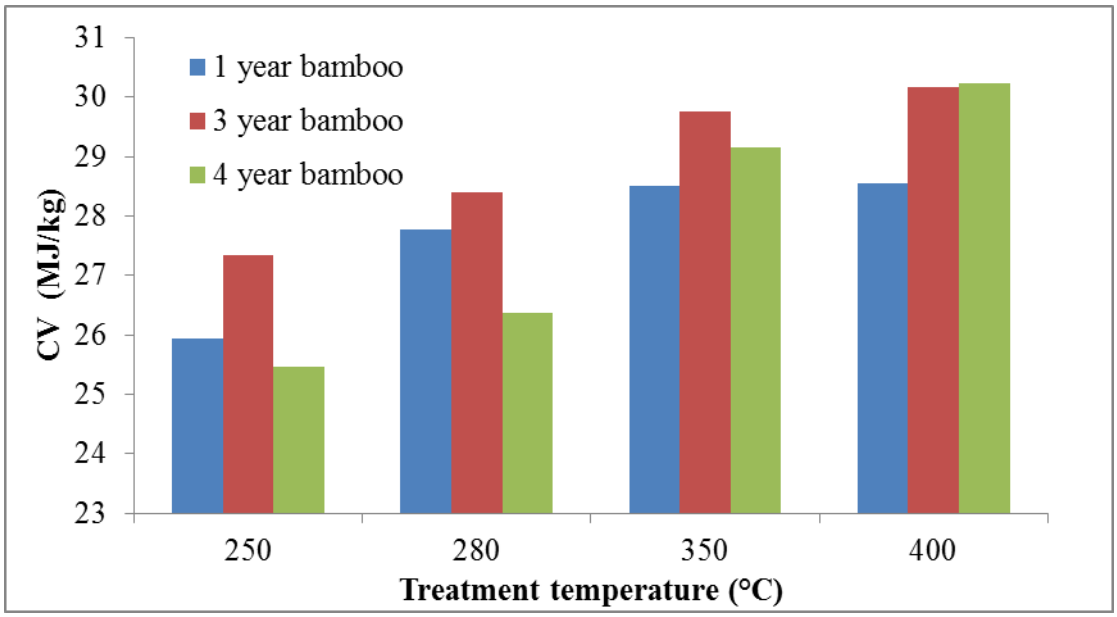

Figure 12: Effect of treatment temperature on calorific value

4.2.Thermal treatment

4.2.1. Mass yield

The mass yield obtained after torrefaction and low temperature carbonisation are presented in Table 7 and Figure 13 below. The mass yield of the torrefied bamboo was higher than that of the carbonised bamboo. This is because the mass loss increases with treatment temperature as a result of the decomposition of bamboo. The decomposition occurs by hemicellulose decomposing within a temperature range of 160°C to 200°C, followed by cellulose within 240°C to 350°C and lignin decomposing within 280°C to 500°C thereby releasing the decomposition products CO, CO_2 and H_2O (Park *et al*, 2012). The torrefied products in this study were found with the highest mass yield, 51%, 40% and 39% for the 4, 3 and 1 year old bamboo, compared to

the carbonized products as seen in Figure 13. Ibrahim *et al* (2013) obtained a higher mass yield of 68.76% on willow torrefied at 270°C for 30 min. Lower mass yields noted in this study was as a result or because of the impact of torrefaction on bamboo, which was similar to that obtained by Rodrigues and Rousset (2009). Meanwhile for carbonisation, Park *et al* (2012) found similar mass yield (32.8%) after carbonisation of woody biomass at 350°C for 30 min.

Table 7: Mass and Energy yield of thermally treated bamboo

Sample ID	Mass loss (%)	n_M	n_E
1 year T250	60.7	0.39	0.55
1 year T280	67.7	0.32	0.48
1 year C350	69.6	0.30	0.47
1 year C400	70.9	0.29	0.45
3 year T250	59.8	0.40	0.64
3 year T280	64.4	0.36	0.59
3 year C350	68.7	0.31	0.55
3 year C400	69.4	0.31	0.54
4 year T250	48.6	0.51	0.74
4 year T280	54.5	0.46	0.68
4 year C350	67.6	0.32	0.54
4 year C400	70.3	0.30	0.51

n_M: Mass yield; n_E: Energy yield

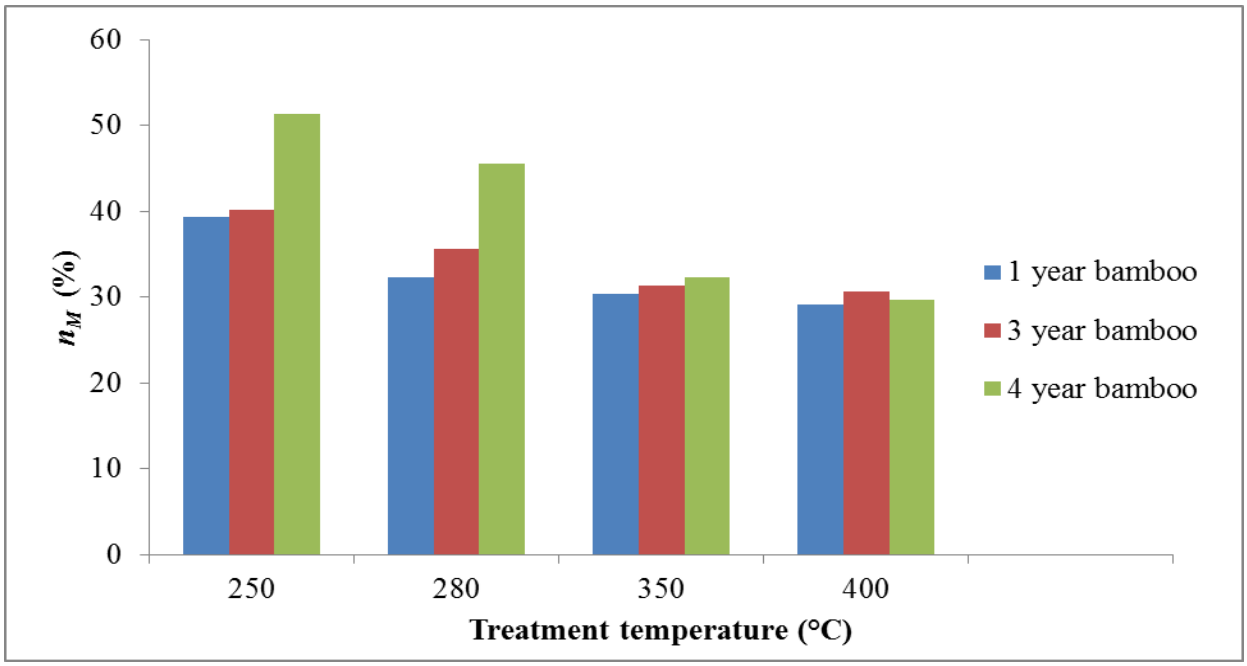

Figure 13: Mass yield at different treatment temperatures

4.2.2. Energy yield

The energy yield results are presented in Table 7 above and Figure 14 below. As can be seen in Figure 14, the energy yield was found to be consistently higher at torrefaction temperatures for all bamboo samples. The torrefied 4 year old bamboo sample had the highest energy yield of 74% and 68% after torrefied at 250°C and 280°C, respectively. Rousset *et al* (2011) found energy yield of 78 and 88.4% on bamboo (*Bambusa vulgaris*) torrefied at 250°C and 280°C, respectively. This is likely to be because of low volatile matter content and high CV value in the 4 year old bamboo sample.

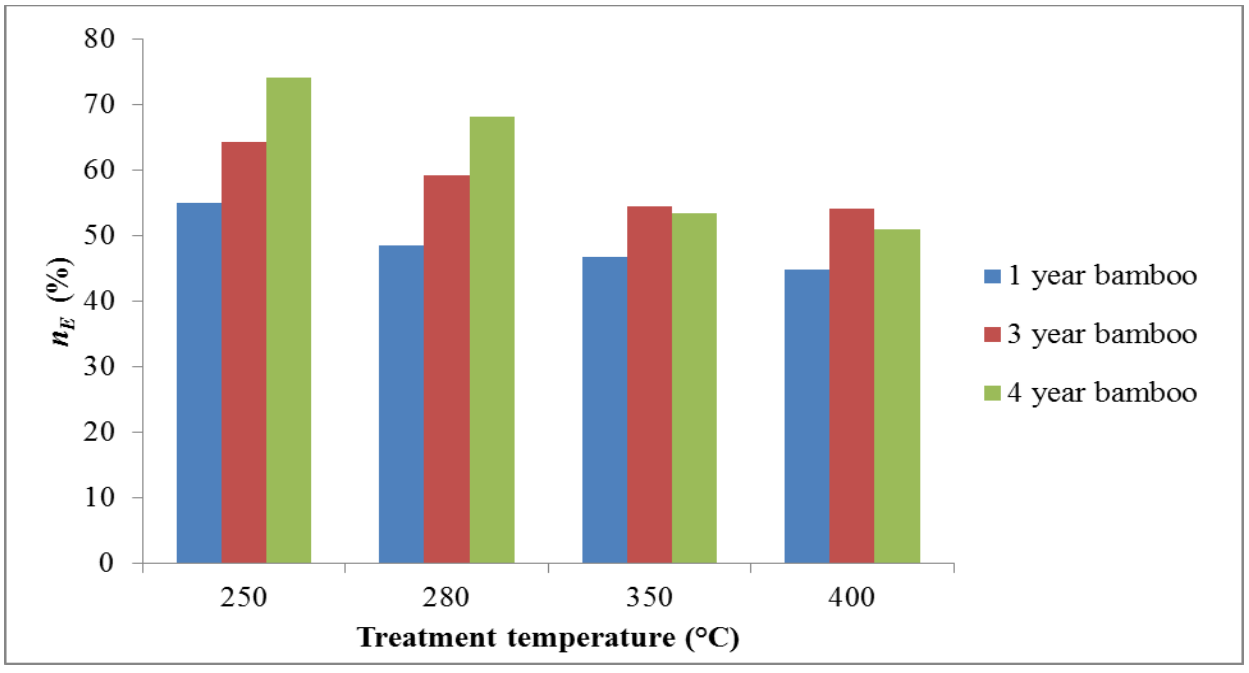

Figure 14: Energy yield at different treatment temperatures

4.3.Grindability

4.3.1. Hardgrove Grindability Index

The process of converting biomass into energy involves grinding of the biomass to fine particles, especially in a pulverized fuel boiler. Therefore, it was essential in this study that the size reduction of bamboo using the Hardgrove Grindability Index (HGI) principle should be investigated, since this, along with other factors might be used in the designing of a mill for pulverizing bamboo. As aforementioned, the HGI was used to measure the grindability of bamboo. The four coal materials of known HGI values were successfully ground in a ball mill machine according to the procedure described in section 3.5. The calibration curve for the four coals is presented in Figure 15. The correlation coefficient (R^2) for the curve is 0.9372.

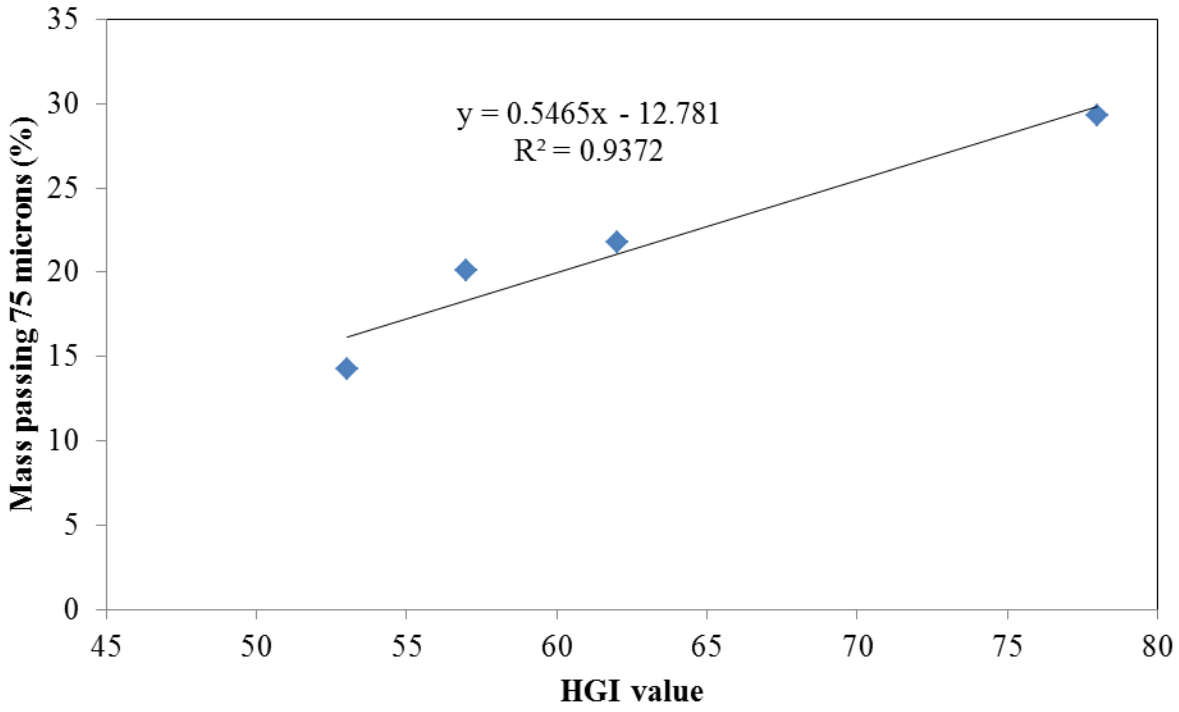

Figure 15: Calibration curve from the four coal samples

The calibration curve above was used to evaluate the equivalent HGI values of the raw and thermally treated bamboo material. The linear equation describing the calibration curve was manipulated to evaluate the equivalent HGI value when the mass of bamboo material passing through the 75µm sieve (m) is known. This is given by Equation 11.

$$\mathrm{HGI_{equiv}} = \frac{\mathrm{m} + 12.781}{0.5465} \quad (11)$$

The equivalent HGI results are shown in Table 8 and Figure 16. It is evident that the raw bamboo performed poorly in these grinding conditions with 0.47% for 1 year old, 0.71% for 3 year old and 0.88% for 4 year old bamboo passing through the 75µm sieve. The corresponding equivalent HGI was 24 for the 1 year old raw bamboo and 25 for both 3 year and 4 year old raw bamboo. The grindability changed remarkably after thermal treatment at all temperatures, with HGI values increasing with the increase in the treatment temperature for all ages of bamboo tested (see Figure 16). This trend is similar to that found by Bridgmen *et al* (2010) for willow and miscanthus energy crops. Ibrahim *et al* (2013) also found a similar trend for eucalyptus and other mixtures of softwoods and hardwoods. All the thermal treatment conditions tested for 1 year and 3 year old bamboo produced thermally treated bamboo with better grindability properties than those of the reference coals used in this work. However, the 4 year old bamboo sample only showed better grindibility relative to the reference coals used in this study at carbonisation temperatures.

Table 8: Equivalent HGI values for the raw and thermally treated bamboo

Sample	Raw		T250		T280		C350		C400	
	m	HGI	m	HGI	M	HGI	m	HGI	m	HGI
1 year	0.47	24	49.70	114	75.63	162	83.88	177	88.50	185
3 year	0.71	25	54.27	123	64.41	141	77.61	165	78.44	167
4 year	0.88	25	12.72	47	22.90	65	51.64	118	56.18	126

HGI: Hardgrove Grindability Index, m: mass of particles passing 75 µm

The equivalent HGI value for 1 year and 3 year old bamboo samples after torrefaction at 250°C was 114 and 123, respectively. This is similar to the HGI value of 122 found by Ohliger *et al*, (2013) on beachwood after torrefaction at 300°C. Meanwhile, after carbonisation at 400°C, an equivalent HGI value of 185 and 167 was achieved for 1 year and 3 year old bamboo, respectively. The 4 year old raw bamboo sample was found to have lower equivalent HGI value at all thermal treatment conditions. After torrefaction at 250°C, the 4 year old bamboo had an equivalent HGI value of 47 which is lower than all the reference coal used in this work.

Moreover, a fuel with an HGI value of 47 is considered to be difficult to grind (Tichanek, 2008 and Ohliger *et al*, 2013). Tichanek (2008) further reports that the preferred HGI value of power station coal is 60 and above. This was achieved after torrefaction at 280°C for a 4 year old bamboo.

It is shown in Figure 16 that there is a significant difference in equivalent HGI values between the 4 year old bamboo and the younger bamboos. There was at least a difference of 24.5% between the 4 year old bamboo and the 3 year old bamboo and an even greater difference when comparing to the 1 year old bamboo. The general trend observed was that a higher equivalent HGI value was achieved for younger bamboo at all treatment conditions and the HGI decreased with an increase in the age of the bamboo with exception of 3 year old bamboo torrefied at 250°C. However, it should be noted that these higher HGI values were achieved at very low mass and energy yields in the younger bamboo.

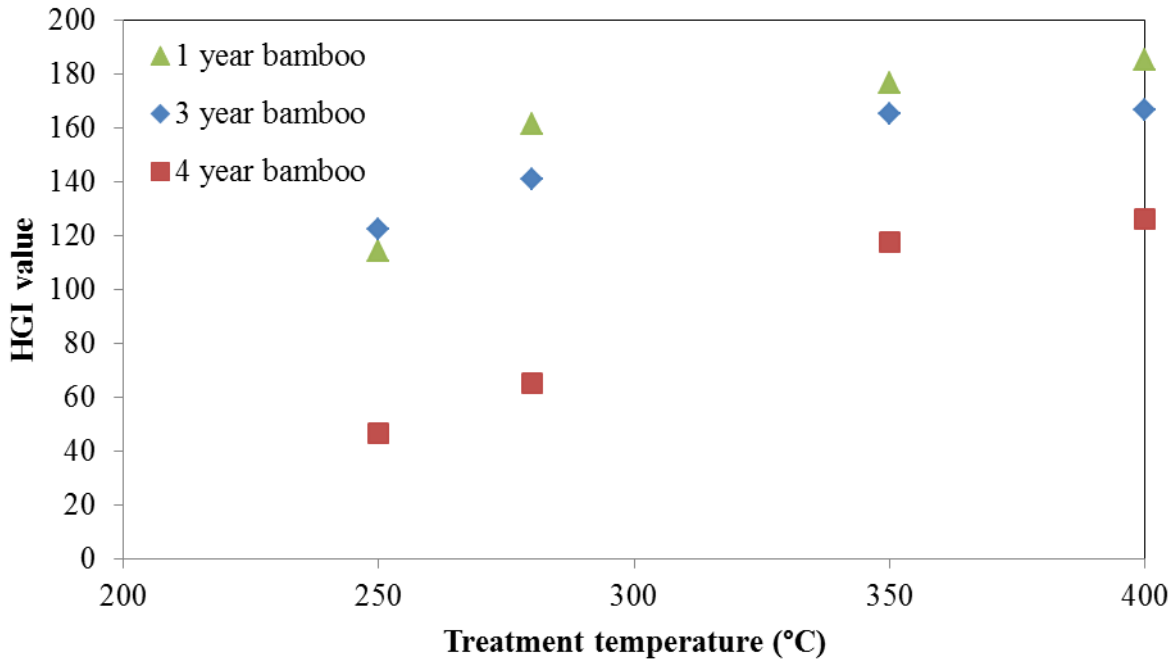

Figure 16: Equivalent HGI values for the torrefied and carbonised bamboo

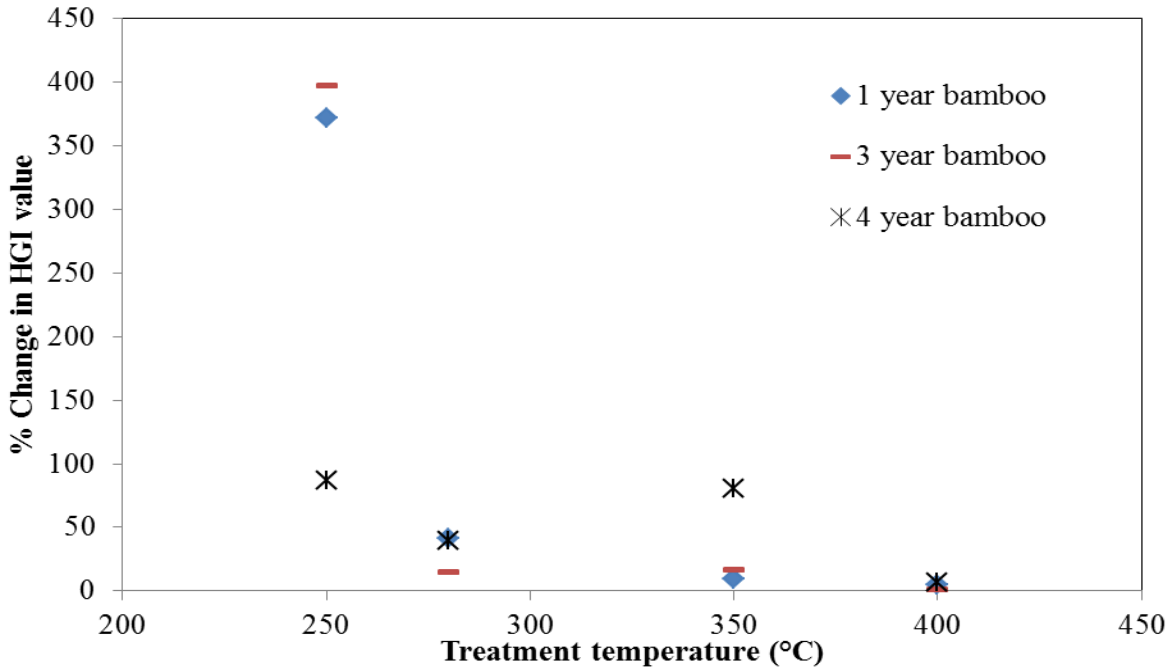

Figure 17: Change in HGI at different treatment temperatures

It is shown in Figure 17 above that increasing thermal treatment temperature has lower impact on the resulting HGI value when in the carbonisation temperature regime. Torrefaction was observed to have more impact on the resulting HGI value or grindability of all bamboos. All bamboos showed the highest percentage change in HGI value at a torrefaction temperature of 250°C. At a carbonisation temperature of 400°C, the highest change in HGI value was 7.04%, which was observed in the 4 year old bamboo. The general trend observed was that treatment temperature becomes less influential on the HGI value as the thermal treatment temperature increases.

4.3.2. Particle size distribution (PSD)

To further complement the HGI results, particle size distribution of the milled raw and the thermally treated bamboo as well as the reference coals were studied. The results for the milled reference coals and raw bamboos are presented in Figure 18 below. It is shown in Figure 18 that the soft coal, given by high HGI value has more fine material and this directly corresponds to more mass passing 75 µm sieve. It has already been demonstrated in this study that the raw bamboo tested has low equivalent HGI values compared to other samples tested. The PSD further confirms that the raw bamboo samples produces less fines after milling indicating poor

grindability. Furthermore, the PSD for all raw bamboos is similar since their equivalent HGI values are also similar.

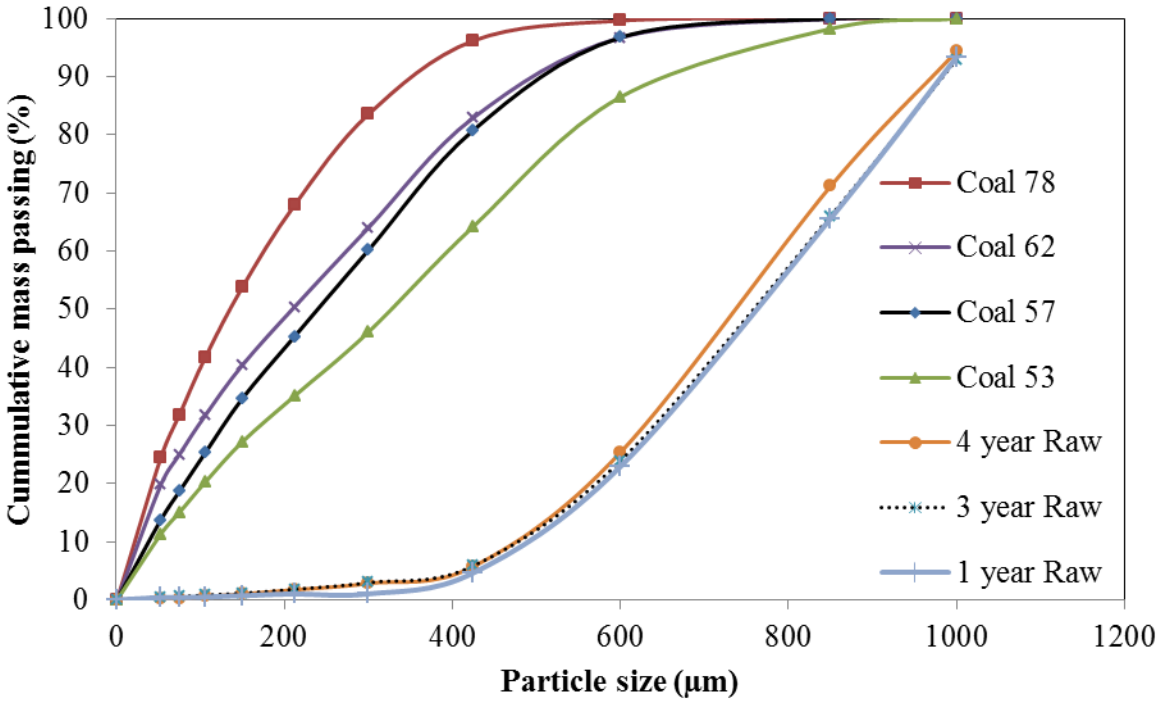

Figure 18: Particle size distribution of the milled reference coal and raw bamboo

Figure 19 below shows the PSD profiles for the milled reference coal and the thermally treated 1 year old bamboo. The PSD profiles show that thermal treatment greatly improved the grindability of the 1 year old bamboo and is in agreement with the equivalent HGI values found. To further illustrate, PSD profiles of the treated 1 year old bamboo presented in Figure 19 have higher weight fraction of fines after milling compared to raw 1 year old bamboo. A fraction of the material with a particle size of -75um for 1 year old bamboo was increased from 0 to above 70% by torrefaction at 280°C and carbonisation at 350°C and 400°C. Also, after torrefaction at 250°C, 1 year old bamboo shows a PSD profile comparable to that of soft coal with an HGI value of 78. This is similar to what Bridgeman *et al* (2010) found on miscanthus torrefied at 290°C. At other higher thermal treatment conditions the PSD profiles for the 1 year old bamboo show that the grindability of the treated bamboo is superior to those of the soft coal used in this study. The PSD profiles for the 3 year and 4 year old bamboo are presented in Figure 20 and Figure 21, respectively.

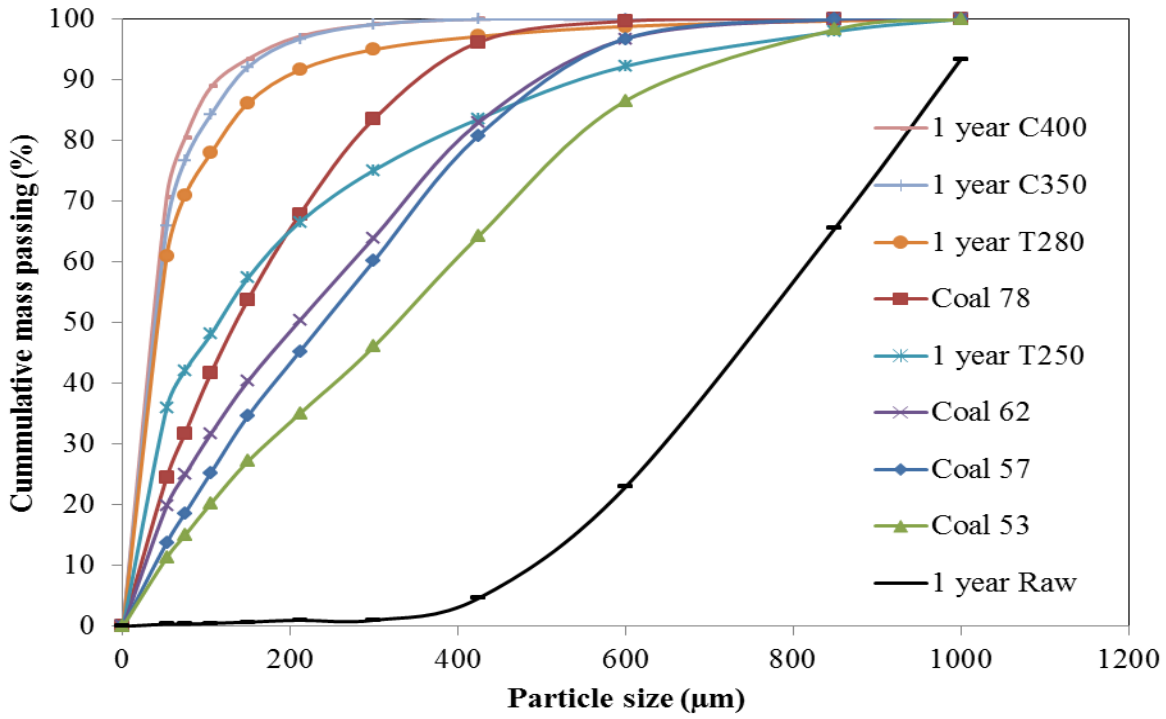

Figure 19: Particle size distribution of the milled reference coal and the thermally treated 1 year old bamboo

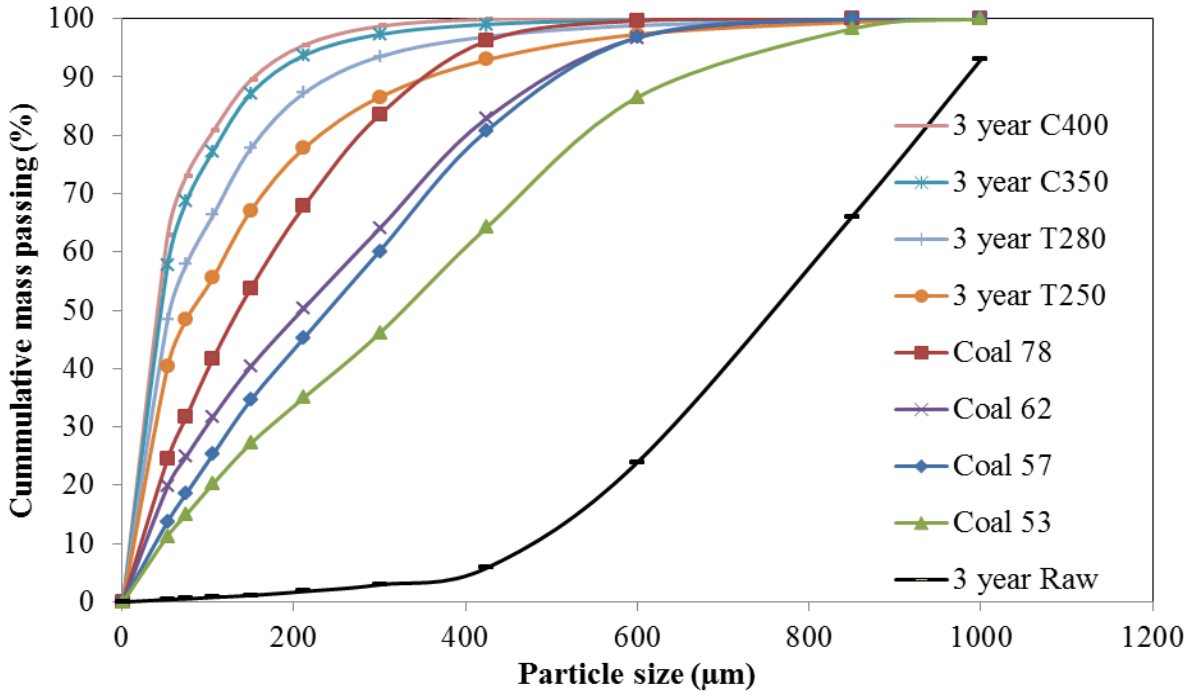

Figure 20: Particle size distribution of the milled reference coal and the thermally treated 3 year old bamboo

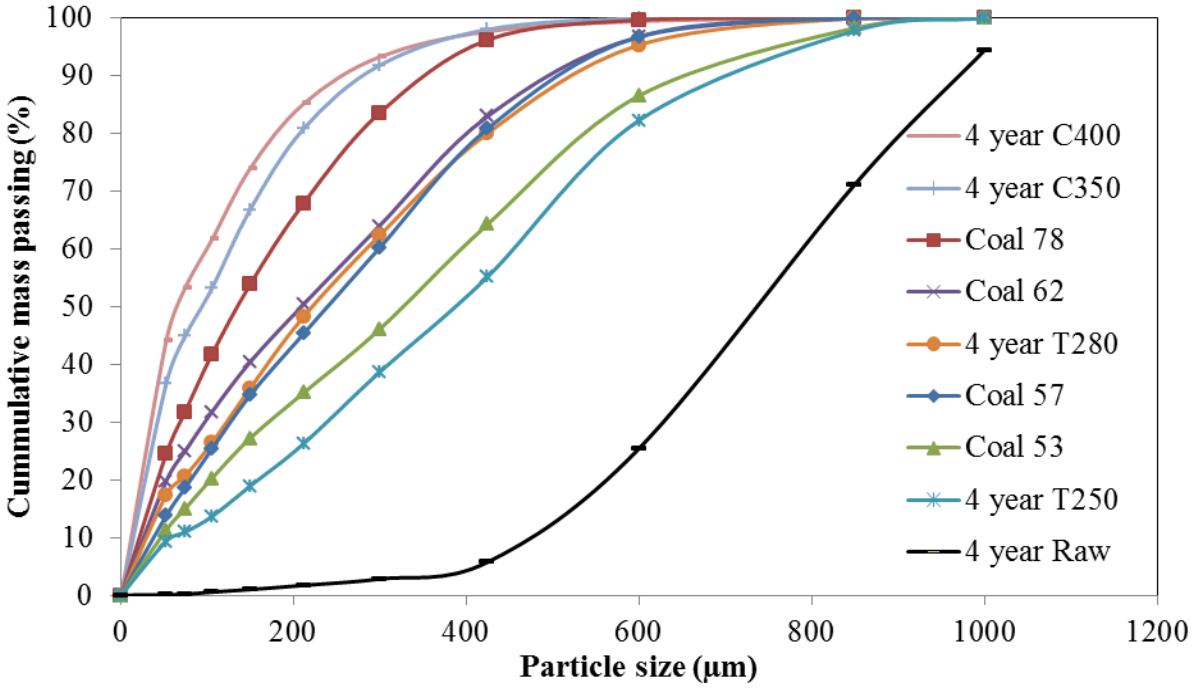

Figure 21: Particle size distribution of the milled reference coal and the thermally treated 4 year old bamboo

The PSD profile for the thermally treated 3 year old bamboo shows similar profiles to that of the treated 1 year old bamboo. Smaller particle sizes were observed in all milled treated 3 year old bamboo than in the soft coal used in this study. For the 4 year old bamboo, only carbonised bamboo showed superior grindability to soft coal, which was expected due to the corresponding HGI values. Four year old bamboo torrefied at 280°C (HGI of 65) showed similar PSD profiles to those of coals with HGI of 57 and 62. It can be said that torrefaction changed the grindability behaviour of bamboo taking it closer to that of coal in this study. The general trend observed is that the particle size distribution profiles are progressively skewed towards the smaller particle sizes with increasing thermal treatment temperature for all bamboos. Phanphanich and Mani (2011) observed similar trends on pine chips and logging residues.

4.4. Thermal Analysis

4.4.1. Repeatability

In order to make comparisons between different samples, factors such as sample quantity, heating rate, and airflow rate were the same between tests. Repeatability checks of the TGA equipment for different test materials used were conducted. The peak temperature (PT) reflects relative reactivities of the fuels and is generally considered to be the most important feature of the DTG curves obtained from TGA experiments. Under the proper conditions, PT should be repeatable to within about 5°C (Norton, 1993). Repeatability for this work was checked and the difference in PT was within 5°C. The graphs for repeatability check studies are presented in Appendix A.

4.4.2. Combustion of coal, raw and thermally treated bamboo

The combustion profiles of raw bamboo and coal are given in Figure 22 below. The critical temperatures are presented again in Table 9. Figure 22 shows that the combustion of bamboo occurs in stages as expected. The first stage was moisture being driven off (25°C to 140°C), followed by devolatilization stage (142°C to 284°C) and thereafter, char combustion (>300°C). Bada *et al* (2014) also demonstrated 3 distinct stages of the combustion of *Bambusa multiplex*. The combustion of raw bamboo is observed to be rapid and occurs at lower temperatures when

compared to that of coal. This is evident from the peak and burnout temperatures of 224-250°C and 460-475°C, respectively, depending on the bamboo age (see Figure 22). Meanwhile, the peak and burnout temperatures of coal are 423°C and 565°C, respectively. Coal was seen with a burnout temperature of at least 90°C higher than that of the raw bamboo. This is expected because coal has higher FC content than all raw bamboo samples. Moreover, it was observed that the reactivity of raw bamboo is at least 4 times more than that of coal (see Table 9) and this is expected from a material of the high volatile matter content. Bamboos with a peak temperature occurring in the lower temperature region on the thermograph or during combustion have the highest reactivity. This is in agreement with what Kastanaki and Vamvuka (2006) found when studying the reactivity of coal, olive and kernel char. Similarly, as other authors found, the coal exhibits a single stage combustion and also the ignition temperature of coal is higher than that of untreated bamboo (Kastanaki and Vamvuka, 2006; and Park *et al*, 2012). In summary, raw bamboos ignite easily at low temperatures and are more reactive than the coal used in this study. Moreover, in terms of reactivity, 1 year old raw bamboo is the better fuel than all other fuels tested.

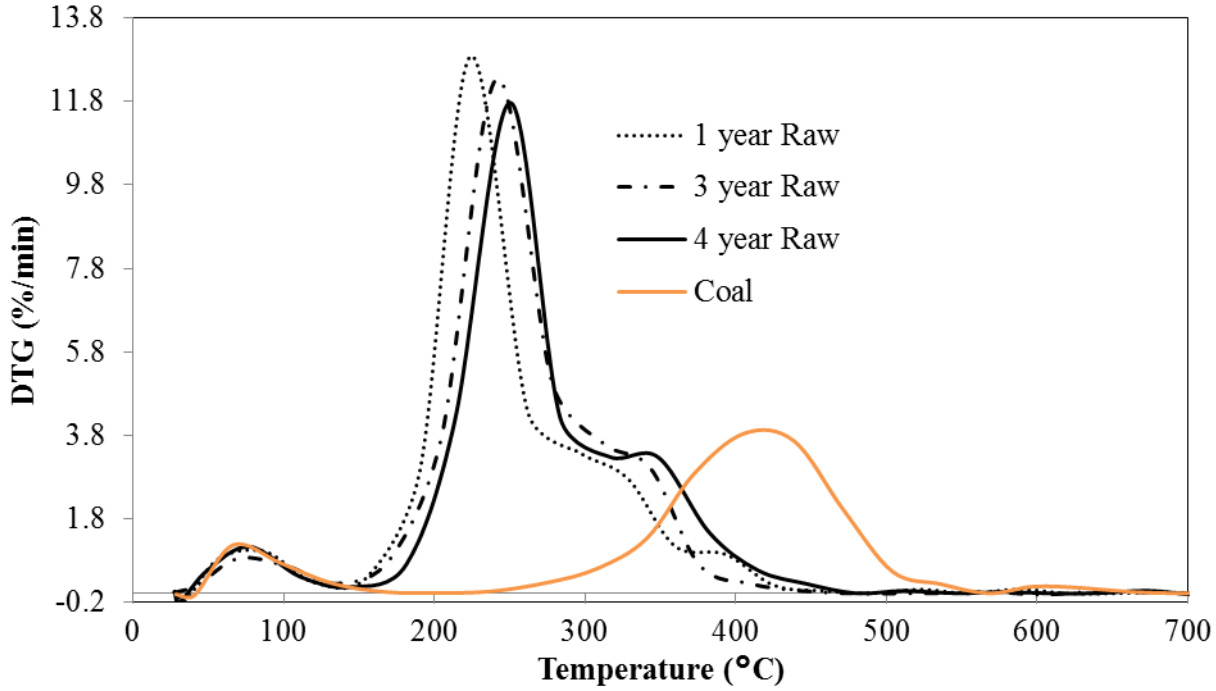

Figure 22: DTG curves for coal and raw bamboo.

Table 9: Ignition, peak and burnout temperature for coal and raw bamboo.

Sample	IT (VM)(°C)	PT (°C)	BT (°C)	*Rm* (%/min/K)	FC (%, db)
1 year Raw	141	224	460	2.59	18.03
3 year Raw	130	241	446	2.40	18.25
4 year Raw	145	250	475	2.25	19.25
Coal	247	423	565	0.55	31.63

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity; FC: Fixed carbon and db: Dry basis.

The DTG curves for 1 year old bamboo at all treatment temperatures are presented in Figure 23 below. The associated critical temperatures and reactivity are shown in Table 10. It was noted that the DTG_{max} of the raw 1 year old bamboo was decreased by 60% after torrefaction at 250°C and decreased even further at higher treatment temperatures as shown in Figure 23. This was expected as the volatile matter content of the thermally treated samples decreased with increased fixed carbon content, suggesting the coal nature of the treated bamboo. The respective combustion profiles of the 1 year old bamboo treated at different temperatures showed 2 peaks, while that of coal showed a single peak (see Figure 23 below). Park *et al* (2012) also observed 2 peaks on the combustion profile of low temperature carbonised woody biomass. Also worth noting is that PT and BT at all temperatures were increased and 1 year old bamboo sample carbonised at 400°C had the highest PT and BT. This could be the result of high FC content in this carbonised sample. However, it should be noted that these PT and BT are still lower than that of coal used in this study. This implies that the combustion of raw and treated 1 year old bamboo will be completed earlier than that of coal.

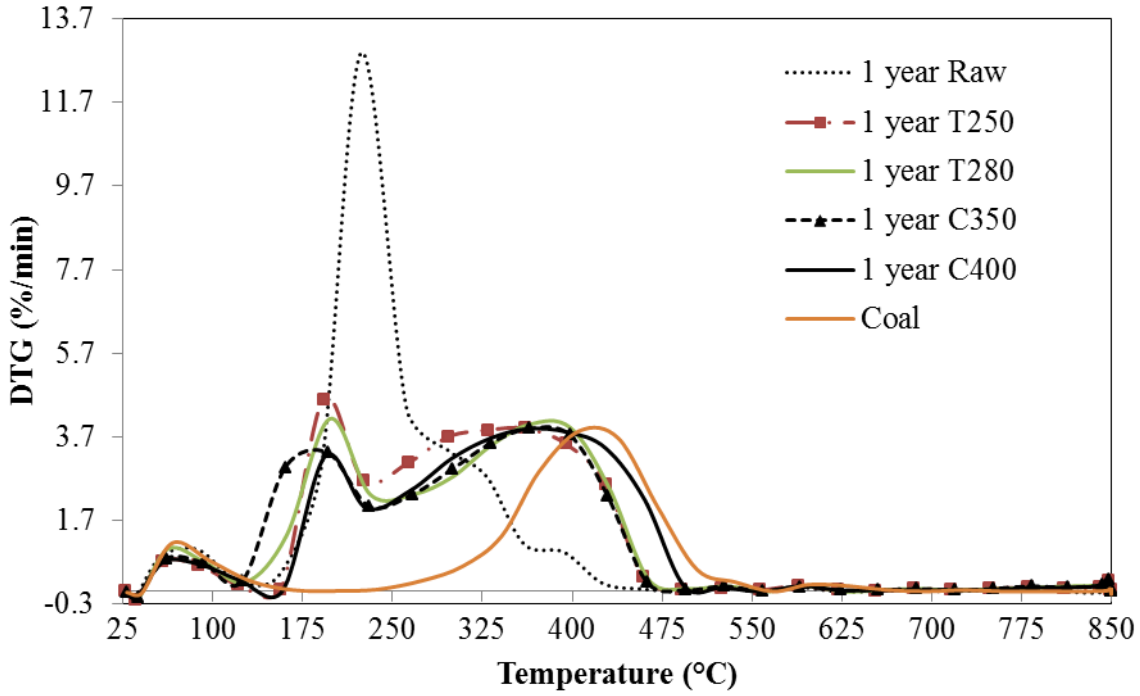

Figure 23: DTG curves for thermally treated 1 year old bamboo and coal.

The reactivities of 1 year old bamboo T280, C350 and C400 within the temperature region (230-496°C) were found to be similar as seen in Figure 23 above and Table 10 below. Meanwhile, that of 1 year old bamboo torrefied at 250°C sample was 62% higher when compare to other thermally treated 1 year old bamboo samples, probably as a result of high VM in this sample**.** It should be noted however that 1 year old raw bamboo still a better fuel in terms of reactivity and lower burnout temperature compared all other thermally treated 1 year old bamboo and coal.

Table 10: Ignition, peak and burnout temperatures for thermal treated 1 year old bamboo

Sample	IT (VM)(°C)	PT (°C)	BT (°C)	*Rm* (%/min/K)	FC (%, db)
1 year Raw	141	224	460	2.59	18.03
1 year T250	160	193	473	0.99	46.16
1 year T280	130	363	474	0.61	50.67
1 year C350	125	364	476	0.61	68.64
1 year C400	161	364	496	0.63	69.94
Coal	247	423	565	0.55	31.63

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity; FC: Fixed carbon and db: Dry basis.

Figure 24 below depicts the DTG curves for the raw and the thermally treated 3 year old bamboo sample. The 3 year old bamboo sample carbonised at 400°C showed a single DTG peak, while the other thermally treated 3 year old bamboo samples showed two peaks. Park *et al* (2012) also made similar observation on the low temperature carbonised woody biomass. The ignition, peak and burnout temperatures of raw and thermally treated 3 year old bamboo are presented in Table 11 below. The IT of the thermally treated 3 year old bamboo samples is higher than that of the raw sample, due to lower VM content present in the treated samples. Park *et al* (2012) also reported on the increase in IT of woody biomass after subjected to thermal treatment. Also, the PT and BT of the torrefied and carbonised 3 year old bamboo samples were also observed to increase as the thermal treatment temperature increases. Bada *et al* (2014) reported a similar observation on *Bambusa multiplex*. Moreover, it should be noted that though the 3 year old bamboo thermally treated at 400°C has similar profile with coal, almost same peak and burnout temperature, it still ignites at lower temperature region compared to coal. The reactivity of the thermally treated 3 year old bamboo sample decreased, which can attributed to the decrease in VM content of the treated samples (see Table 11 below).

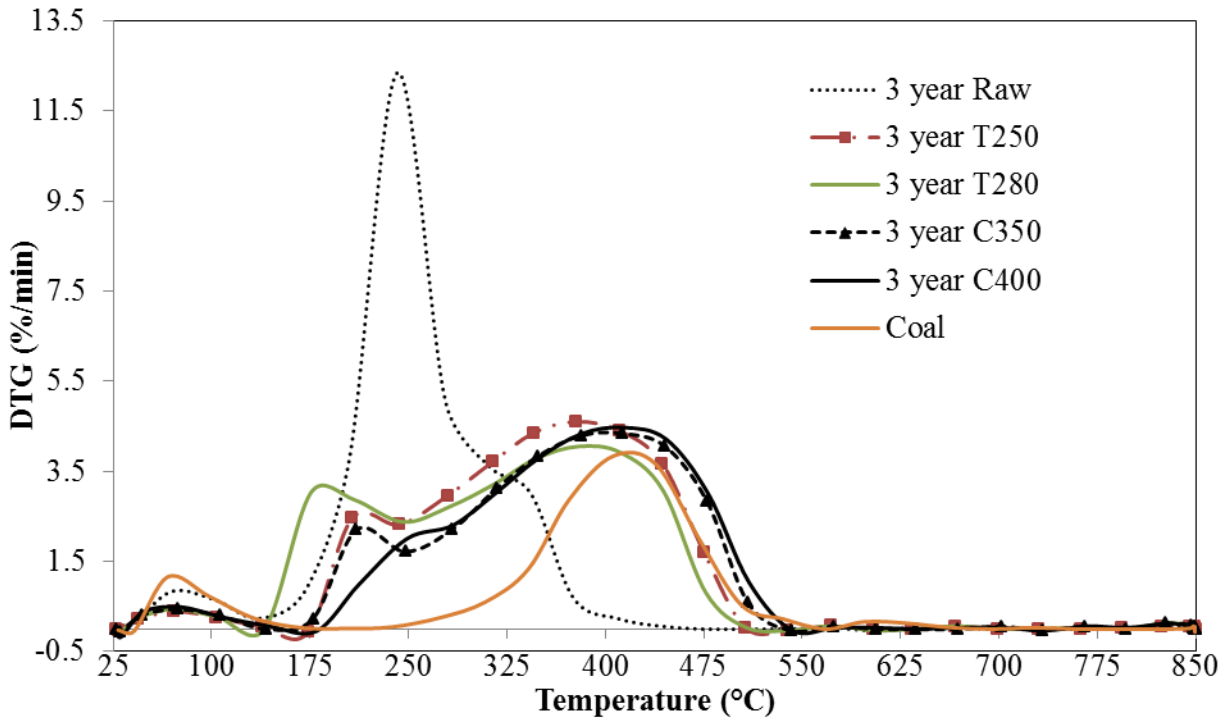

Figure 24: DTG curves for thermally treated 3 year old bamboo and coal

Table 11: Ignition, peak and burnout temperatures for thermal treated 3 year old bamboo

Sample ID	IT (VM)(°C)	PT (°C)	BT (°C)	*Rm* (%/min/K)	FC (%, db)
3 year Raw	130	241	446	2.40	18.25
3 year T250	174	377	507	0.71	53.97
3 year T280	145	379	509	0.61	66.71
3 year C350	176	412	542	0.63	68.60
3 year C400	189	414	543	0.65	71.42
Coal	247	423	565	0.55	31.63

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity; FC: Fixed carbon and db: Dry basis.

The DTG curves for the thermally treated 4 year old bamboo samples are presented in Figure 25 below, with the corresponding critical temperatures given in Table 12. The 4 year old bamboo sample carbonised at 400°C showed a single DTG peak and similar profile as that of coal. The burnout characteristics of the low temperature carbonised 4 year old bamboo samples are almost similar to that of coal and still ignites and burnout at a lower temperature than that of coal. The 4 year old bamboo carbonised at 400°C also showed higher peak temperature compared to coal, probably due to high FC content in this sample. Also, the combustion of the 4 year old bamboo carbonised at 400°C sample (4 year C400) occurs over a wider temperature area than that of coal and the raw bamboo sample, which corresponds to longer burnout times and could also be as a result of higher carbon content. Again, the 400°C carbonised 4 year old bamboo sample has better reactivity than coal (see Table 12 below). In general, it can be concluded that the burnout temperature of the raw and the thermally treated bamboo samples are influenced by the FC content of the samples.

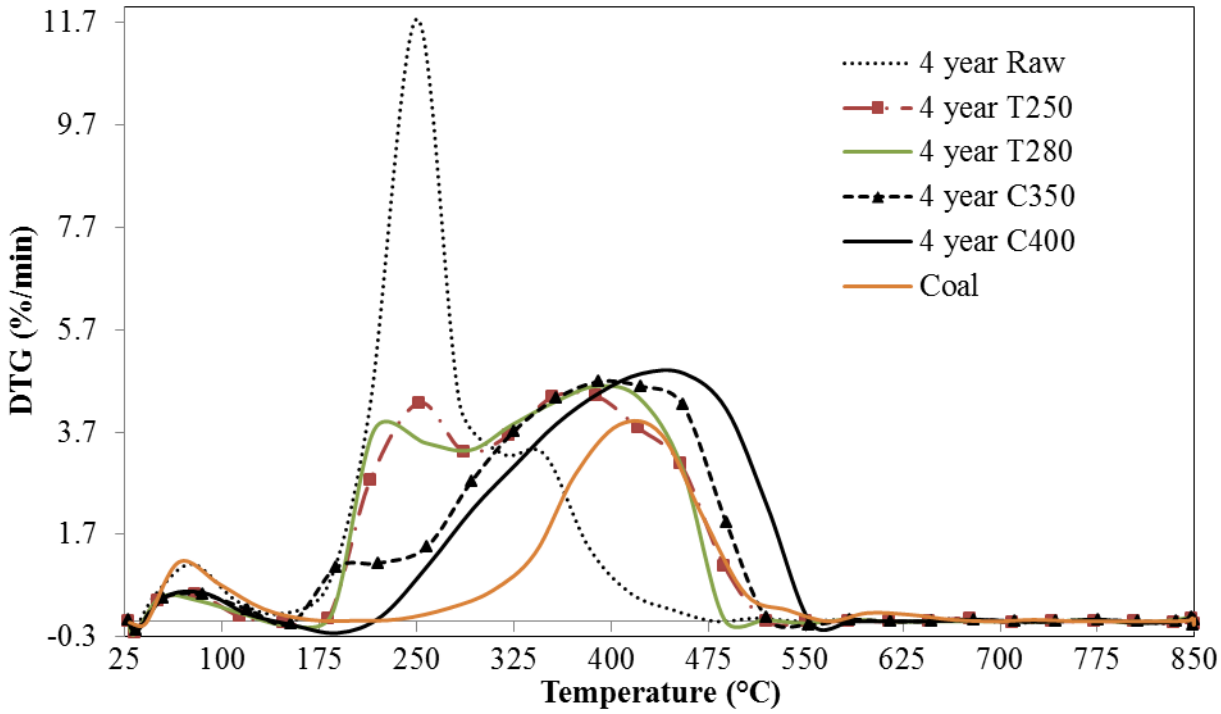

Figure 25: DTG curves for thermally treated 4 year old bamboo and coal.

Table 12: Ignition, peak and burnout temperatures for thermal treated 4 year old bamboo

Sample ID	IT (VM)(°C)	PT (°C)	BT (°C)	Rm (%/min/K)	FC (%, db)
4 year Raw	145	250	475	2.25	19.25
4 year T250	181	388	520	0.67	58.58
4 year T280	183	390	490	0.69	63.64
4 year C350	153	391	522	0.71	73.14
4 year C400	219	456	552	0.66	76.60
Coal	247	423	565	0.55	31.63

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity; FC: Fixed carbon and db: Dry basis.

4.4.3. Co-combustion profiles of raw bamboo and coal

Raw bamboo (1, 3 and 4 year old) and coal were co-combusted in a TGA furnace. The blends studied were 75% raw bamboo + coal, 50% raw bamboo + coal and 25% raw bamboo + coal, for each respective age of the bamboo. The co-combustion profiles of 1 year, 3 year and 4 year old raw bamboo with coal are presented in Figure 26, Figure 27 and Figure 28, respectively.

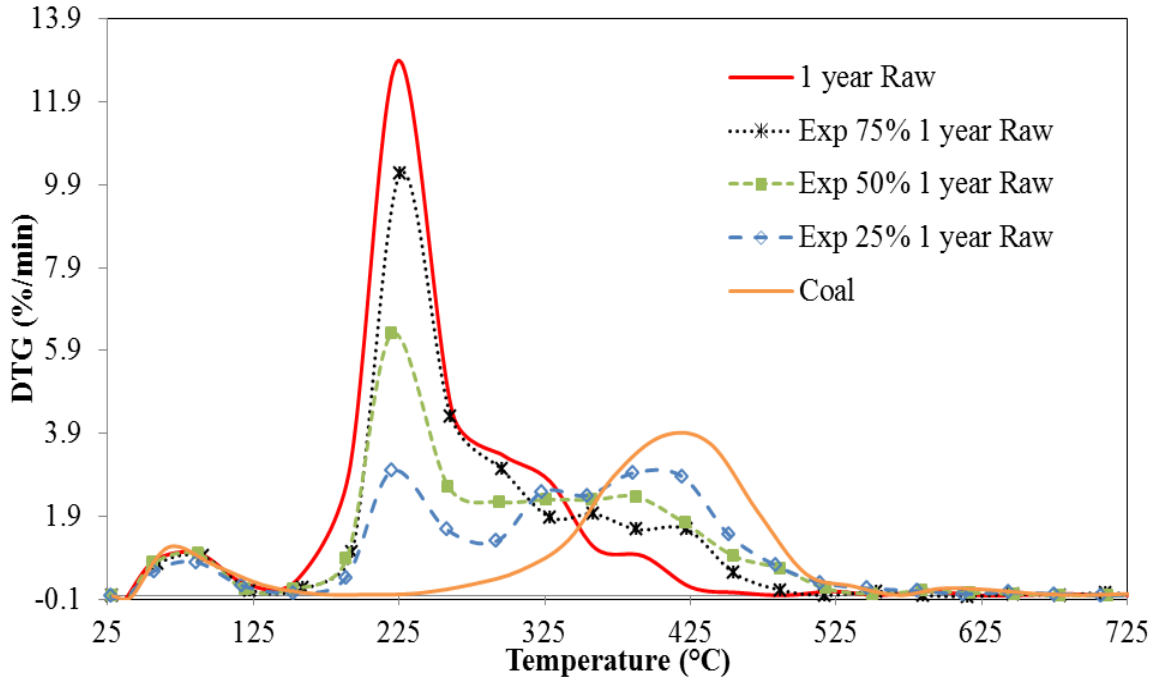

Figure 26: DTG curves of co-combustion of raw 1 year old bamboo with coal.

It was observed that for blends of 1 year old raw bamboo and coal, the maximum rate of mass loss (DTG_{max}) decreased significantly with the decrease in the weight percentage of bamboo in the bamboo/coal blend (see Figure 26 above), probably due to decrease in VM content of the blend. Also, the difference in peak temperatures (220°C-226°C) of these blends was little, where these maximum rates of mass loss occur. A blend containing 25% 1 year old raw bamboo + 75% coal is seen to have the highest ignition and burnout temperature compared to other blends as can be seen in Figure 26 above, however these temperature are still less than that of coal. The above observation is probably as a result of the higher carbon content and lower VM content in the blend. Also, a combustion profile of a 75% 1 year old raw bamboo + 25% coal blend is similar to that of 1 year old raw bamboo combusted alone.

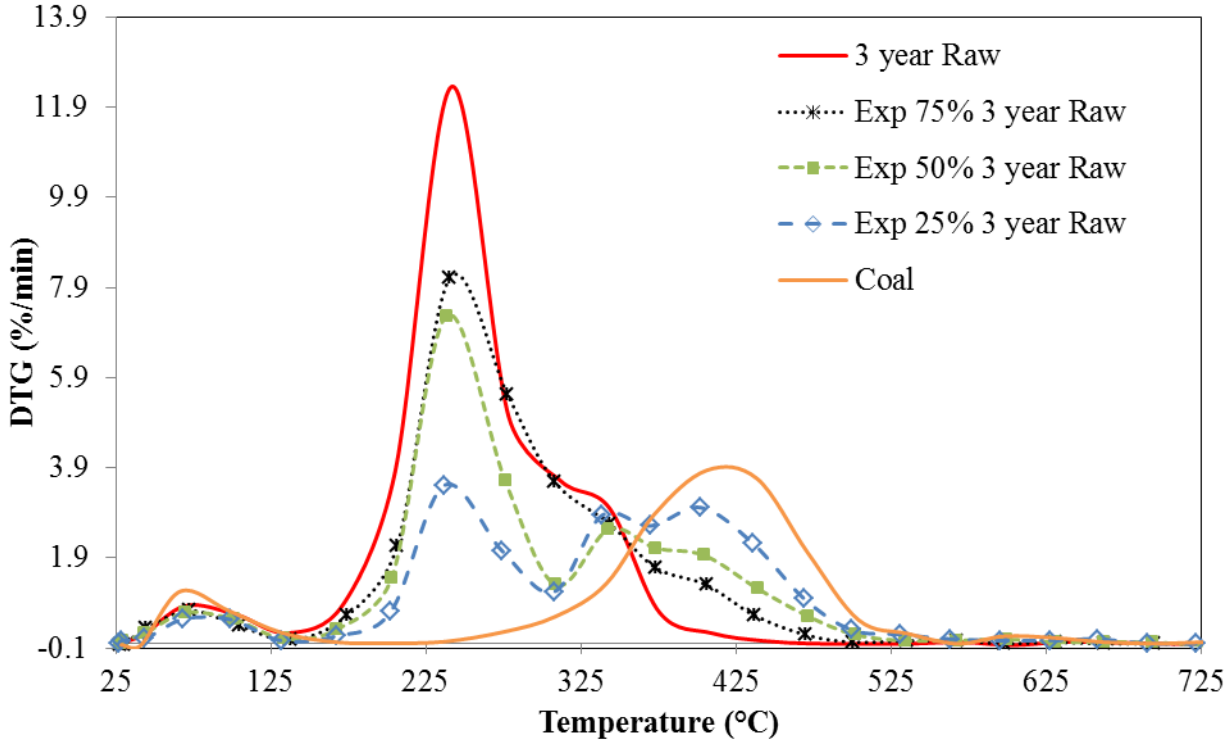

Figure 27: DTG curves of co-combustion of raw 3 year old bamboo with coal

The co-combustion profiles of 3 year old raw bamboo with coal are presented in Figure 27 above. The DTGmax is seen to decrease with increase in weight percentage of coal in the blend, probably due to change in the VM in the blend. It was also observed that BT of the blends increases with the increase in weight percentage of coal in the blend, probably because carbon content in the blend is also increased. A blend containing the highest weight percentage of coal, i.e. (25%, 3 year old raw bamboo + 75% coal) was seen to have higher BT, however still lower than that of coal.

Figure 28 below depicts the co-combustion profiles of 4 year old raw bamboo with coal. All the blends of 4 year old raw bamboo and coal ignited at lower temperatures compared to that of coal. Also, the combustion of the blends was completed long before that of coal (lower BT) as can be seen in Figure 28 and Table 13 below.

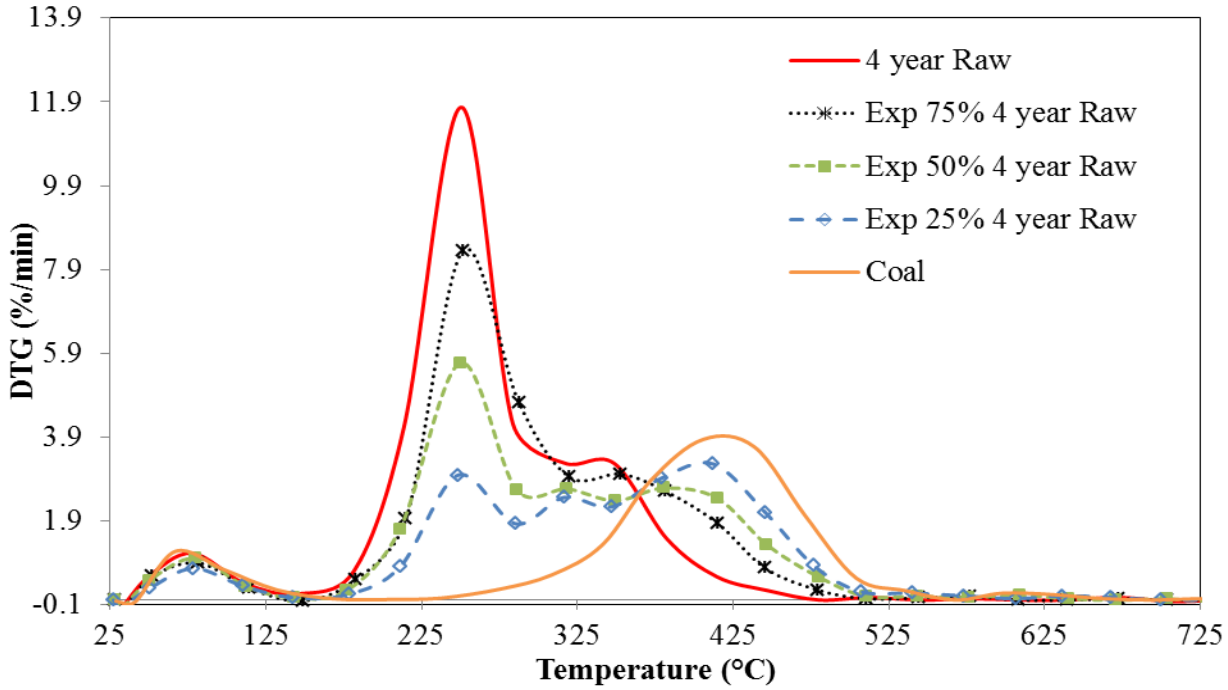

Figure 28: DTG curves of co-combustion of raw 3 year old bamboo with coal

Table 13: Ignition, peak and burnout temperatures of raw bamboo/coal co-combustion

Sample ID	IT (VM)(°C)	PT (°C)	BT (°C)	DTG_{Max} (%/min)	R_m (%/min/K)
1 year raw	141	224	460	12.89	2.59
75% 1 year raw + 25% coal	137	226	502	10.17	2.04
50% 1 year raw + 50% coal	134	220	535	6.3	1.28
25% 1 year raw + 75% coal	153	220	540	2.99	0.61
3 year raw	130	241	446	12.35	2.40
75% 3 year raw + 25% coal	137	240	502	8.11	1.58
50% 3 year raw + 50% coal	134	238	515	7.27	1.42
25% 3 year raw + 75% coal	132	237	520	3.51	0.69
4 year raw	145	250	475	11.77	2.25
75% 4 year raw + 25% coal	151	251	510	8.35	1.59
50% 4 year raw + 50% coal	143	250	512	5.66	1.08
25% 4 year raw + 75% coal	142	412	515	3.25	0.47
Coal	247	423	565	3.92	0.56

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity

There were similarities observed from the thermographs of the respective blends of raw bamboo with coal. All the blends combusted in stages and this maybe because bamboo, like other biomass, is heterogeneous and combusts in stages (Gil *et al*, 2010). Also, the blends containing

25% raw bamboo (irrespective of age) + 75% coal showed the highest BT and still burnout before coal. The temperatures of interest from the thermographs investigated are reported in Table 13 above. The blends containing 75% raw bamboo + coal were seen to have higher reactivity and the profiles were similar to that of the 100% raw bamboo sample. It is suspected that this is due to the high VM in the blend, introduced by the higher weight percentage of the raw bamboo. It must also be noted that the peak temperature of all blends is lower than that of coal and coal had the lowest reactivity. Kastanaki and Vamvuka (2006) also reported that low peak temperatures are associated with high reactivity. Therefore raw bamboo can be co-fired with low ranking coals to improve their burning efficiencies, with 1 year old raw bamboo being the most suitable.

4.4.4. Co-combustion profiles of the thermally treated 1 year old bamboo and coal

Torrefied and low temperature carbonised bamboo samples were blended with coal at different weight ratios (25% bamboo + 75% coal, 50% bamboo + 50% coal and 75% bamboo + 25% coal) and co-fired. The combustion profiles for blends of 1 year old T250 and coal are presented in Figure 29 below. As seen in Figure 29, the profiles of all blends of 1 year old T250 and coal, i.e. (75% T250 + 25% coal), (50% T250 + 50% coal) and (25% T250 + 75% coal) samples showed two DTG peaks of the moisture removal stage, which occurs in the temperature range of 25 to 125°C. Also, these profiles are similar but coal exhibits a burning profile different from the other fuels. There was little difference observed in ignition temperatures between 1 year old T250 and all blends. However, the IT for a single combustion of 1 year old T250 sample was at least 87°C lower than that of coal. It was noted from Figure 29 that as the coal content in the blend increases, the first peak was seen to decrease and peak temperature increased. These observations can be attributed to the increase in the carbon content and a decrease in the VM content of the blend. Park *et al* (2012) also reported a similar observation on the co-combustion of torrefied woody biomass and coal. The burning profile of (75% T250 + 25% coal) sample closely matches that of T250, with both profiles having a peak temperature of 191-193°C and a burnout temperature of 491°C. Also worth mentioning is that the reactivity is higher for blends with higher biomass content. This is expected, since biomass is known to be more reactive than coal. Moreover, the reactivity of the blends was observed to decrease as the coal content in the blend increased.

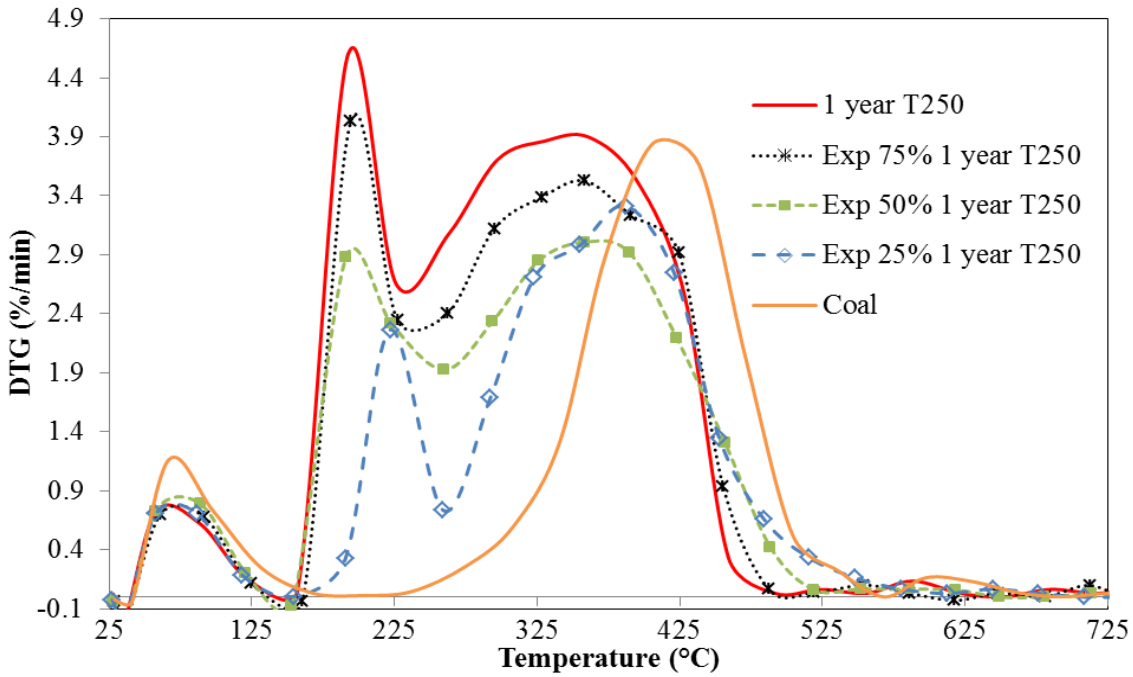

Figure 29: DTG curves of co-combustion of 1 year old T250 and coal.

The co-combustion profiles of 1 year old T280 and coal blends are presented in Figure 30 below. It can be expected from Figure 30 that a blend of (75% T280 + 25% coal) will have the highest reactivity due to highest peak (DTG_{max}) observed. Also, this blend showed lowest BT compared to all other fuels and similar to T280. A (25% T280 + 75% coal) blend in Figure 30 had a DTG profile closest to that of coal and this point to close compatibility elements of the thermally treated bamboo. However, it should be noted that this blend burns to completion at a higher temperature than coal probably as a result of a higher FC content in the blend. Bada *et al* (2015) also reported that blending *Bambusa balcooa* thermally treated at 280°C or higher with high ash coal shows close co-combustion compatibility attributes.

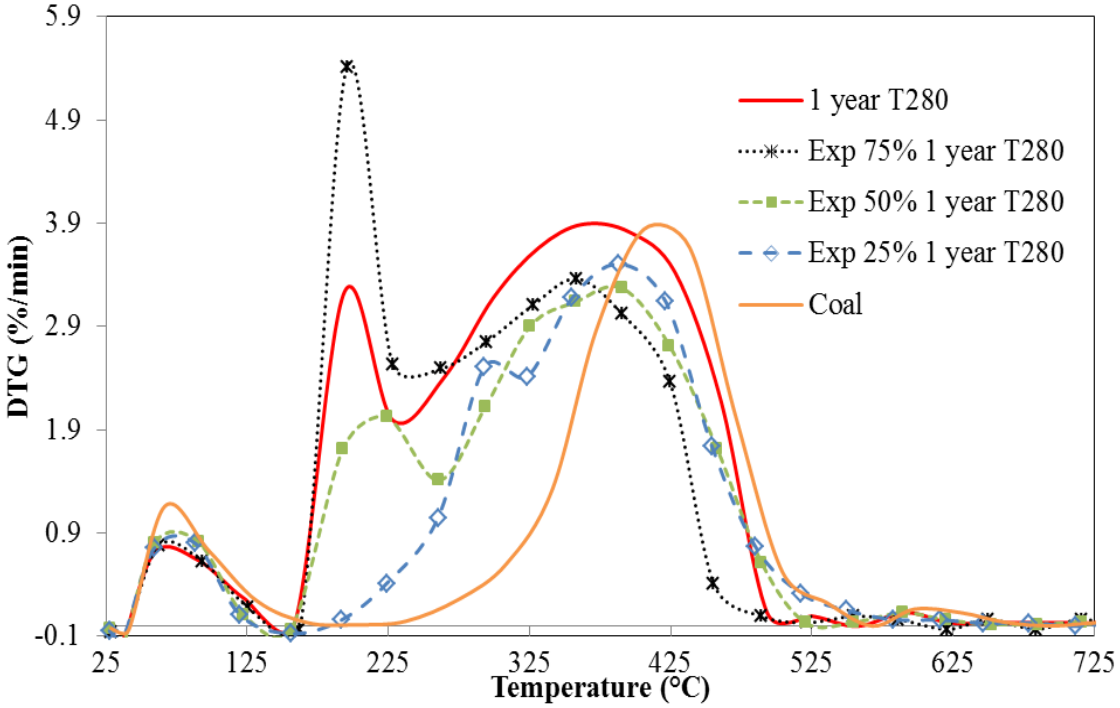

Figure 30: DTG curves of co-combustion of 1 year old T280 and coal

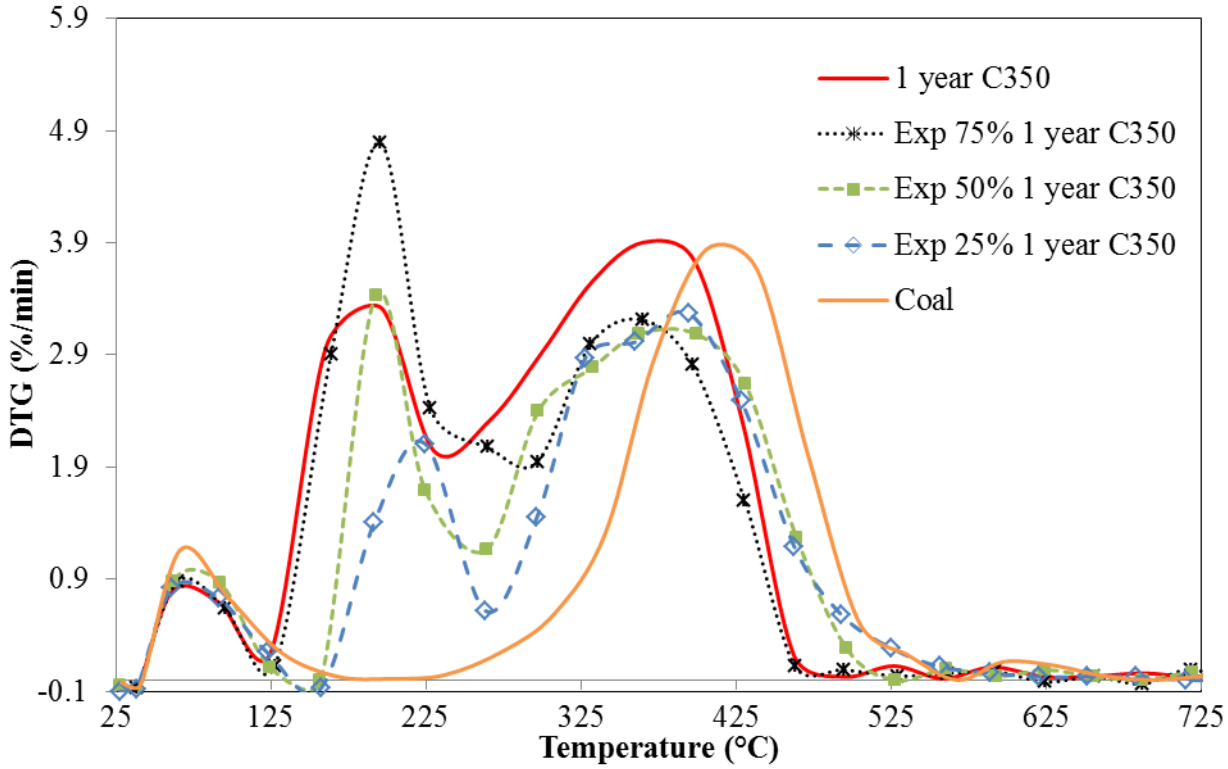

Figure 31: DTG curves of co-combustion of 1 year old C350 and coal

Figure 31 above shows the co-combustion profiles of 1 year old C350 with coal. Similar to a blend of 75% (T280) + 25% coal in Figure 30 above, a blend of C350 and coal with the same proportion was observed to have highest peak (DTG_{max}) with a lower PT as can be seen in Figure 31 above. Also, a blend of (75% C350 + 25% coal) showed lower IT and BT similar to that of C350, however the reactivity was almost double that of C350 and coal, respectively (see Table 14 below). The devolatilization peak in Figure 31 above was observed to decrease with the increase in the weight proportion of coal in the blend, probably as a result of less VM available in the blend as the coal proportion is increased.

The co-combustion profiles of 1 year old C400 with coal are shown in Figure 32 below. Just as with other thermally treated 1 year old bamboo blended at a proportion of (75% bamboo + 25% coal) already discussed above, a blend of (75% C400 + 25% coal) had the highest DTG peak compared to other blends of the same sample with coal. As expected, this blend had the highest reactivity compared to other fuels of the same sample (see Table 14 below). It should be noted that this DTG peak obtained decreases as the coal weight proportion of the blend increased.

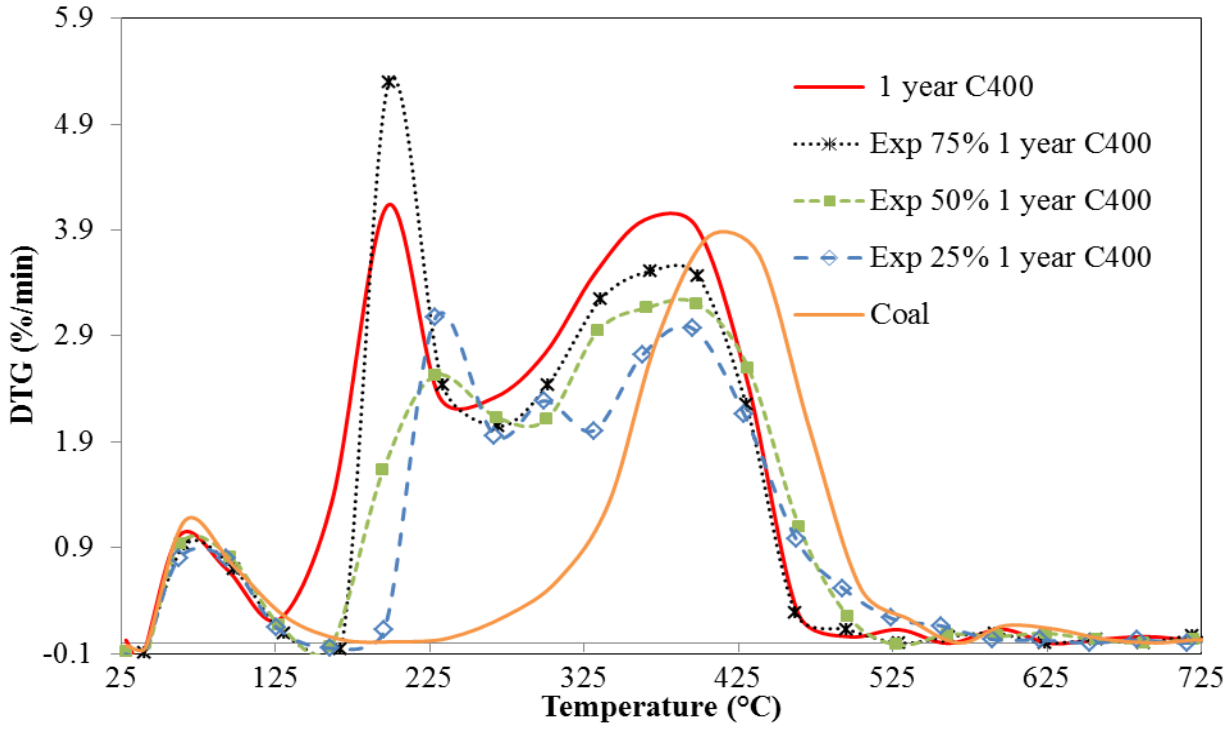

Figure 32: DTG curves of co-combustion of 1 year old C400 and coal

It should be noted that all blends of the thermally treated 1 year old bamboo at respective temperatures with coal showed two stage combustion whereby, burning of volatiles is probably responsible for the 1st stage and cellulose and lignin conversion is responsible for the 2nd stage. In terms of reactivity, 1 year old bamboo thermally treated at 280°C or higher when blended with coal in the proportion of (75% bamboo + 25% coal) had the highest reactivity. It can also be seen from Table 14 that these blends ignite before coal, have low PT and also burnout at a lower temperature than other fuel blends.

Table 14: Ignition, peak and burnout temperatures of the treated 1 year old bamboo/coal co-combustion

Sample ID	IT (VM)(°C)	PT (°C)	BT (°C)	DTG_{Max} (%/min)	R_m (%/min/K)
1 year T250	157	193	491	4.60	0.99
75% 1 year T250 + 25% coal	160	195	491	4.04	0.86
50% 1 year T250 + 50% coal	156	358	519	3.31	0.53
25% 1 year T250 + 75% coal	160	387	612	3.01	0.46
1 year T280	158	363	519	3.89	0.61
75% 1 year T280 + 25% coal	163	196	519	5.41	1.15
50% 1 year T280 + 50% coal	158	390	520	3.27	0.49
25% 1 year T280 + 75% coal	191	388	616	3.51	0.53
1 year C350	125	364	468	3.90	0.61
75% 1 year C350 + 25% coal	126	196	467	4.79	1.02
50% 1 year C350 + 50% coal	157	399	527	3.09	0.46
25% 1 year C350 + 75% coal	158	394	589	3.27	0.49
1 year C400	125	197	496	4.13	0.88
75% 1 year C400 + 25% coal	168	199	525	5.30	1.12
50% 1 year C400 + 50% coal	160	398	527	3.20	0.48
25% 1 year C400 + 75% coal	192	228.79	589.08	3.07	0.61
Coal	247	423	565	3.92	0.56

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity

4.4.5. Co-combustion profiles of the thermally treated 3 year old bamboo and coal

The co-combustion profiles of the torrefied 3 year old bamboo samples T250 and T280 with coal are shown in Figure 33 and Figure 34, respectively. In Figure 33 below, it can be seen that all blends of T250 with coal have lower peaks compared that of a T250 sample. A blend of (75% T250 + 25% coal) was seen in Figure 33 with DTG profile closest to that of a T250 sample. Moreover, the DTG profiles are seen to move away from that of T250 sample and progressively moving closer to the profile of coal as the weight of proportion of coal is increased. Apart from the shoulder observed on the DTG profile of (75% T250 + 25% coal), this blend is a better fuel compared to coal and other blends shown in Figure 33 because of lower IT and BT. Also, in terms of reactivity, it is expected that this fuel will burn faster than coal and other blends because its DTG profile showed the highest DTG peak after T250 sample. A blend sample of 25% T250 + 75% coal had the highest IT after coal, low DTG peak and higher BT than coal, probably because of less VM and increased FC content in the blend.

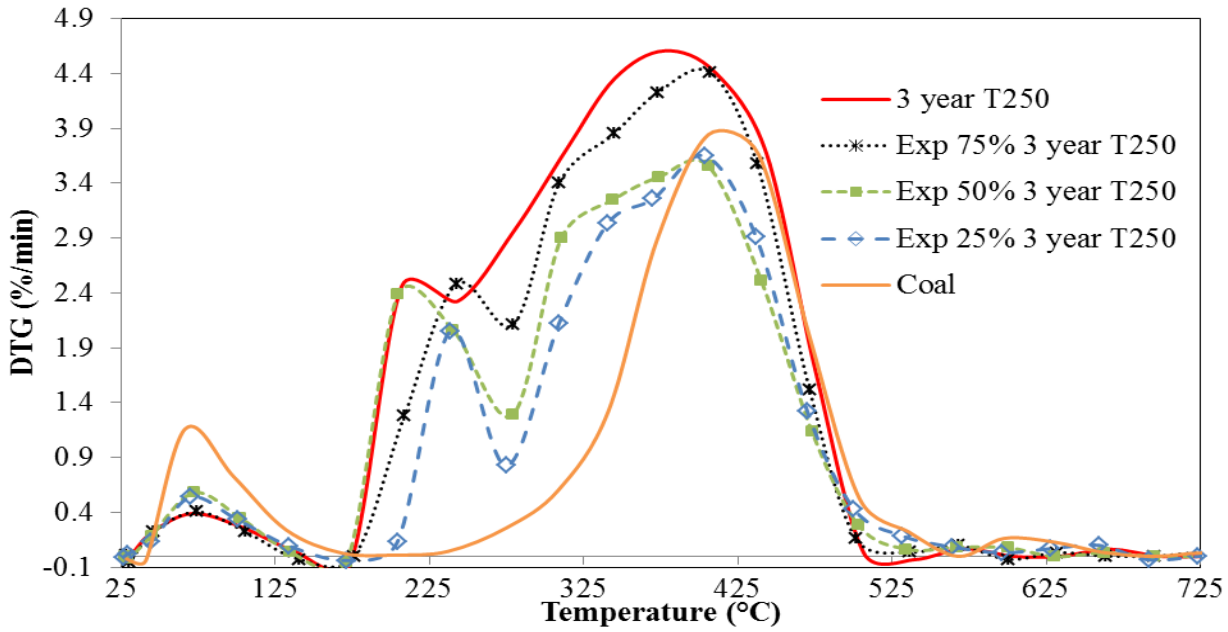

Figure 33: DTG curves of co-combustion of 3 year old T250 and coal

Figure 34 below shows the co-combustion profiles of 3 year old T280 with coal. The DTG profiles of the blends are seen to move away from that of T280 sample and leaning towards that of coal as the weight proportion of coal in blend is increases. Also, IT, PT and BT were seen to increase as the weight proportion of coal in the blend increases. This is probably as a result of

lesser VM and higher FC content in the blends. The DTG peak of a (75% T280 + 25% coal) blend was the highest, followed by that of (50% T280 + 50% coal) fuel. It should be noted that higher DTG peaks are associated with reactivities. The aforementioned observation can be probably attributed to more VM and lesser FC content in the two fuels.

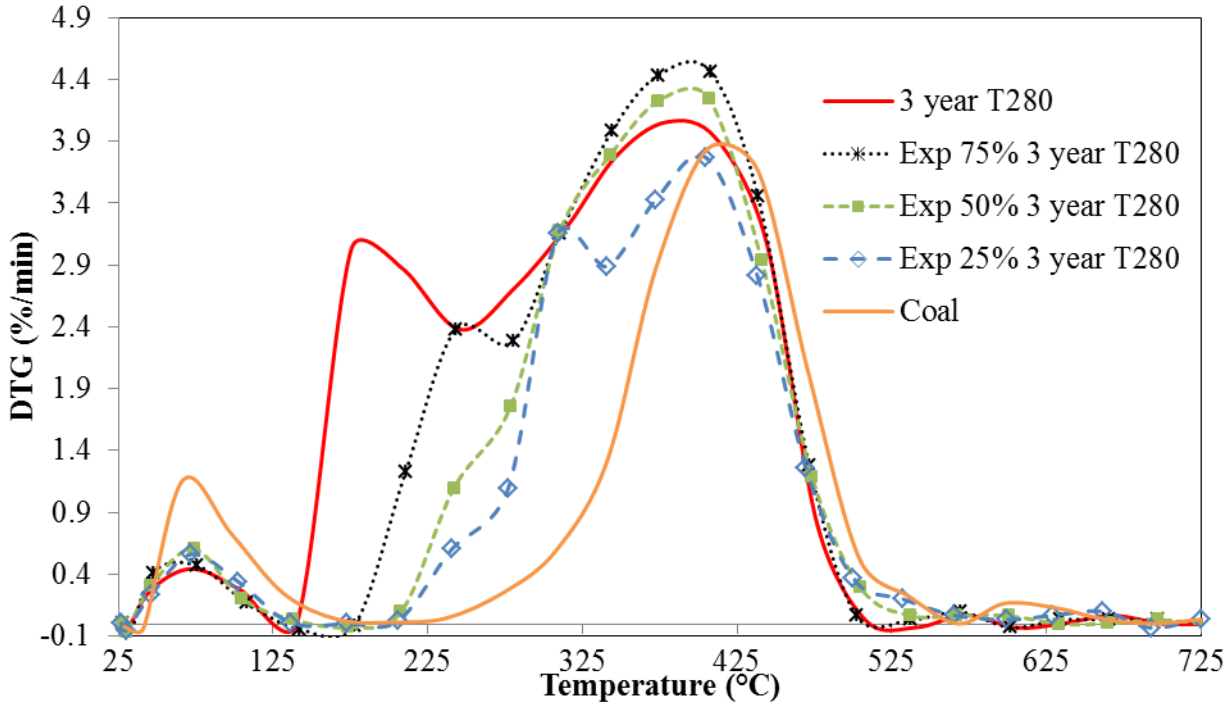

Figure 34: DTG curves of co-combustion of 3 year old T280 and coal

Figure 35 and Figure 36 show the co-combustion profiles of coal with 3 year old low temperature carbonised bamboo C350 and C400, respectively. The peak temperature of all blends of C350 with coal was almost the same and at least 15-17% lower than that of coal. Also, the DTG peaks of (50% C350 + 50% coal), (25% C350 + 75% coal) and coal are almost the same. However the DTG peak of (75% C350 + 25% coal) fuel is higher and almost the same as that for C350, as seen in Figure 35 below. This higher DTG peak is probably attributed to higher VM content in this fuel. A blend of (25% C350 + 75% coal) ignites almost at the same temperature as coal.

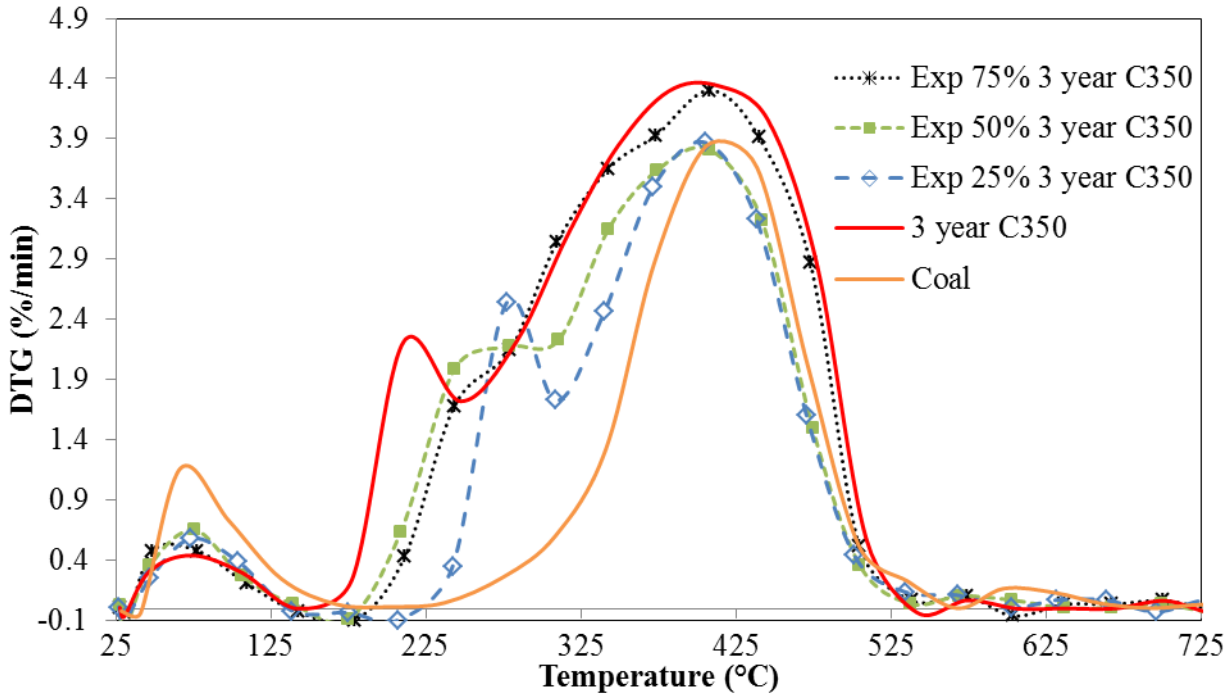

Figure 35: DTG curves of co-combustion of 3 year old C350 and coal

The co-combustion profiles of 3 year old C400 with coal are shown in Figure 36 below. A fuel consisting of 25% C400 + 75% coal showed single peak combustion profile, suggesting coal like burning characteristics. The same observation was made by Park *et al* (2012) on blends of thermally treated woody biomass and coal. Therefore, it can be concluded that above fuel will be closely compatible to coal during combustion. It can be seen from Figure 36 below that all fuels had almost similar PT and the reactivity of all fuels is higher than that of coal. However, it must be noted that (75% C400 + 25% coal) and (50% C400 + 50% coal) fuels ignites at the lower temperature region and burns to completion long before coal and other fuels.

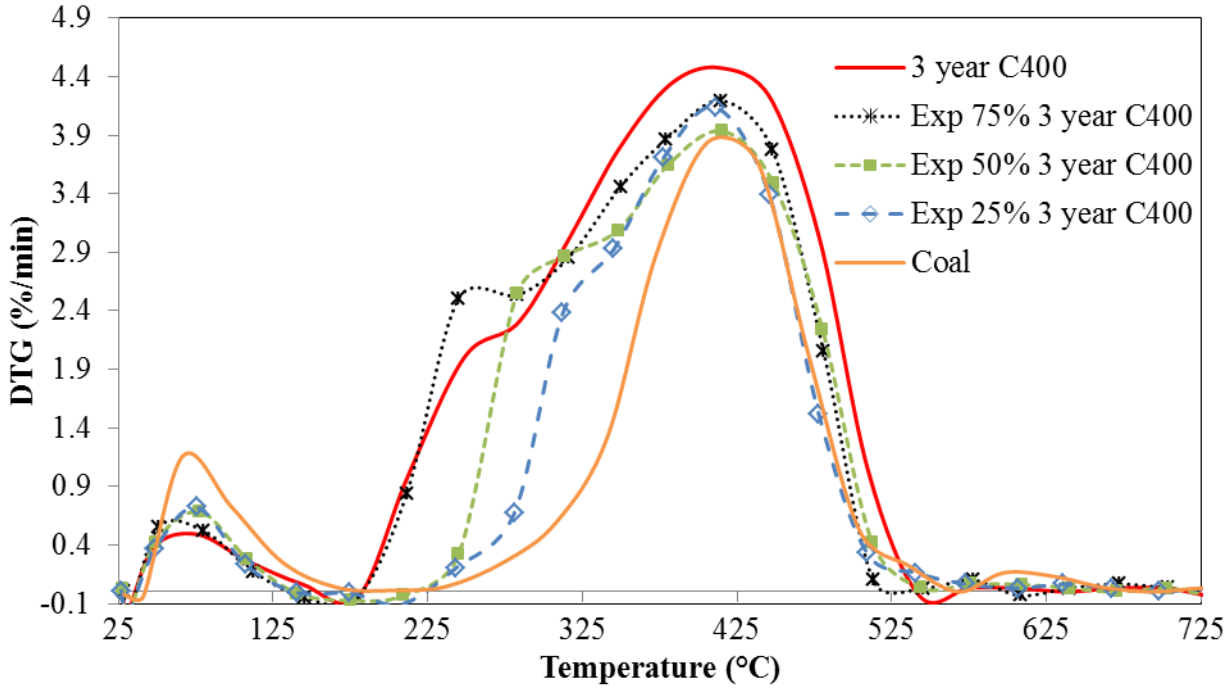

Figure 36 DTG curves of co-combustion of 3 year old C400 and coal

The burning characteristic temperatures of the thermally treated 3 year old bamboo blended to with coal are presented in Table 15 below. The DTG profile of 3 year old bamboo carbonised at 400°C sample and when blended with coal, showed PT, and BT comparable to that of coal, showing attributes of close compatibility. Moreover, (25% C400 + 75% coal) is the most compatible ahead of other fuels of 3 year old bamboo, and also burns faster than coal as shown in Table 15 below. Ignition and burnout temperatures were increased when weight proportion of coal was increased for all blends. In terms of reactivity, 3 year old bamboo torrefied at 280°C blended with coal in the weight proportion of (75% T280 + 25% coal) takes superiority. This fuel also burns in the low temperature regions, i.e. lowest burnout temperature, which would be beneficial for reducing the NO_x emissions in a PF boiler using low temperature burners or a CFB boiler

Table 15: Ignition, peak and burnout temperatures of treated 3 year old bamboo/coal co-combustion

Sample ID	IT (VM)(°C)	PT (°C)	BT (°C)	DTG_{Max} (%/min)	R_m (%/min/K)
3 year T250	174	377	507	4.61	0.71
75% 3 year T250 + 25% coal	176	407	537	4.41	0.65
50% 3 year T250 + 50% coal	171	406	534	3.56	0.52
25% 3 year T250 + 75% coal	189	404	596	3.65	0.54
3 year T280	145	379	509	4.06	0.62
75% 3 year T280 + 25% coal	178	408	502	4.46	0.66
50% 3 year T280 + 50% coal	203	409	537	4.24	0.62
25% 3 year T280 + 75% coal	205	410	599	3.77	0.56
3 year C350	176	412	542	4.34	0.63
75% 3 year C350 + 25% coal	182	408	538	4.30	0.63
50% 3 year C350 + 50% coal	177	407	537	3.81	0.56
25% 3 year C350 + 75% coal	225	406	603	3.87	0.57
3 year C400	189	414	543	4.48	0.65
75% 3 year C400 + 25% coal	180	414	525	4.20	0.61
50% 3 year C400 + 50% coal	223	415	543	3.94	0.57
25% 3 year C400 + 75% coal	225	411	606	4.14	0.60
Coal	247	423	565	3.84	0.55

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity

4.4.6. Co-combustion profiles of the thermally treated 4 year old bamboo and coal

The combustion profiles of the blends of torrefied 4 year old bamboo and coal are shown in Figure 37 and Figure 38 below. Just as it was observed for the other blends of treated 1 year old and 3 year old bamboo, the DTG profile of (25% T250 + 75% coal) was the closest to matching that of coal as can be seen in Figure 37 below. The same observation was made in Figure 38 for a blend consisting of (25% T280 + 75% coal). Also, the IT and BT were seen to increases as the weight proportion of coal in the blend was increased in both Figure 37 and Figure 38 below. These observations can be attributed to higher FC and lower VM content in the blend. Bada *et al* (2014) also reported the same observations for co-combustion of torrefied *Bambusa multiplex* and coal.

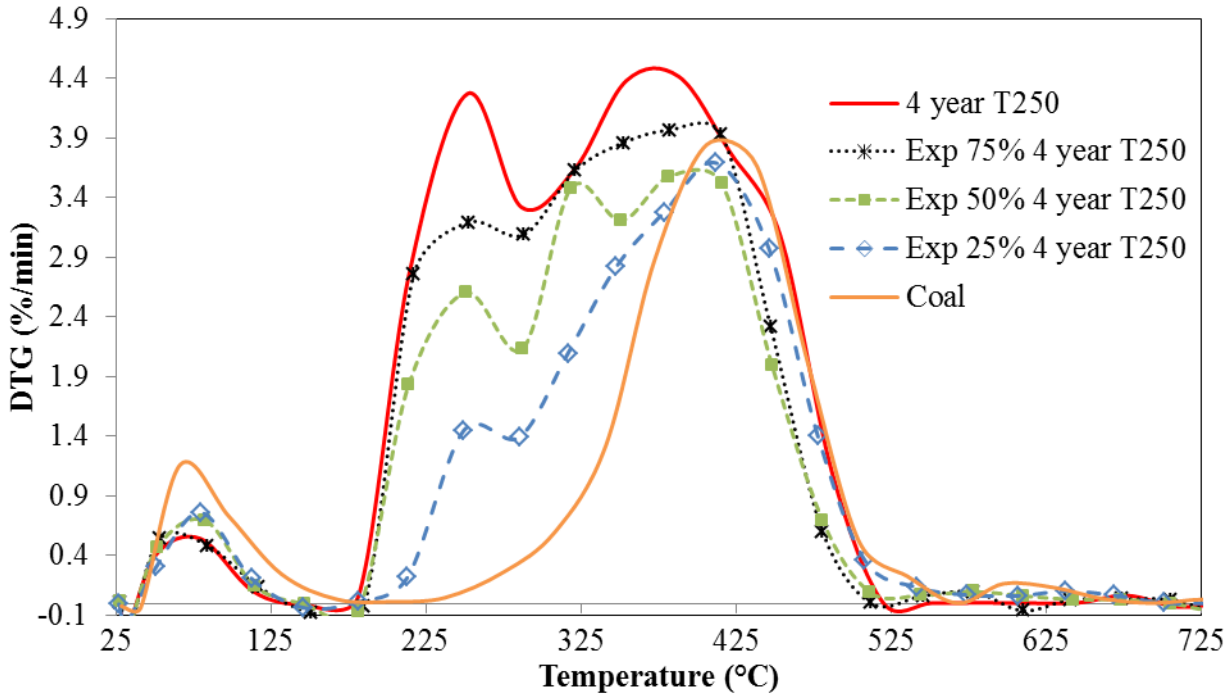

Figure 37: DTG curves of co-combustion of 4 year old T250 and coal

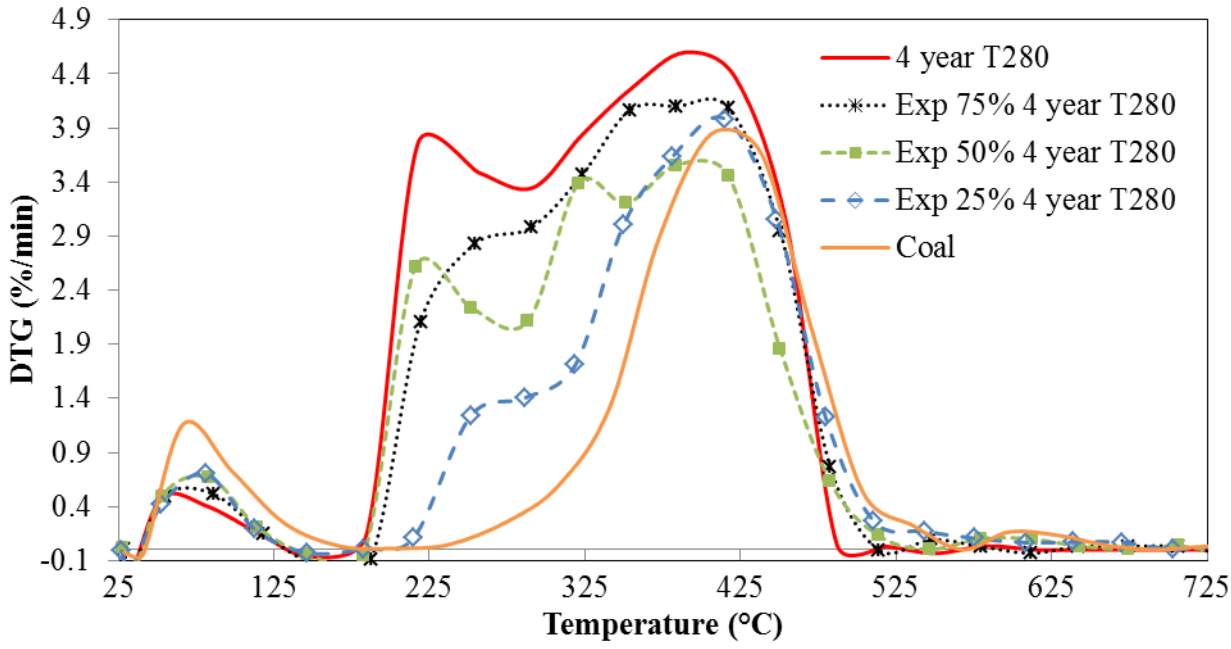

Figure 38: DTG curves of co-combustion of 4 year old T280 and coal

The co-combustion profiles of 4 year old C350 with coal are shown in Figure 39. The respective DTG profiles of (75% C350 + 25% coal) and (50% C350 + 50% coal) fuels showed a smaller devolatilization stage peak (small shoulder), suggesting there is still a small amount of VM in the blends. A single combustion stage was observed for (25% C350 + 75% coal) fuel, which points to coal like nature. Also, as expected (25% C350 + 75% coal) fuel, had the highest IT after coal. Moreover, there is minimal difference between profiles of all blends in Figure 39 below, in terms of PT and BT.

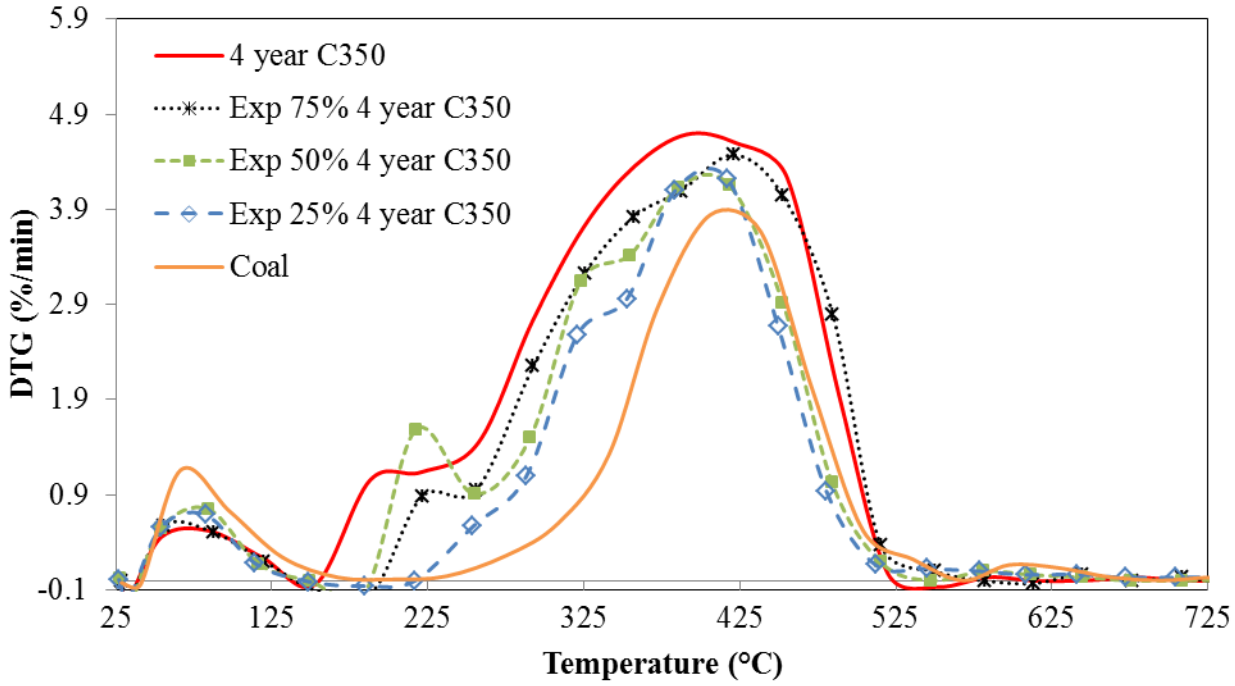

Figure 39: DTG curves of co-combustion of 4 year old C350 and coal

Figure 40 below shows that the combustion of carbonized 4 year old bamboo (C400) solely, and its co-combustion with coal had single peaks like that of coal. Park *et al* (2012) also reported single stage combustion for low temperature carbonized woody biomass. The same observation was made by Bada *et al* (2015) on combustion and co-combustion of *Bambusa balcooa* with high ash coal. It is suspected that the single combustion observed here is possible because all the active volatiles in the bamboo were already released, by low temperature carbonization. The 4 year old C400 sample has the highest FC content and low VM, therefore these physicochemical properties are probably responsible for high IT, PT and BT during combustion. As can be seen in Figure 40, the DTG curve of (25% C400 + 75% coal) fuel is closely matched to that of coal, with

almost same IT, DTG peaks and BT (also see Table 16 below), which are all indicators of close compatibility. It should also be noted that the DTG peaks decreased with the increase in weight proportion of coal in the blend.

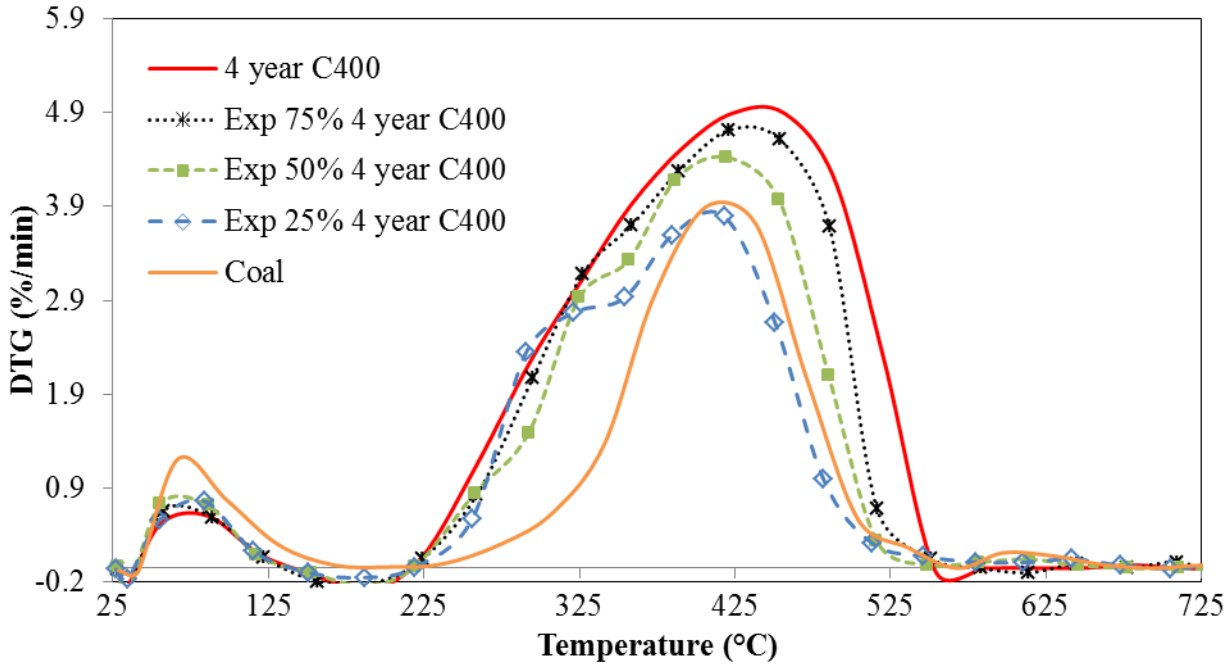

Figure 40: DTG curves of co-combustion of 4 year old C400 and coal

The critical temperatures from the DTG curves studied in this section are given in Table 16 below. From the IT, PT and BT given in Table 16, it can concluded that 4 year old C400 is the most compatible to be co-fired with coal for electricity generation. Also, blends with the highest proportion of C400 had better reactivities. Therefore, bamboo can be blended with coal to improve the burning efficiency.

Table 16: Ignition, peak and burnout temperatures of treated 4 year old bamboo/coal co-combustion

Sample ID	IT (VM)(°C)	PT (°C)	BT (°C)	DTG_{Max} (%/min)	R_m (%/min/K)
4 year T250	181	388	520	4.41	0.67
75% 4 year T250 + 25% coal	181	397	512	4.13	0.62
50% 4 year T250 + 50% coal	187	401	544	3.99	0.59
25% 4 year T250 + 75% coal	200	412	573	3.69	0.54
4 year T280	183	390	490	4.60	0.69
75% 4 year T280 + 25% coal	189	383	513	4.10	0.62
50% 4 year T280 + 50% coal	185	383	546	3.55	0.54
25% 4 year T280 + 75% coal	202	415	607	3.98	0.58
4 year C350	153	390	522	4.69	0.71
75% 4 year C350 + 25% coal	191	420	550	4.47	0.64
50% 4 year C350 + 50% coal	187	418	547	4.15	0.60
25% 4 year C350 + 75% coal	216	417	608	4.21	0.61
4 year C400	219	456	552	4.84	0.66
75% 4 year C400 + 25% coal	223	421	583	4.66	0.67
50% 4 year C400 + 50% coal	219	419.6	549	4.37	0.63
25% 4 year C400 + 75% coal	218	418	579.6	3.74	0.54
Coal	247	423	565	3.84	0.55

IT: Ignition temperature; VM: Volatile matter; PT: Peak temperature; BT: Burnout temperature, *Rm*: Reactivity

4.4.7. Interaction study of coal and bamboo

The combustion performance of all the raw bamboo samples /coal blends were explored in order to investigate if an interaction occurred between the individual fuels during combustion. In order to determine this, a theoretical DTG curve was calculated based on identical temperature history of the two components of the blend. The calculated and experimental DTG curves for the respective blends of 1 year, 3 year and 4 year old raw bamboo with coal are shown in Figure 41, Figure 42 and Figure 43, respectively. The correlation coefficient of the calculated and experimental DTG data of each blend was calculated and the results are reported in Table 17 below. It can be seen from Figure 41 below that there were no significant deviations between the experimental and calculated DTG curves for all blend ratios investigated. This is further supported by the calculated correlation coefficient showing values close to 1 as reported in Table 17. This means that combustion performance of a blend of 1 year old raw bamboo sample and

coal, could be predicted based on the performance of the individual fuel. Therefore, the interaction between the two fuels can be noted as being an additive reaction.

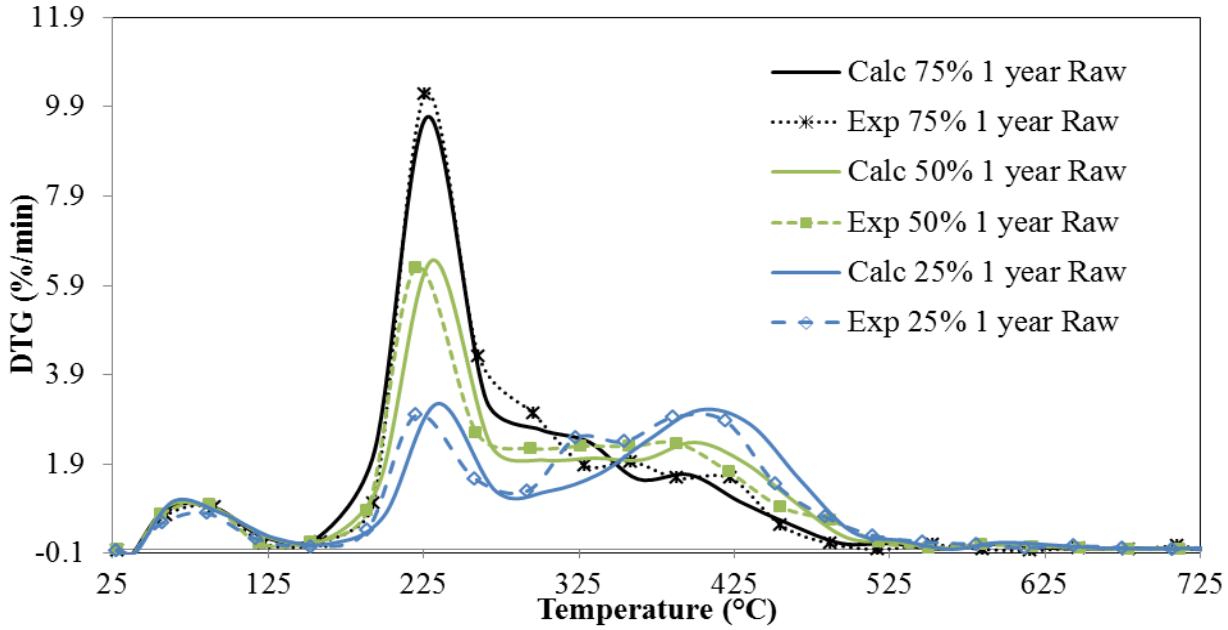

Figure 41: Experimental and calculated DTG curves of 1 year old raw bamboo and coal blends

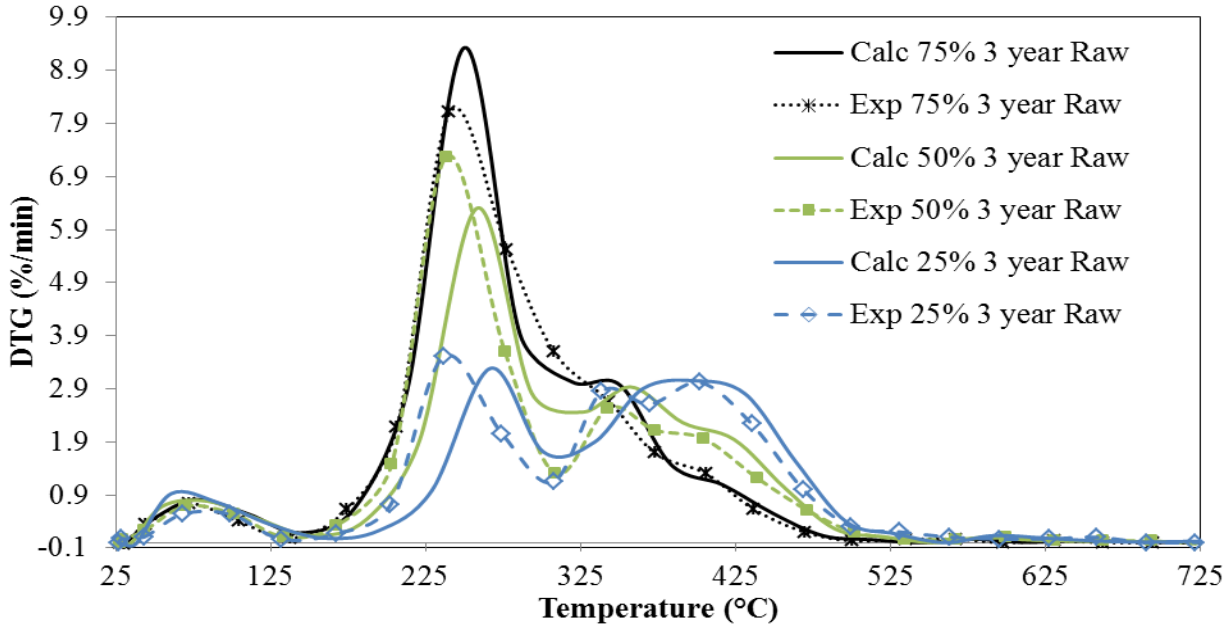

Figure 42: Experimental and calculated DTG curves of 3 year old raw bamboo and coal blends

The 3 year old raw and 4 year old raw bamboo samples blended with coal also showed the same behaviour as illustrated in Figure 42 and Figure 43, respectively. The correlation coefficient was also observed to decrease as the coal content in the respective blends increased. The same result was obtained by Gil *et al* (2010) and Sadhukhan *et al* (2008) from the additive behaviour of pine sawdust and coal, and lignite coal and waste wood fines blends, respectively. However, it should be noted that the latter study was carried out under pyrolysis conditions.

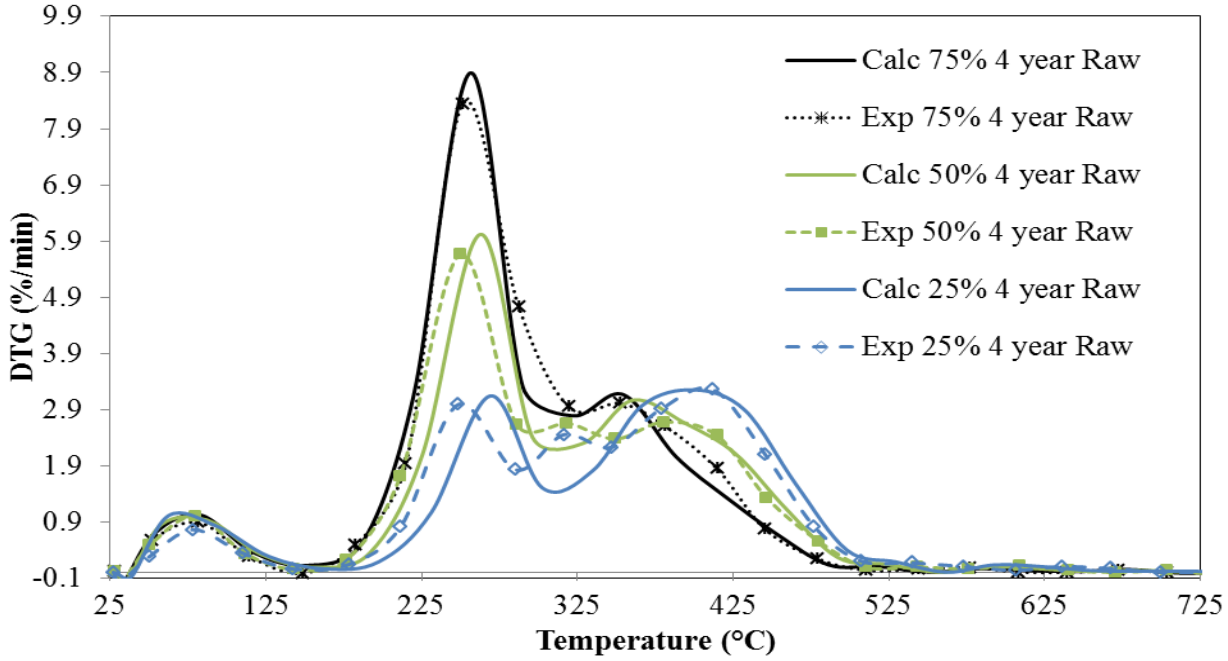

Figure 43: Experimental and calculated DTG curves of 4 year old raw bamboo and coal blends

Table 17: Correlation coefficient between experimental and calculated DTG data

Sample ID	R^2				
	Raw	T250	T280	C350	C400
75% 1yr bamboo + 25% coal	0.9691	0.4389	0.3681	0.2802	0.3142
50% 1yr bamboo + 50% coal	0.9572	0.5815	0.5941	0.4913	0.6311
25% 1yr bamboo + 75% coal	0.8020	0.6760	0.8667	0.5948	0.6167
75% 3yr bamboo + 25% coal	0.9875	0.3478	0.3461	0.2351	0.3582
50% 3yr bamboo + 50% coal	0.8296	0.5548	0.5091	0.6379	0.4745
25% 3yr bamboo+ 75% coal	0.8124	0.8026	0.7760	0.9150	0.7440
75% 4yr bamboo+ 25% coal	0.9758	0.5303	0.4658	0.1857	0.1302
50% 4yr bamboo+ 50% coal	0.9392	0.6965	0.6436	0.4704	0.4152
25% 4yr bamboo+ 75% coal	0.8495	0.8714	0.8586	0.7787	0.8763

R^2: correlation coefficient

The combustion performance of torrefied and low temperature carbonised 4 year old bamboo/coal blends were also explored in order to investigate the interaction between the components during combustion. The experimental and calculated DTG curves of co-combustion of (4 year T250 + coal) blends are presented in Figure 44, (4 year T280 + coal) in Figure 45, (4 year C350 + coal) in Figure 46 and (4 year C400 + coal) in Figure 47. The correlation coefficients for all DTG curves are, however, reported in Table 17 above. It can be seen from both the correlation coefficients presented in Table 17 and the DTG curves presented in Figure 44 that the deviation between experimental and calculated DTG data of (4 year T250 + coal) blends is significant. Also, the deviation is observed to increase with increasing biomass content in the blend, as indicated by decreasing R^2 values. This indicates that there is a synergistic behaviour between the fuels in the blend. Sahu *et al* (2013) also reported synergistic behaviour when co-combusting low temperature sawdust char and coal or low temperature corn cob char and coal.

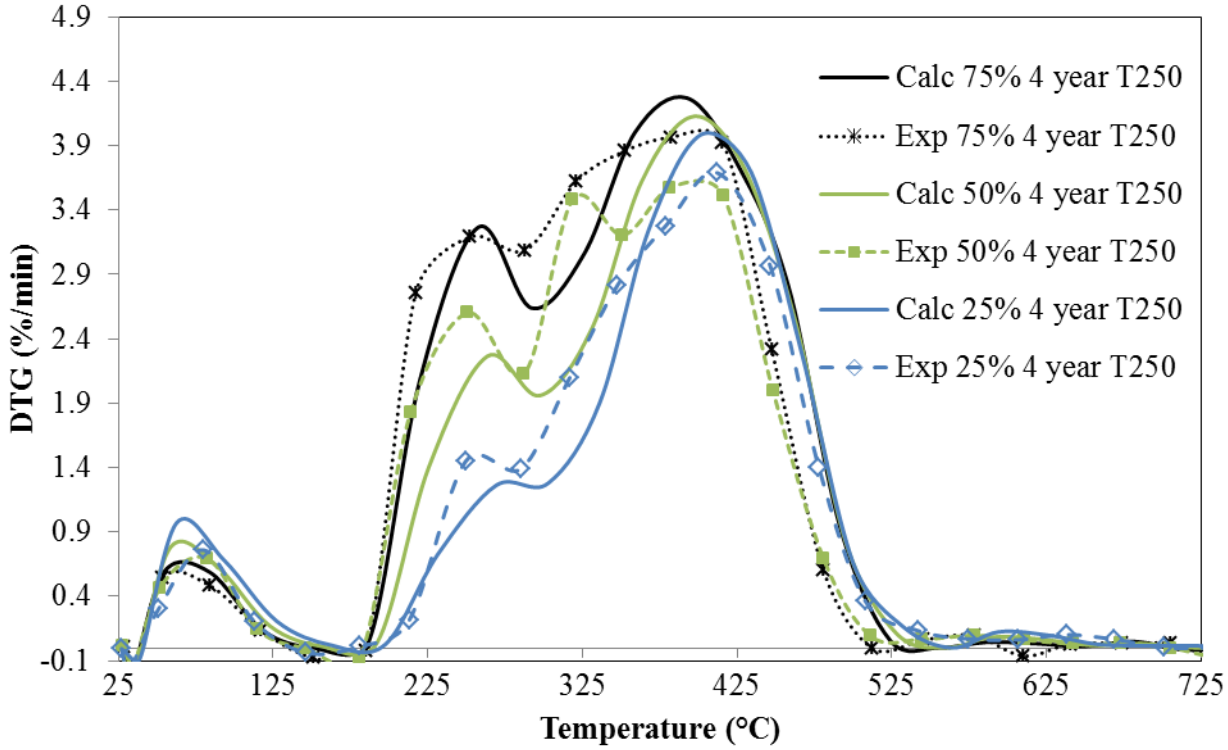

Figure 44: Experimental and calculated DTG curves of 4 year old T250 and coal blends

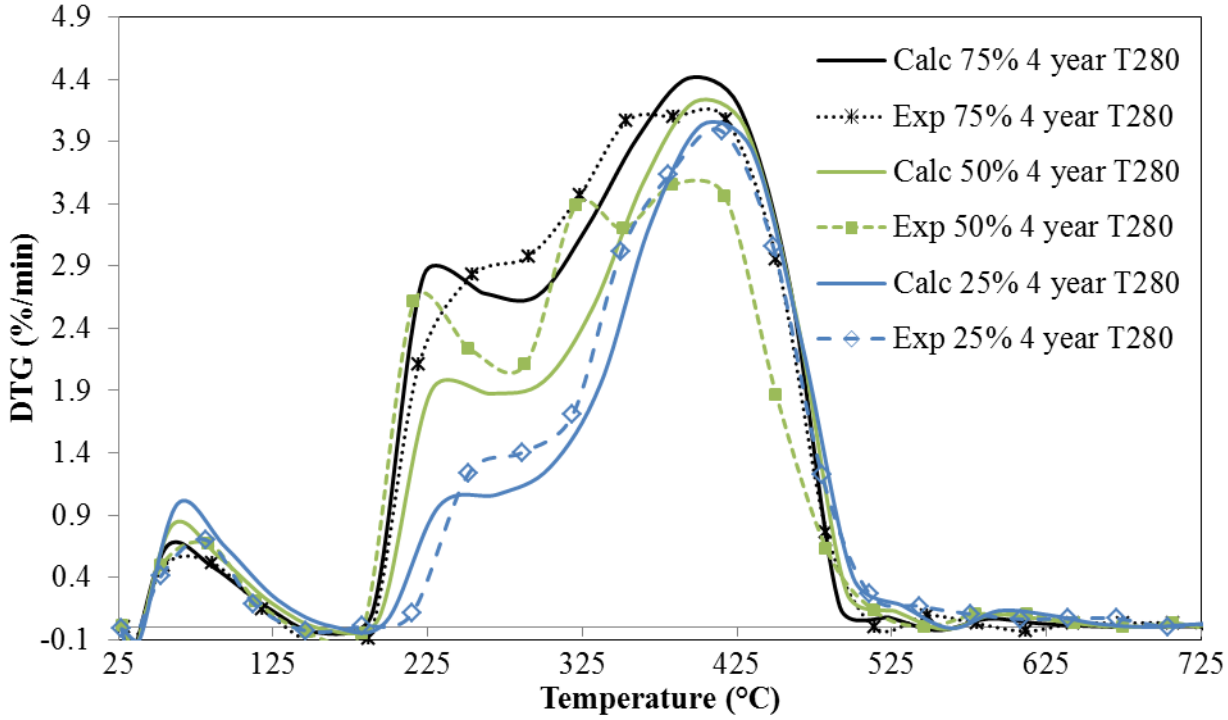

Figure 45: Experimental and calculated DTG curves of 4 year old T280 and coal blends

It can be seen from Figure 45 above that the blends of (4 year T280 + coal) show similar behaviour as that of (4 year T250 + coal). Also with (4 year T280 + coal) blends, the deviation between experimental and calculated DTG curves is more significant, except for (25% 4 year T280 + 75% coal) blend. The associated correlation coefficients (R^2) are 0.4658 and 0.6436 for (75% 4 year T280 + 25% coal) and (50% 4 year T280 + 50% coal) blends, respectively. Meanwhile, that for a (25% 4 year T280 + 75% coal) blend is 0.8586 indicating a behaviour approaching additive behaviour.

Experimental and calculated DTG curves for the low temperature carbonised 4 year bamboo co-combusted with coal are given in Figure 46 and Figure 47 below. As seen from the correlation coefficients presented in Table 17 and DTG curves in Figure 46, there is a significant deviation between experimental and calculated DTG curves for co-combustion of (4 year C350 + coal) blends reflecting an interaction between the two fuels. However, the deviation is less pronounced for a (25% 4 year C350 + 75 % coal) blend indicated by an R^2 value of 0.7787. Similar observations were made for the co-combustion of (4 year C400 + coal) blends shown in Figure 47. The deviation was greater in blends containing a higher weight percentage of bamboo.

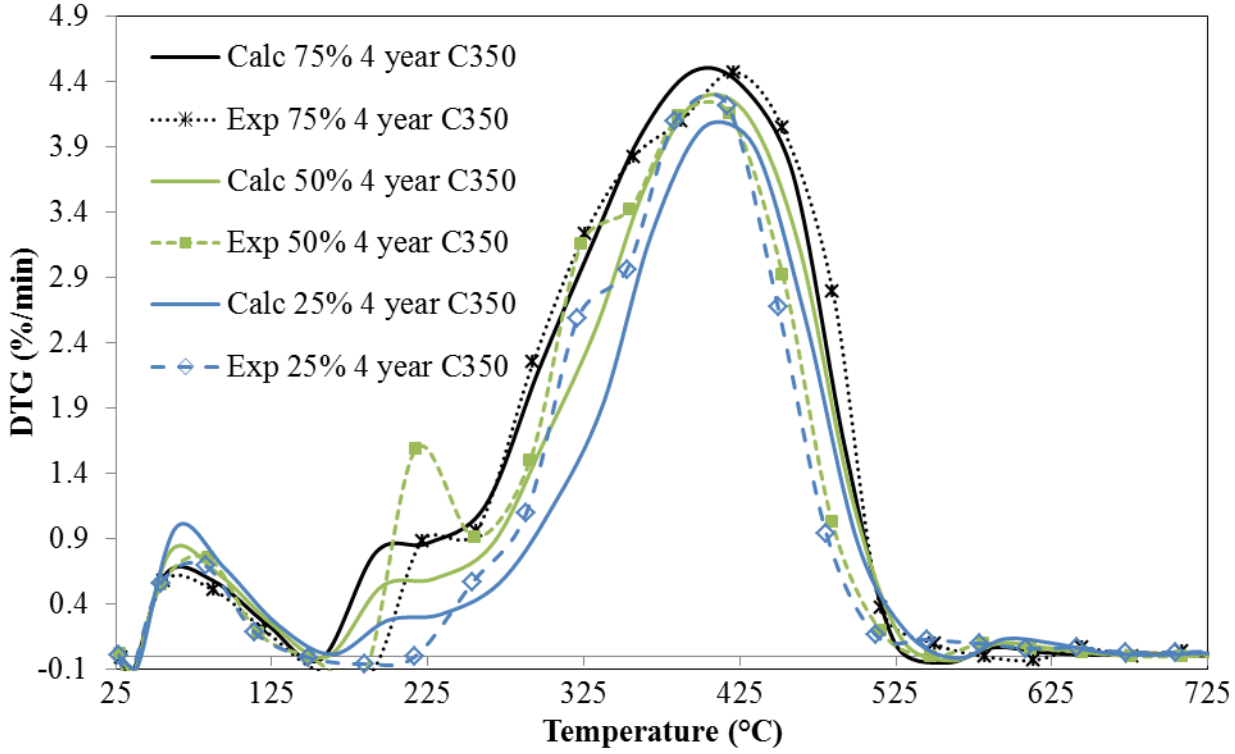

Figure 46: Experimental and calculated DTG curves of 4 year C350 and coal blends

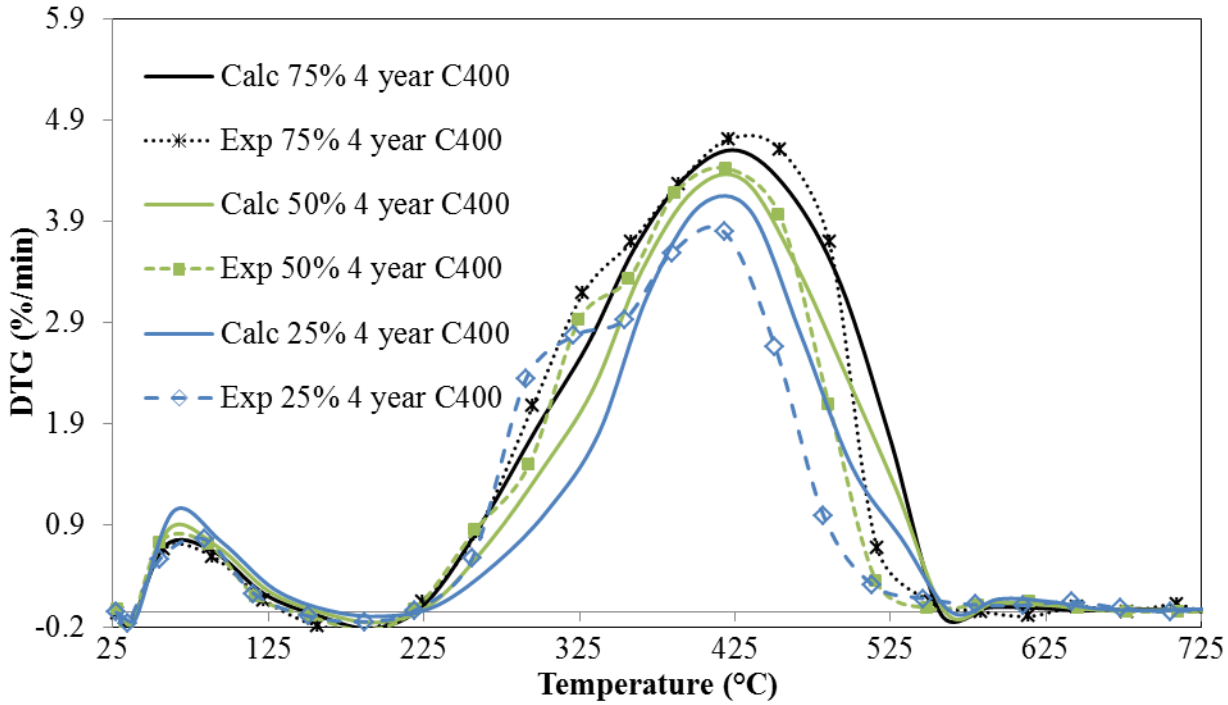

Figure 47: Experimental and calculated DTG curves of 4 year old C400 and coal blends

The interaction between other thermally treated bamboo (1 and 3 year old) and coal was also studies and the respective DTG curves are presented in Appendix B. It is evident from Table 17 above that almost all the experimental co-combustion DTG curves of thermally treated 1 year old bamboo + coal blends and treated 3 year old bamboo + coal blends deviated from the theoretically predicted DTG curves, suggesting that there was an interaction between the respective blends during co-firing. The deviation between experimental and theoretical DTG curves of co-combustion of (25% 1 year T280 + 75% coal), (25% 3 year T250 + 75% coal) and (25% 3 year C350 + 75% coal) was less pronounced. It can be concluded that increasing the weight percentage of coal in the blend promotes less interaction between the fuels during co-combustion, suggesting the behaviour approaches that of additive nature.

4.4.8. Kinetic analysis

Kinetic study on the combustion of different bamboo samples, solely and their co-combustion with coal was conducted. Model free kinetic methods were used to evaluate one parameter of the kinetic triplet, i.e. activation energy. Ozawa and Kissinger models were chosen as the model free methods to determine the combustion activation energy of raw bamboo, thermally treated bamboo and their blends with coal. As already discussed in section 2.9, the two methods require at least 3 heating rates. The DTG curves obtained from each heating rate have a characteristic peak, i.e. the corresponding peak temperature. Figure 48 below presents the DTG curves for the combustion of 1 year old raw bamboo sample at 3 different heating rates of 5, 10 and 15 °C/min. The heating rates, denoted as (B) and peak temperatures (PT) obtained from DTG curves shown in Figure 48 were used to plot the Ozawa plot and Kissinger plot presented in Figure 49. The slope of the respective plot was used to determine the activation energy. The same procedure was used for all fuels tested. It should be noted that the activation energy was only determined for the combustion of coal, raw bamboo samples (1, 3 and 4 year old), torrefied bamboo at 250°C and low temperature carbonised bamboo at 400°C. Meanwhile, for co-combustion, only the 4 year old raw bamboo/coal blend and the thermally treated sample/coal blend were evaluated. The activation energies obtained from the combustion of different fuels are presented in Table 18 below. The DTG curves and the respective Ozawa and Kissinger plots used to determine the activation energies of other fuels reported in Table 18 are presented in Appendix C.

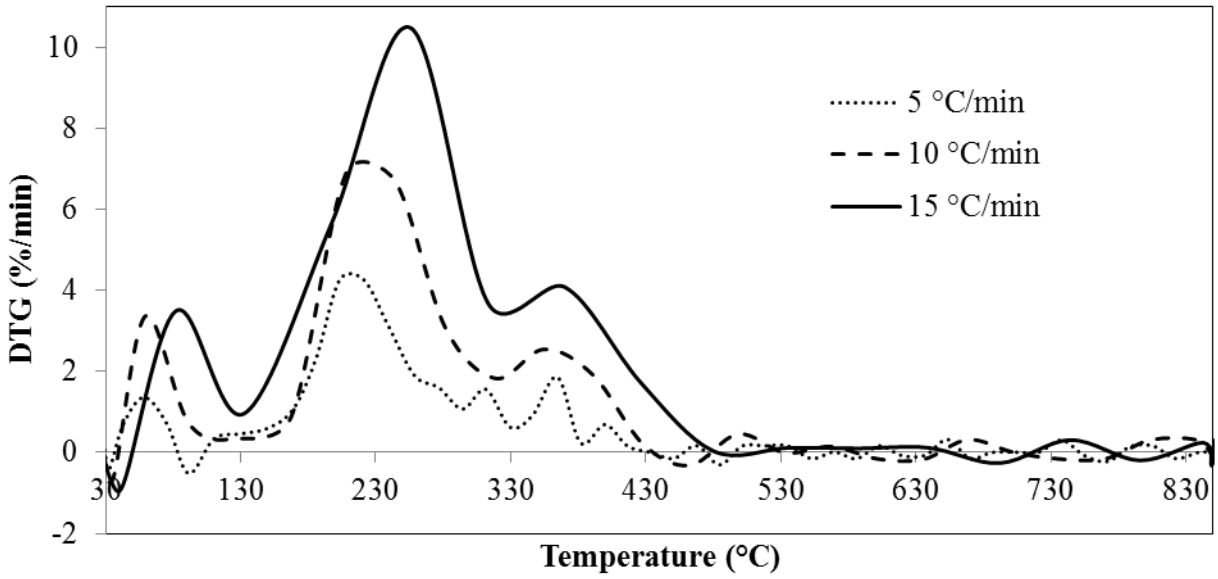

Figure 48: DTG curves of 1 year old raw bamboo at different heating rates

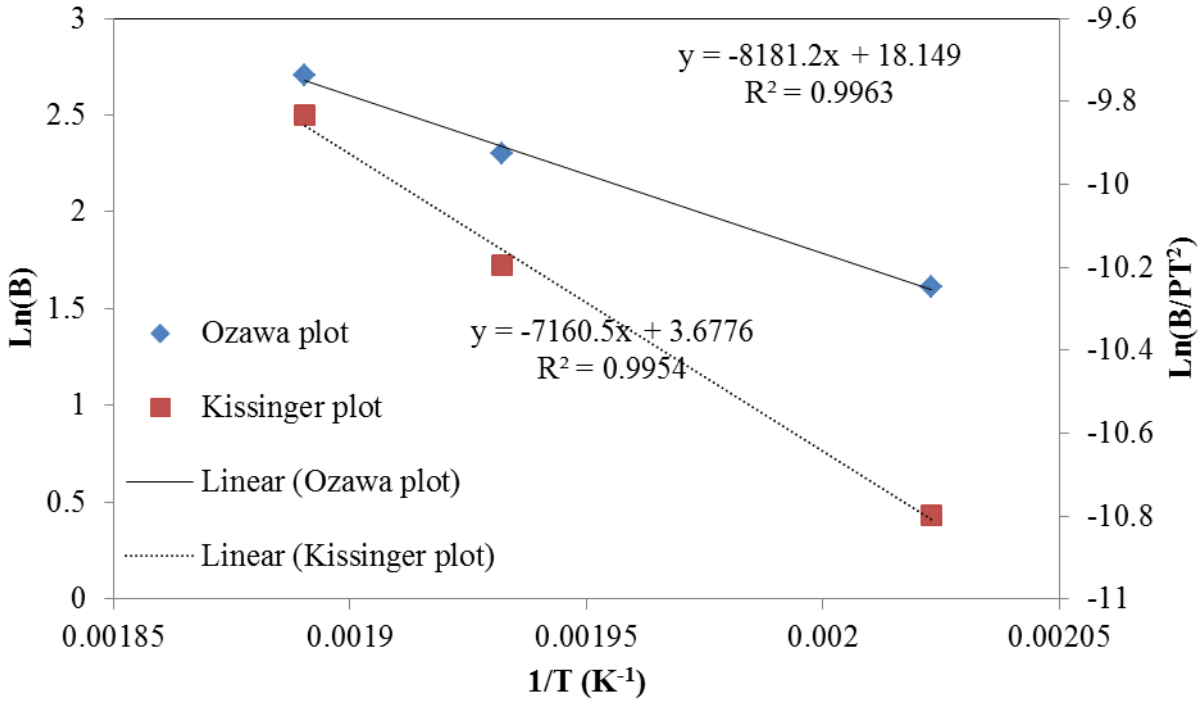

Figure 49: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 1 year old raw bamboo

Table 18: Activation energies of coal, raw and thermally treated bamboo

Sample ID	Temperature range (°C)	Ozawa Ea (kJ/mol)	R^2	Kissinger Ea (kJ/mol)	R^2
Coal		90	0.9108	83	0.8886
1 year Raw	132-313	65	0.9963	60	0.9954
1 year T250	199-441	280	0.9399	285	0.936
1 year C400	203-541	289	0.8154	294	0.8053
3 year Raw	162-341	69	0.9529	64	0.9391
3 year T250	231-456	125	0.9744	122	0.9703
3 year C400	246-464	259	0.8693	263	0.8602
4 year Raw	179-356	56	0.9576	50	0.9407
4 year T250	185-470	71	0.9533	63	0.9359
4 year C400	253-532	110	0.9618	105	0.954

R^2: correlation coefficient; Ea: activation energy

It can be seen from Table 18 that the activation energy of all different ages of raw bamboo is lower than that of coal, suggesting that less energy will be required for the combustion of raw bamboo. High VM content in the raw bamboo samples might be responsible for this low activation energies. The activation energy for the raw bamboo varied from 56 to 65 kJ/mol and from 50 to 60 kJ/mol, as obtained from the Ozawa and Kissinger model, respectively. Sadhukhan *et al* (2008) reported activation energies of between 68-76 kJ/mol for waste wood, which are comparable to that reported in the present work. Meanwhile, Yao *et al* (2008) reported activation energies between 150-175 kJ/mol for different natural fibres including bamboo. However, it should be noted that the activation energy reported by the author are from the thermal decomposition process under high purity nitrogen atmosphere with only 0.5 % oxygen content.

The activation energy for the combustion of the thermally treated bamboo as observed in this investigation was found to be higher than that of the raw bamboo. For all different ages of the raw bamboo, the activation energy was observed to increase with the thermal treatment temperature. This can be attributed to the less volatile matter present in the thermally treated bamboo samples. The activation energy for the torrefied 1 year old bamboo is 280 kJ/mol using Ozawa model and 285 kJ/mol using Kissinger model. In term of treatment temperature, the activation energy of the respective age of bamboo was observed to increase with treatment temperature, probably because of higher FC content and less VM in the treated bamboo sample. Kopczynski *et al* (2015) also observed increasing activation energy of the main combustion stage

as the thermal treatment temperature of the fuel was increased. Table 19 presents the activation energies for the respective co-combustion of raw and thermally treated 4 years old bamboo with coal. The DTG curves and corresponding Ozawa and Kissinger plots used to evaluate the activation energy for the co-combustion are presented in Appendix C.

Table 19: Activation energies for the co-combustion of 4 year old raw and thermally treated bamboo with coal.

Sample ID	Ozawa		Kissinger	
	Ea (kJ/mol)	R^2	Ea (kJ/mol)	R^2
75% 4 year Raw + 25% coal	33	0.9770	26	0.9571
50% 4 year Raw + 50% coal	33	0.9983	25	0.9973
25% 4 year Raw + 75% coal	79	0.9759	71	0.9673
75% 4 year T250 + 25% coal	40	0.9731	30	0.9517
50% 4 year T250 + 50% coal	35	0.9014	25	0.8149
25% 4 year T250 + 75% coal	75	0.9835	67	0.9770
75% 4 year T280 + 25% coal	39	0.9716	29	0.9482
50% 4 year T280 + 50% coal	34	0.9054	25	0.8184
25% 4 year T280 + 75% coal	76	0.9794	68	0.9716
75% 4 year C350 + 25% coal	73	0.9516	65	0.9366
50% 4 year C350 + 50% coal	75	0.9755	67	0.9668
25% 4 year C350 + 75% coal	86	0.9738	79	0.9633
75% 4 year C400 + 25% coal	43	0.8814	34	0.8025
50% 4 year C400 + 50% coal	73	0.9797	65	0.9721
25% 4 year C400 + 75% coal	70	0.9722	62	0.9604

R^2: correlation coefficient; Ea: activation energy

It can be seen from Table 19 that the activation energy of all bamboo/coal blends containing a higher coal weight proportion possesses higher activation energy than that with lower coal proportion. This is probably because of more carbon introduced by coal as the proportion of coal in the blend increases. Park *et al* (2012) reported a decreasing activation energy as torrefied woody biomass weight proportion in the blend increased. A similar observation was made by the same author on a blend of coal and low temperature carbonised woody biomass, which is in agreement with result obtained in this study. Yanfen and Xiaoqian (2010) also reported a decreasing activation energy as the weight proportion of paper sludge in the blend increased.

The activation energy is between 33-79 kJ/mol, 40-75 kJ/mol and 43-73 kJ/mol for the blends of coal with raw bamboo, torrefied T250 bamboo and low temperature carbonised C400 bamboo, respectively. The activation energy of the blends was lower than that for coal and also lower than the calculated average of the combined coal and respective fuel. This further supports the observation that most of the fuels tested in this study show synergistic behaviour. The lowest R^2 value was 0.8814 using Ozawa model. The activation energies obtained from the Kissinger model are slightly lower to the ones obtained using the Ozawa model.

It can be concluded that raw bamboo samples require less energy to ignite, possibly because of higher VM content. Also, the high FC content and low VM might be responsible for high activation energy in the thermally treated samples. Overall, the activation energy is strongly influenced by carbon content and VM of the sample. It was seen that the activation energy of the blends increases with the increase in the weight proportion of coal, suggesting the introduction of more carbon from coal might be responsible for this increase.

CHAPTER 5: CONCLUSIONS

The aim of this research work was to study the physical properties of raw, torrefied and carbonised bamboo to establish the potential of these materials as suitable biomass sources for co-firing with coal. The proximate and ultimate analyses and the DTG profiles were used to study in detailed the combustion and co-combustion characteristics of raw and thermally treated bamboo and their blends with coal. The grindability of this material was also evaluated using Hardgrove Grindability Index method. The following conclusions were drawn from the data:

1. It was demonstrated that thermal treatment can be used to improve fuel properties for bamboo biomass. Higher mass and energy yield were achieved for torrefied bamboo compared to low temperature carbonised bamboo. The calorific value was also increased significantly by thermal treatment and was highest at carbonisation temperatures. The calorific value of 1 year, 3 year and 4 year old bamboo plants was increased by low temperature carbonisation from 18.53 MJ/kg to 28.54 MJ/kg for 1 year old bamboo, 17.10 MJ/kg to 30.17 MJ/kg for 3 year old bamboo and 17.63 MJ/kg to 30.24 MJ/kg for 4 year old bamboo.

2. The VM/FC ratio of bamboo was also reduced to below 1 by thermal treatment, matching the ratios found for coal. At carbonisation temperatures, the FC for all ages of bamboo was increased to above 66% db, matching high quality coal. After carbonisation at 400°C, the VM of the 1 year, 3 year and 4 year old bamboo plants was decreased significantly, namely, from 74.6 to 26.9% for 1 year old bamboo, 73.6 to 18.9% for 3 year old bamboo and 72.8 to 17.8% for 4 year old bamboo.

3. Thermal treatment also improved the grindability of bamboo. Untreated biomass was difficult to pulverise but thermal treatment altered the physical properties bamboo thereby generating significant size reduction using this process. 1 year old bamboo sample was easier to pulverise than 3 and 4 year old bamboo samples at most of the treatment temperatures. In comparison, 4 year old bamboo was difficult to grind at all treatment temperature. However, at the temperature of 280 °C, the grindability was comparable to, and sufficient for, application in a power station.

4. In regard to the combustion characteristics of bamboo, the raw sample has the highest fuel reactivity and the lowest devolatilisation, ignition, peak and burnout temperatures compared to all heat treated fuels. The peak and burnout temperatures of the heat treated bamboo samples shifted to right of the diagram, namely to higher temperatures, probably as a result of molecular alteration in the hemicellulose structure of the treated samples. The DTG curve for the 4 year old C400 sample closely matched that for coal, followed by that of 3 year old C400. This result suggests that the 4 year old sample C400 is more compatible with coal. The burnout temperatures for all heat treated bamboo samples were lower than that for coal, i.e. it would appear that all bamboo samples burn out sooner than coal.

5. The blending of raw bamboo with coal in different weight ratios produced a wide range of ignition, peak and burnout temperatures, all of which were found to be lower than those for coal except for the burnout temperature for the blend containing 75 % coal. In other words, as the weight percentage of coal in the blend increases, the DTG profiles were found to move away progressively from raw bamboo and to approach that of coal. The same observation was made for blends with treated bamboo.

6. A blend of low temperature carbonised 4 year old bamboo with coal resulted in a DTG profile characterised by a single peak which closely matched that of coal. This was the only blend in comparison to all other blends to do so. This result suggests that carbonised 4 year old C400 bamboo has the most similar combustion characteristics to coal and may therefore be the most compatible candidate for co-firing with coal. However, almost all blends showed clear interaction between fuels as indicated by the variations in combustion profiles during co-firing, thereby suggesting synergistic behaviour.

7. The activation energy of raw bamboo was lower than that for coal, probably because raw bamboo ignites and burns out easily due to its high VM content. However, the activation energy of the heat treated bamboo was found to increase with increasing treatment temperature. The activation energy of the blends was lower than that for coal and also

lower than the calculated average of the combined coal and respective fuel. This further supported the finding of synergistic behaviour.

In summary, it was demonstrated that thermal treatment is paramount for improving the fuel and combustion characteristics of bamboo as well increasing its ease of grindability. In terms of combustibility, the torrefied bamboo was shown in this research to burn at lower temperatures relative to coal and to exhibit high reactivity, which could serve as useful fuel in low temperature combusting environments such as fluidised bed boilers. Carbonised 4 year old bamboo is likely to be the preferred alternative source of fuel for firing alone or co-firing with coal in high temperature pulverised boilers in South Africa due to their high calorific values, higher energy yields, ease of grindability and coal-like combustion characteristics.

CHAPTER 6: RECOMMENDATIONS

Based on the successful demonstration that torrefaction and low temperature carbonisation can improve the physicochemical and combustion properties of raw bamboo both when fired alone or as a co-fired fuel with coal, the following recommendations are made for further investigation;

1. A life cycle analysis should be carried to establish (i) the benefit of growing bamboo as a CO_2 sink and a low carbon or neutral renewable source of fuel for power generation, and (ii) to compare the carbon footprint and other greenhouse gas emission when burning bamboo relative to coal in power generating facilities. .

2. Life cycle studies of rehabilitation sites using bamboo as the biofuel crop of choice should be investigated on a pilot scale to establish the growth patterns of selected bamboo species and the potential for developing this plant as a low carbon source of fuel for power generation in the country. .
3. Techno-economic studies should be carried out to determine the feasibility and impact of this approach on social and economic benefits.

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APPENDICES A

8.1. Repeatability graphs of coal and raw bamboo samples (1, 3 and 4 year old).

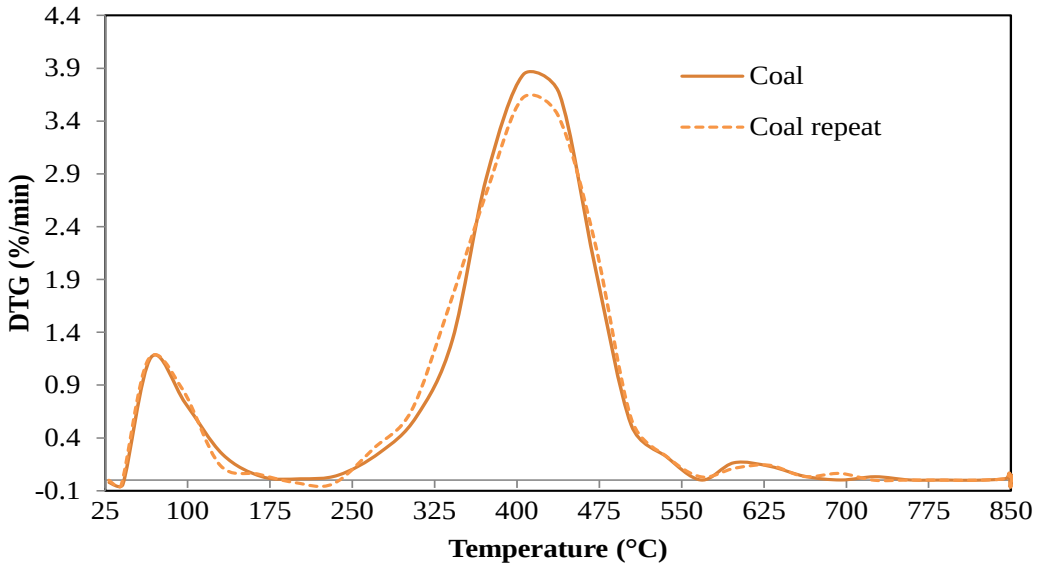

Figure 50: Repeatability check for the combustion of coal in a TGA

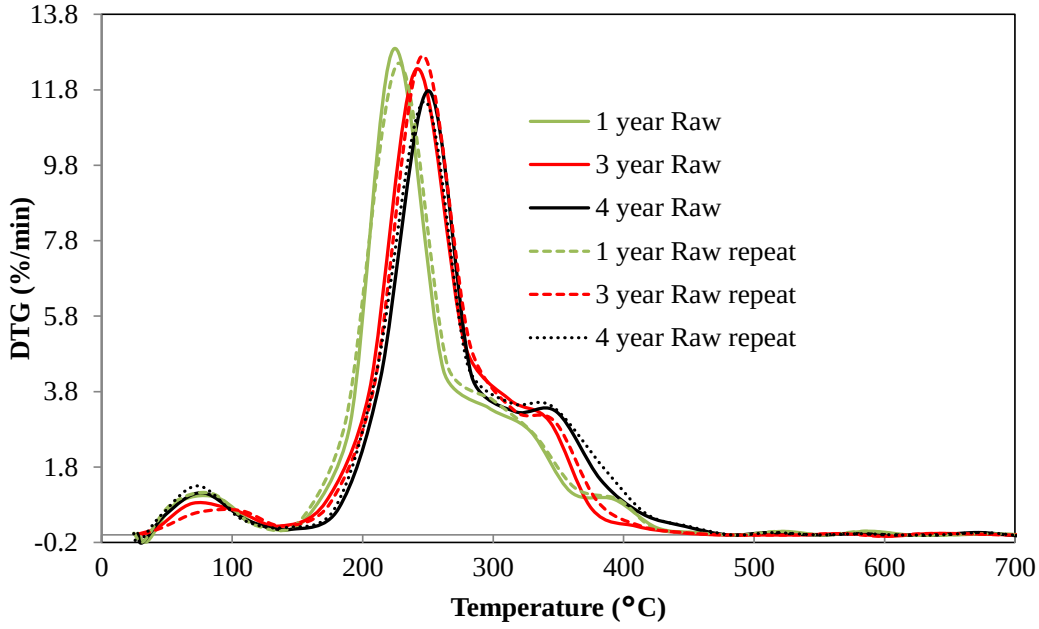

Figure 51: Repeatability check for the combustion of raw bamboo (1, 3 and 4 year old) in a TGA

8.2. Repeatability graphs of thermally treated bamboo samples (1, 3 and 4 year old).

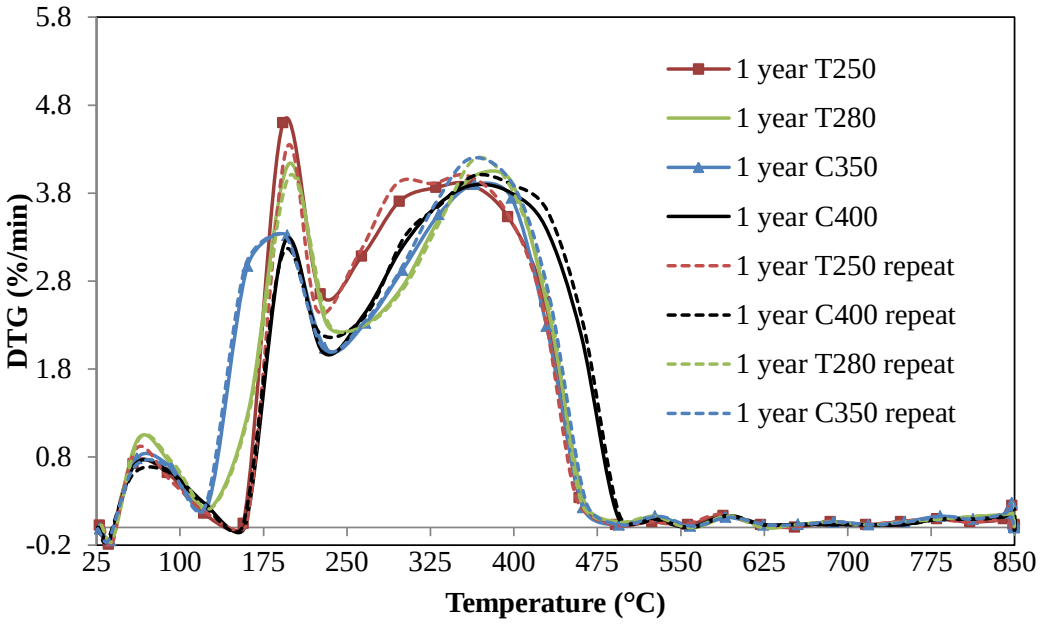

Figure 52: Repeatability check for the combustion of thermally treated 1 year old bamboo in a TGA

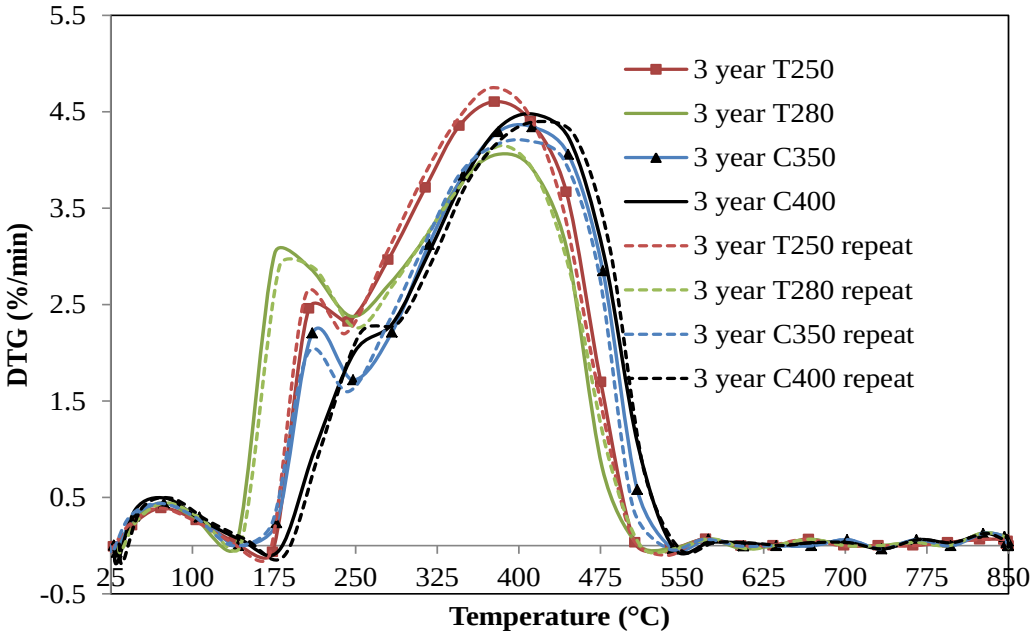

Figure 53 Repeatability check for the combustion of thermally treated 3 year old bamboo in a TGA

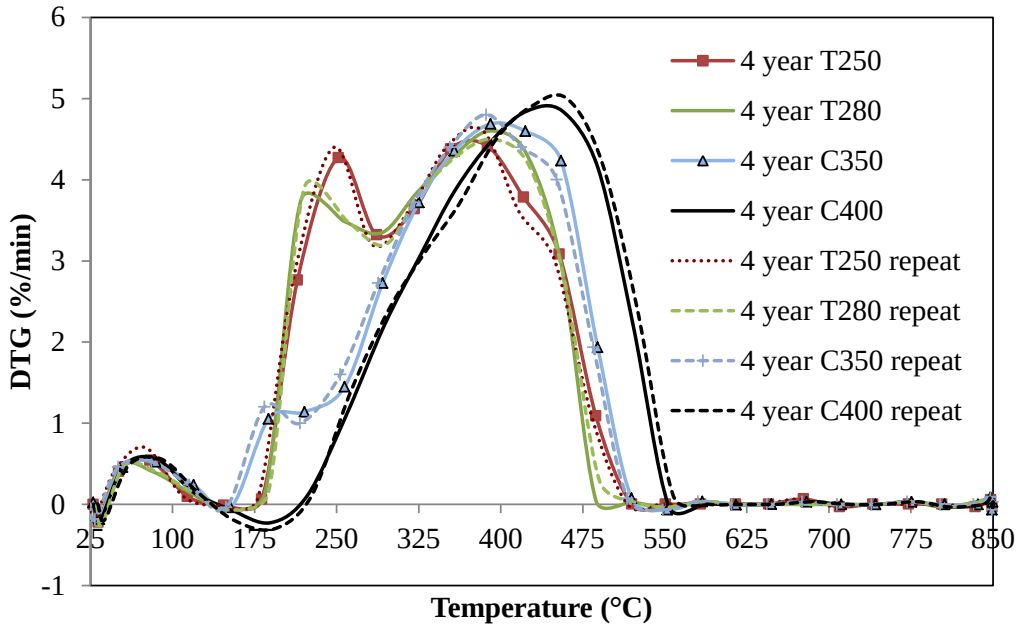

Figure 54: Repeatability check for the combustion of thermally treated 4 year old bamboo in a TGA

APPENDICES B

8.3. Experimental and calculated differential thermogravimetric profiles for the co-combustion of thermally treated 1 year old bamboo with coal

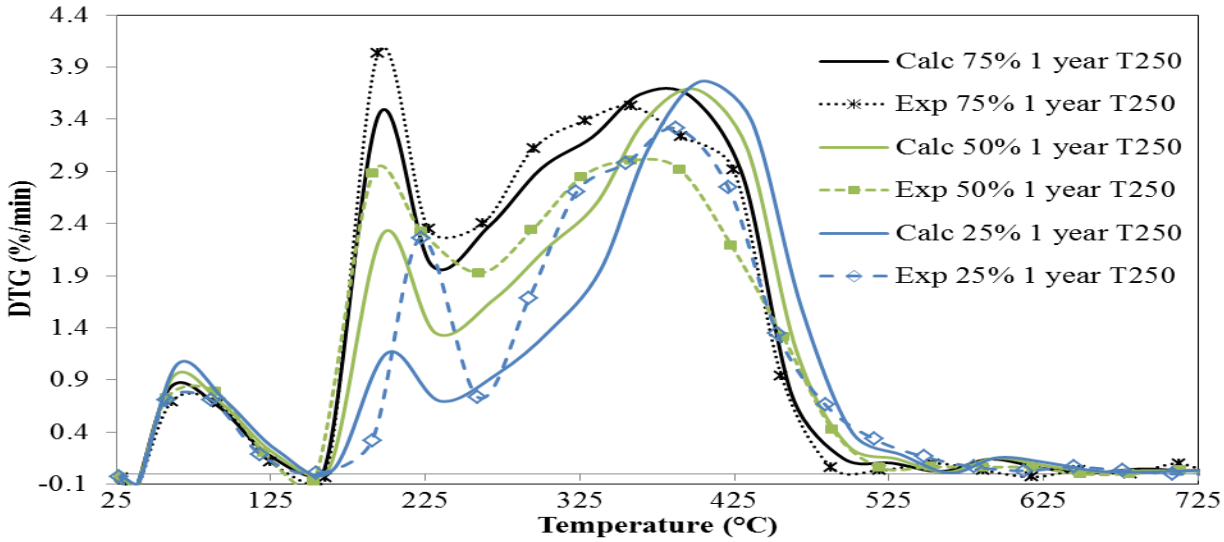

Figure 55: Experimental and calculated DTG curves of 1 year old T250 and coal blends

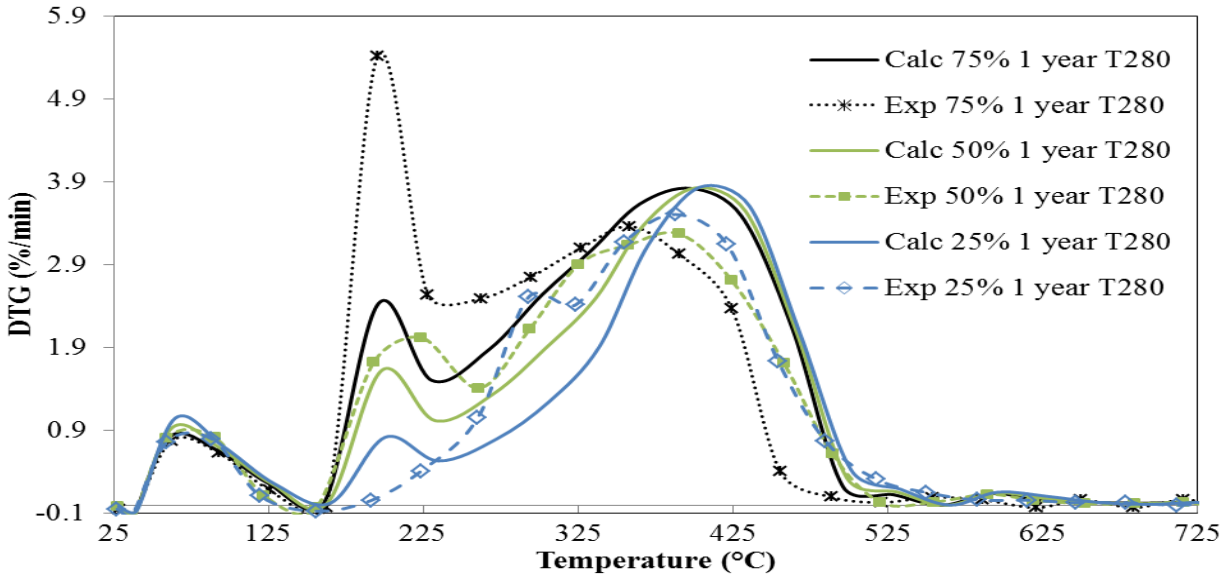

Figure 56: Experimental and calculated DTG curves of 1 year old T280 and coal blends

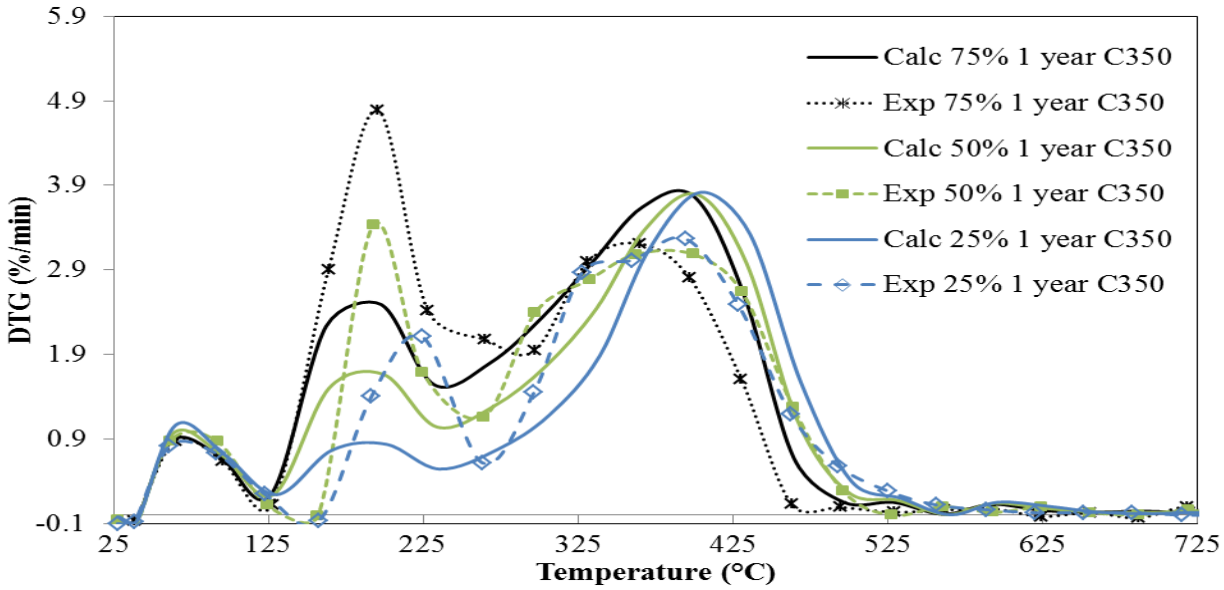

Figure 57: Experimental and calculated DTG curves of 1 year old C350 and coal blends

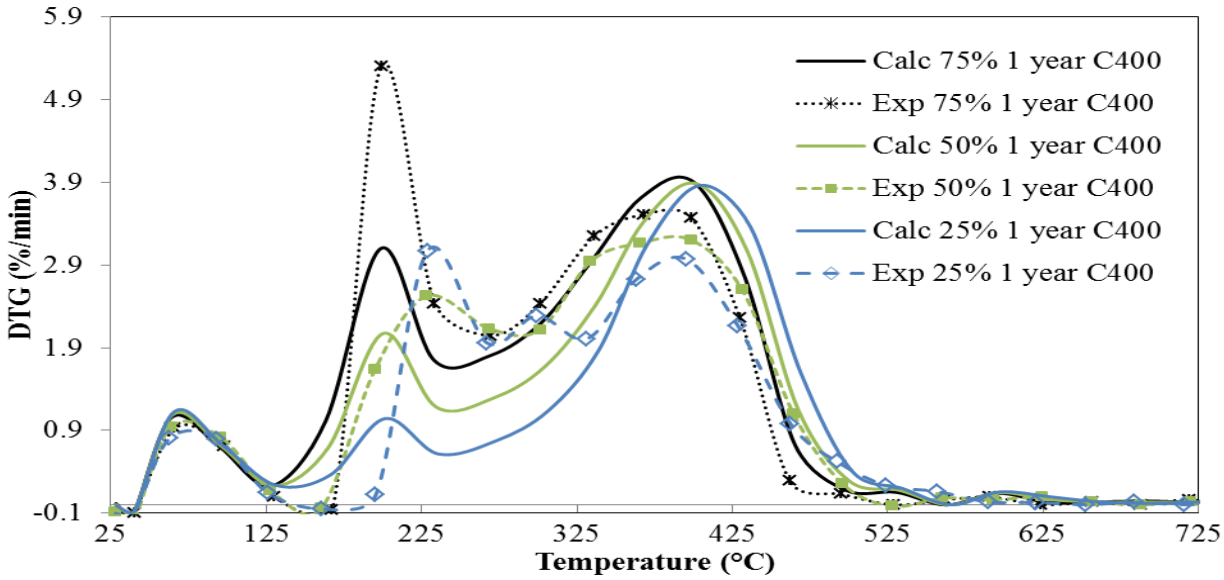

Figure 58: Experimental and calculated DTG curves of 1 year old C400 and coal blends

8.4. Experimental and calculated differential thermogravimetric profiles for the co-combustion of thermally treated 3 year old bamboo with coal

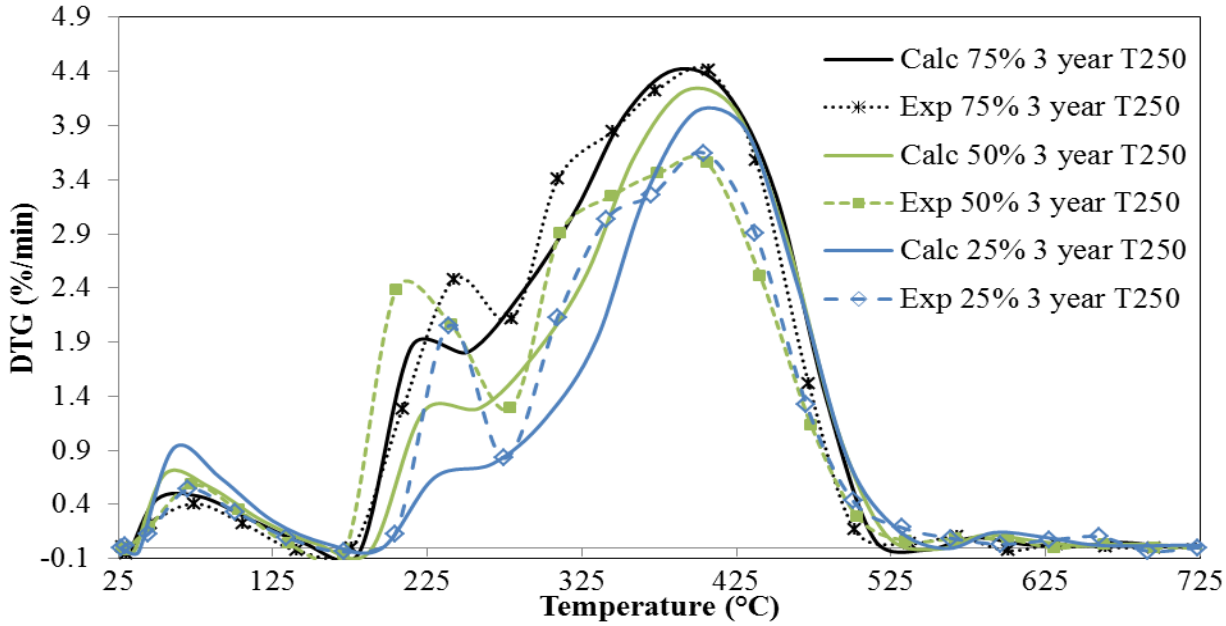

Figure 59: Experimental and calculated DTG curves of 3 year old T250 and coal blends

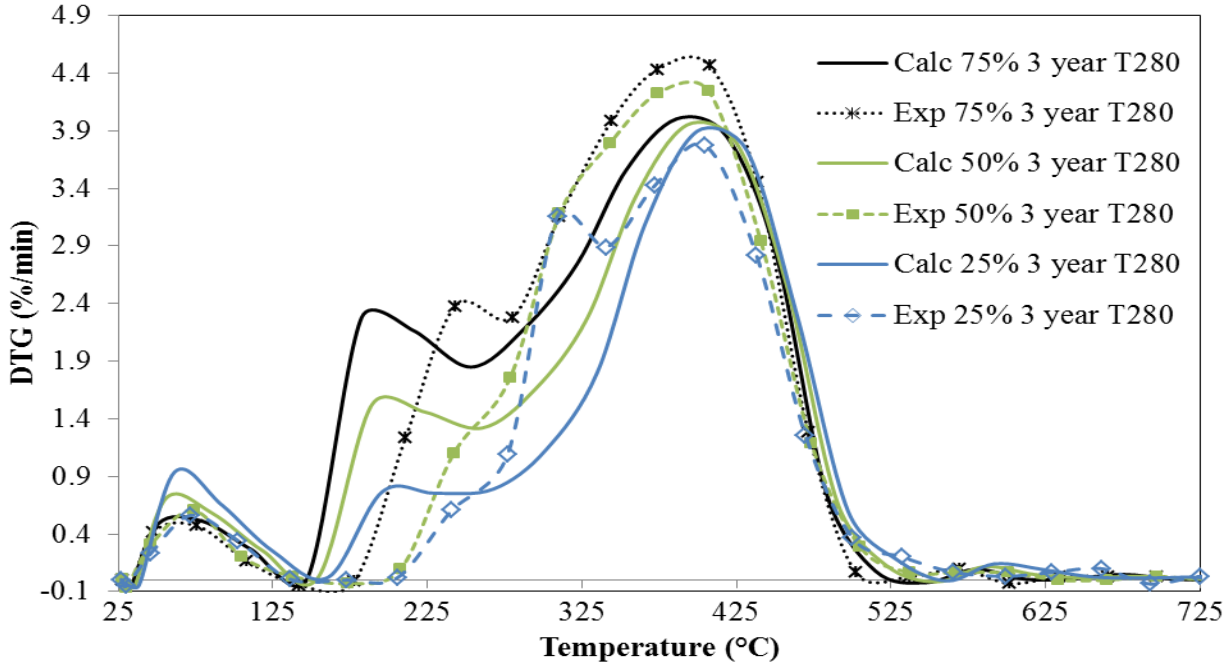

Figure 60: Experimental and calculated DTG curves of 3 year old T280 and coal blends

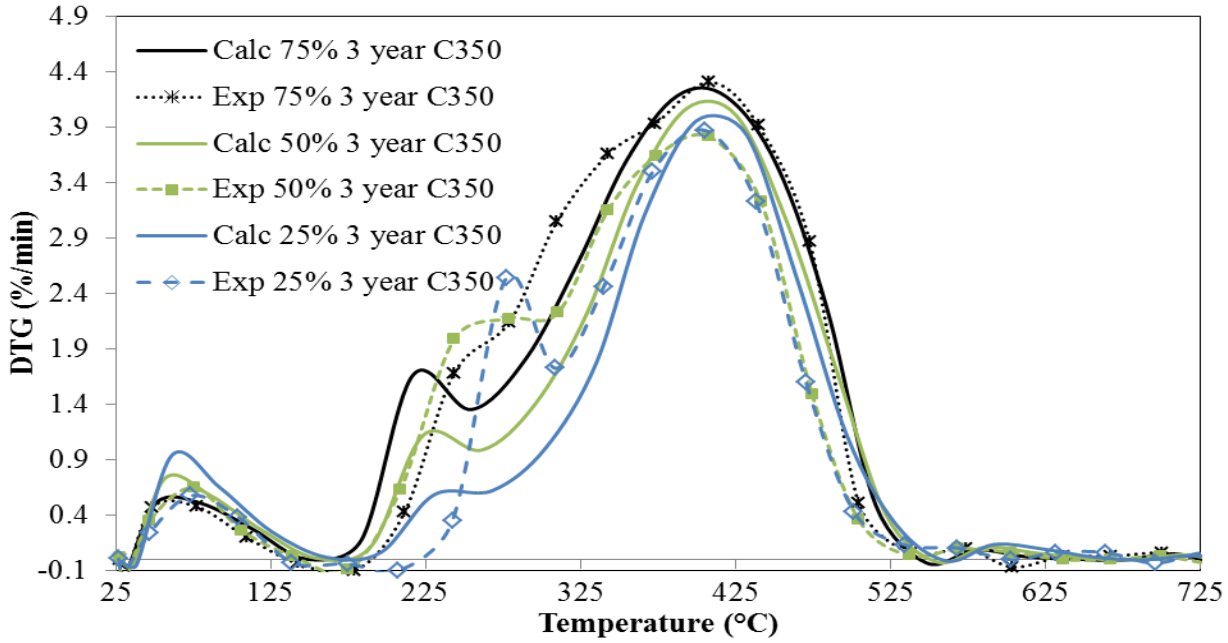

Figure 61: Experimental and calculated DTG curves of 3 year old C350 and coal blends

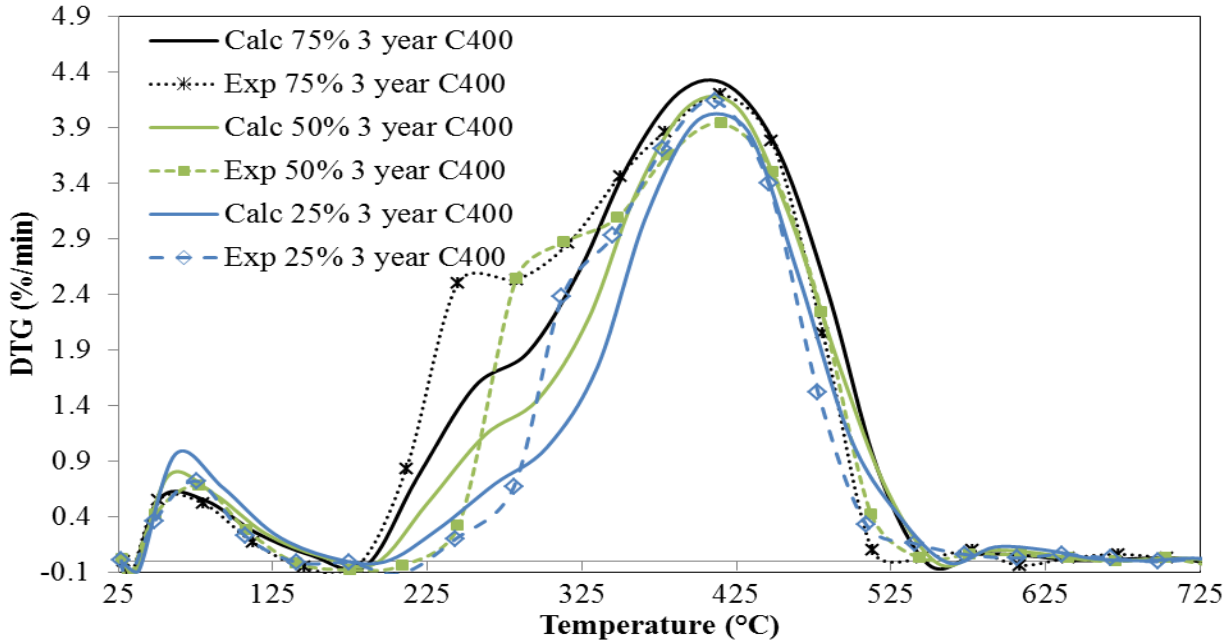

Figure 62: Experimental and calculated DTG curves of 3 year old C400 and coal blends

APPENDICES C

8.5. Differential thermogravimetric profiles for the combustion of raw and treat bamboo at varying heating rates and kinetic plots (Ozawa and Kissinger plots).

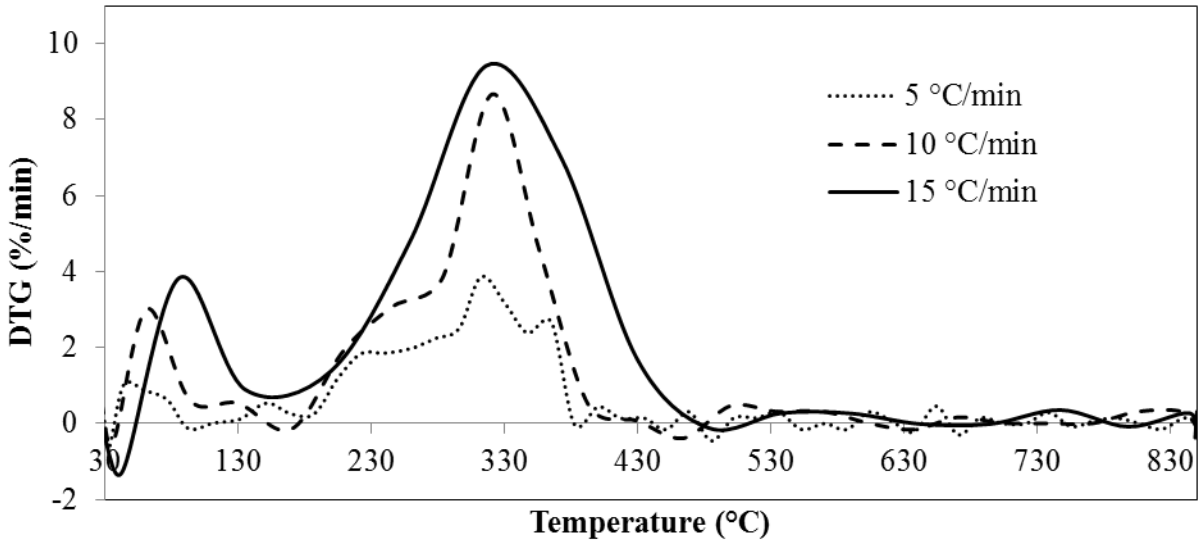

Figure 63: DTG curves of 1 year old T250 bamboo at different heating rates

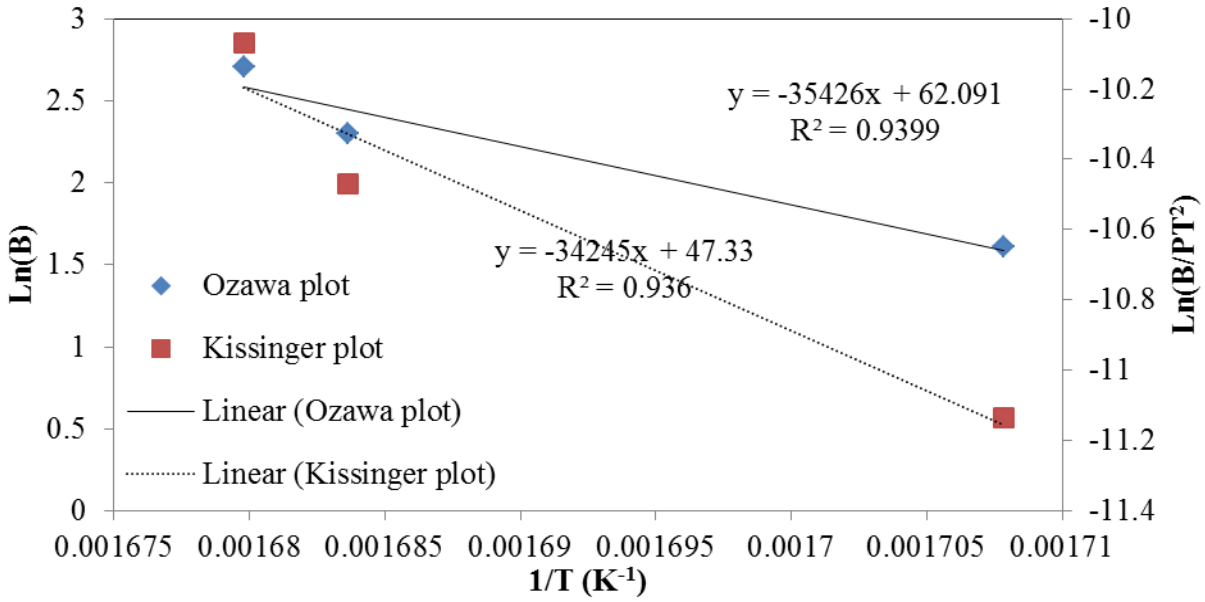

Figure 64: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 1 year old T250 bamboo

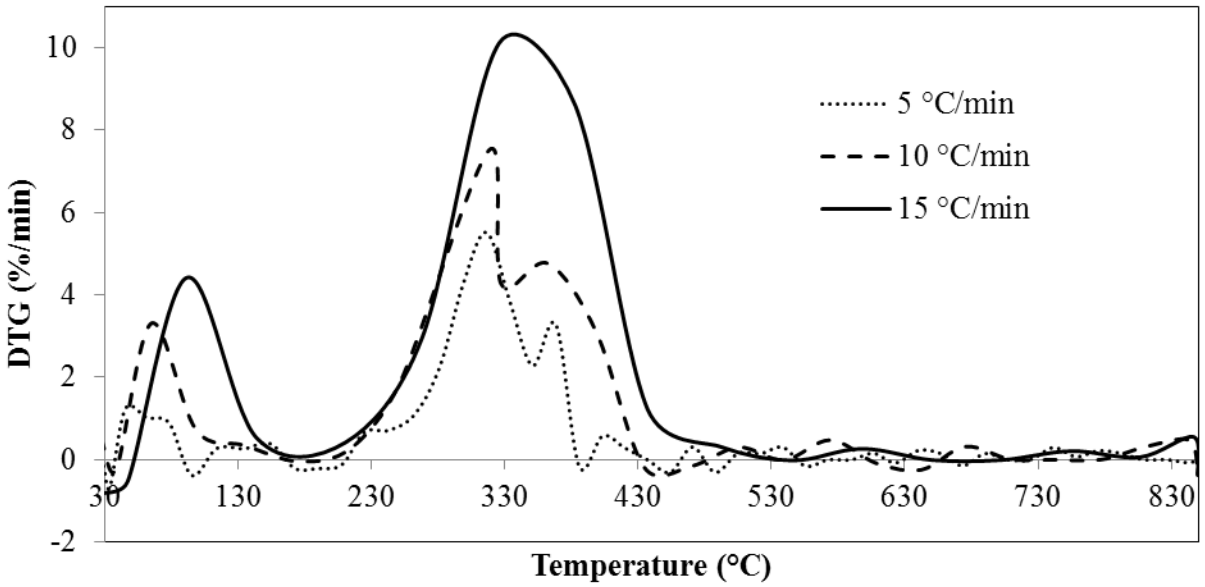

Figure 65: DTG curves of 1 year old C400 bamboo at different heating rates

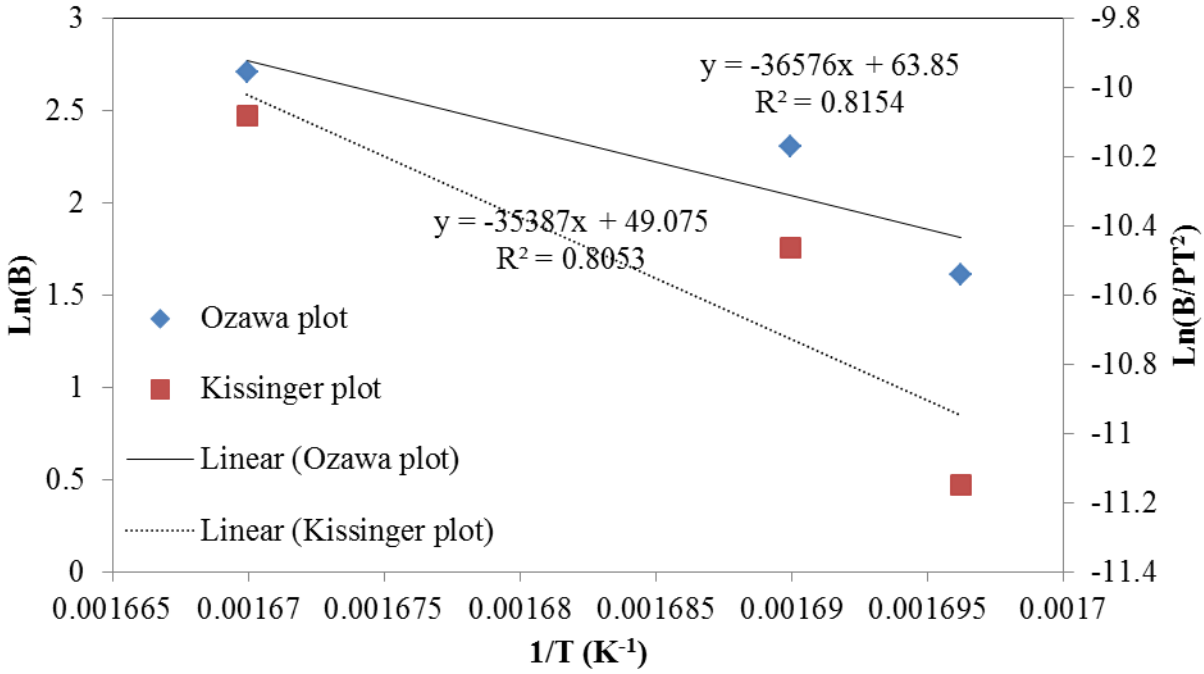

Figure 66: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 1 year old C400 bamboo

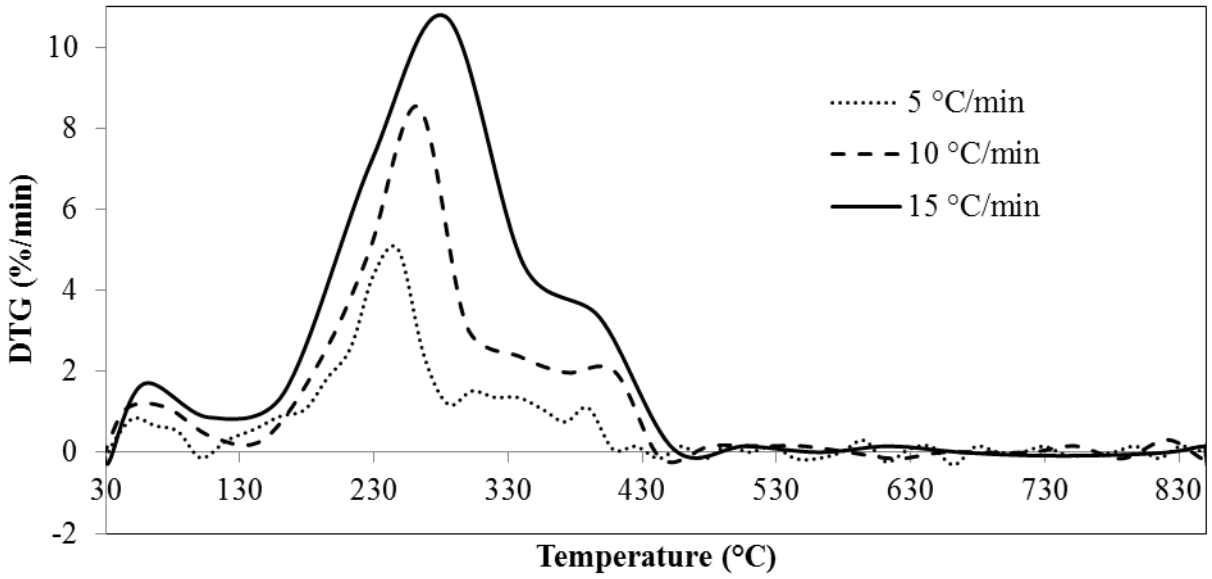

Figure 67: DTG curves of 3 year old raw bamboo at different heating rates

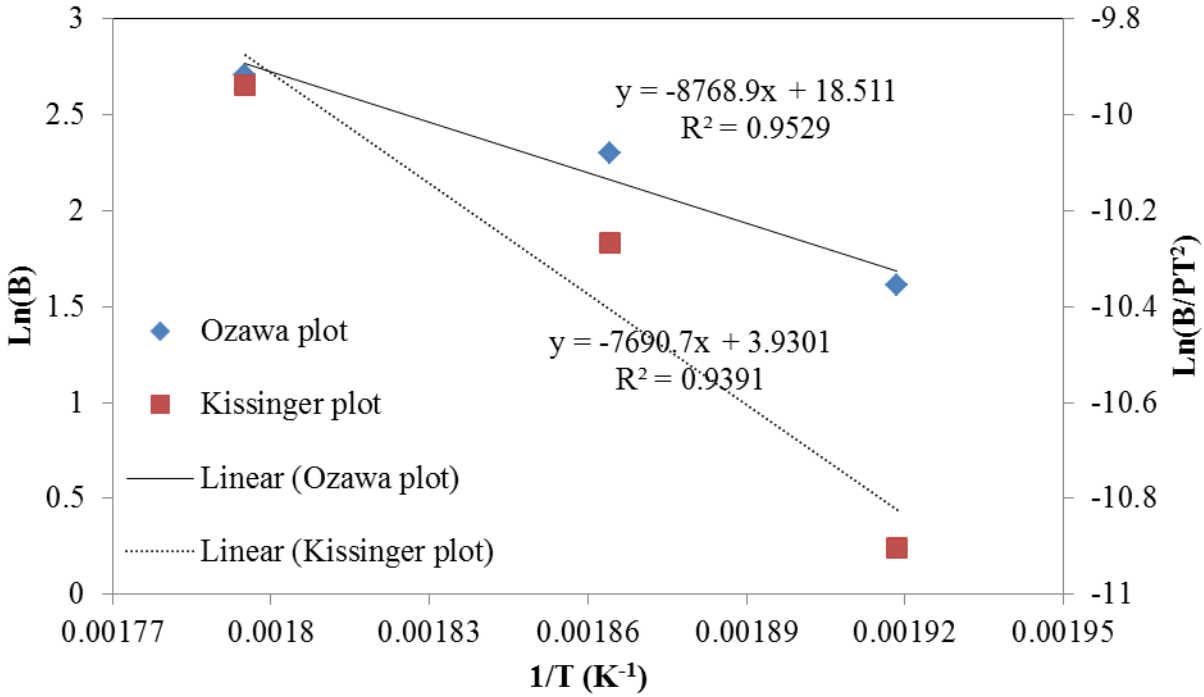

Figure 68: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 3 year old raw bamboo

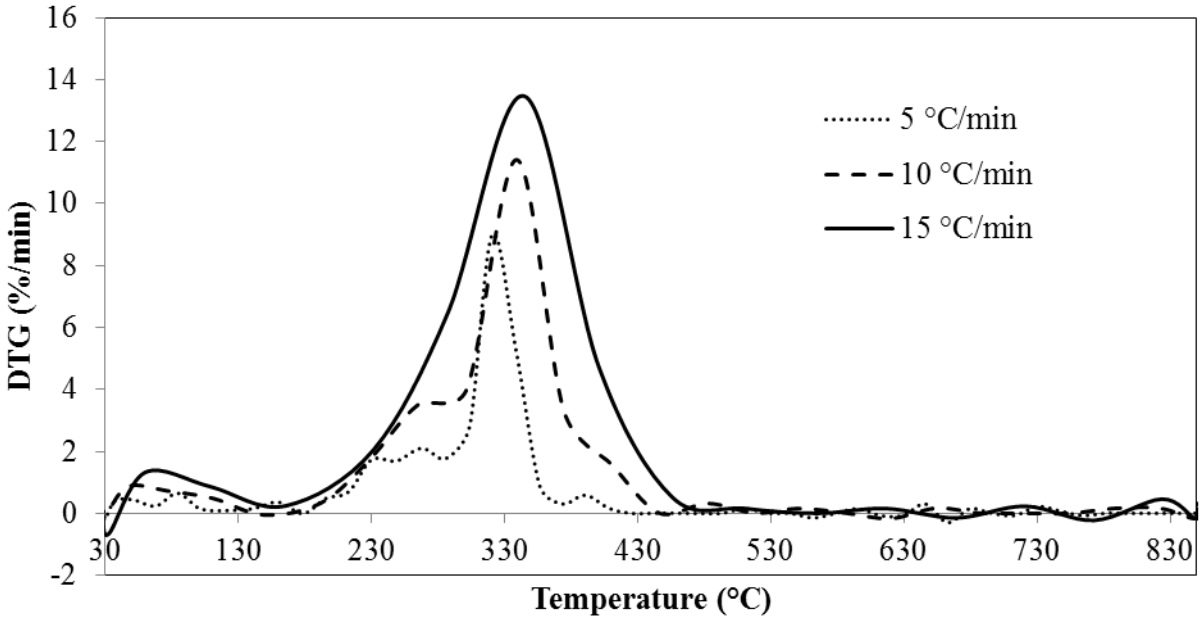

Figure 69: DTG curves of 3 year old T250 bamboo at different heating rates

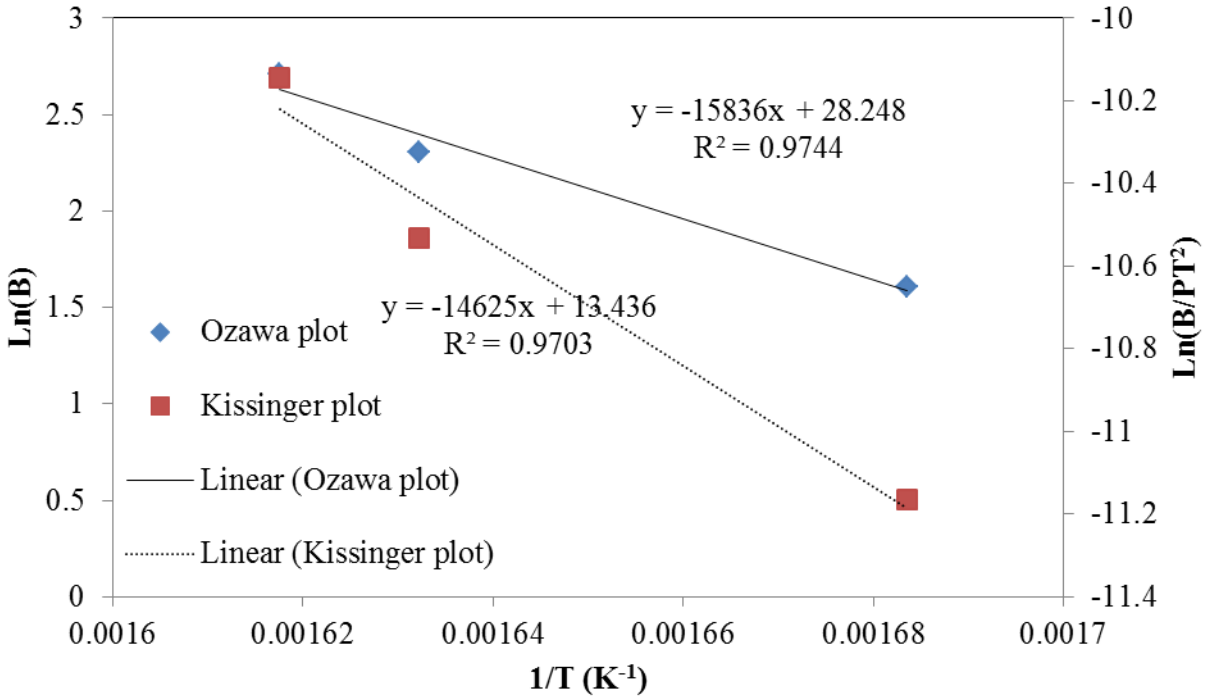

Figure 70: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 3 year old T250 bamboo

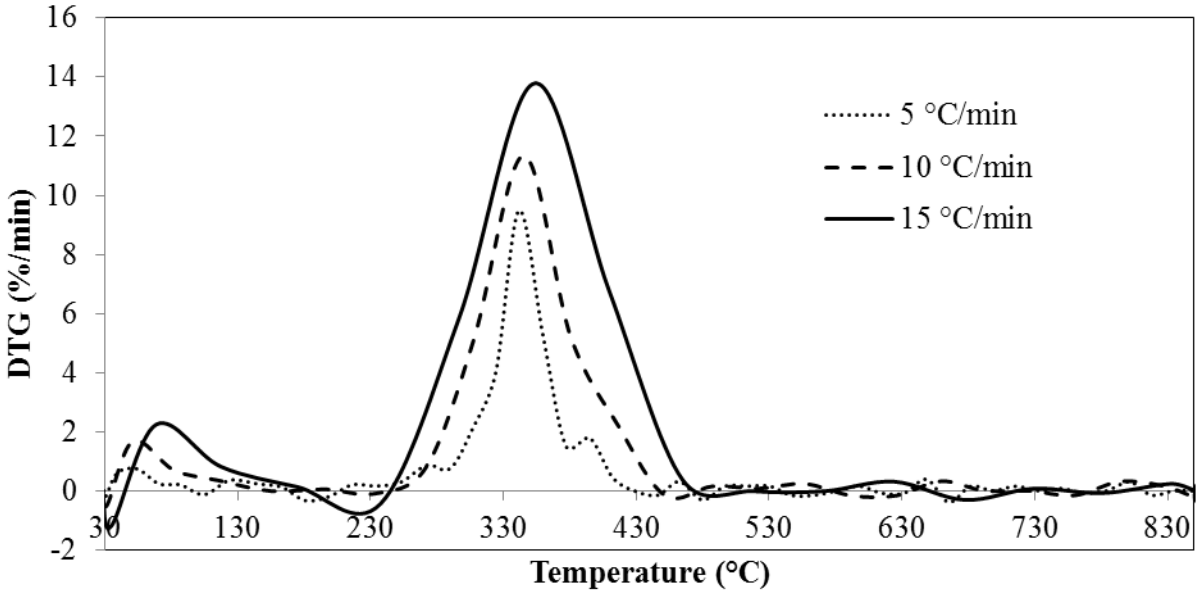

Figure 71: DTG curves of 3 year old C400 bamboo at different heating rates

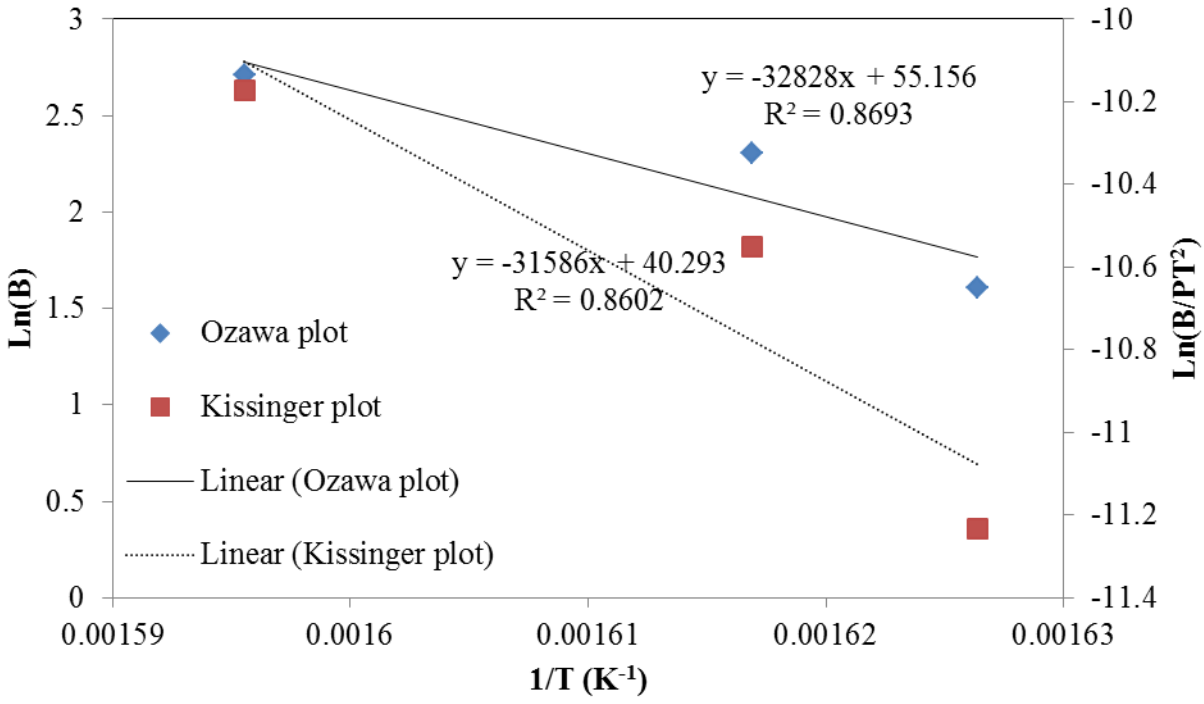

Figure 72: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 3 year old C400 bamboo

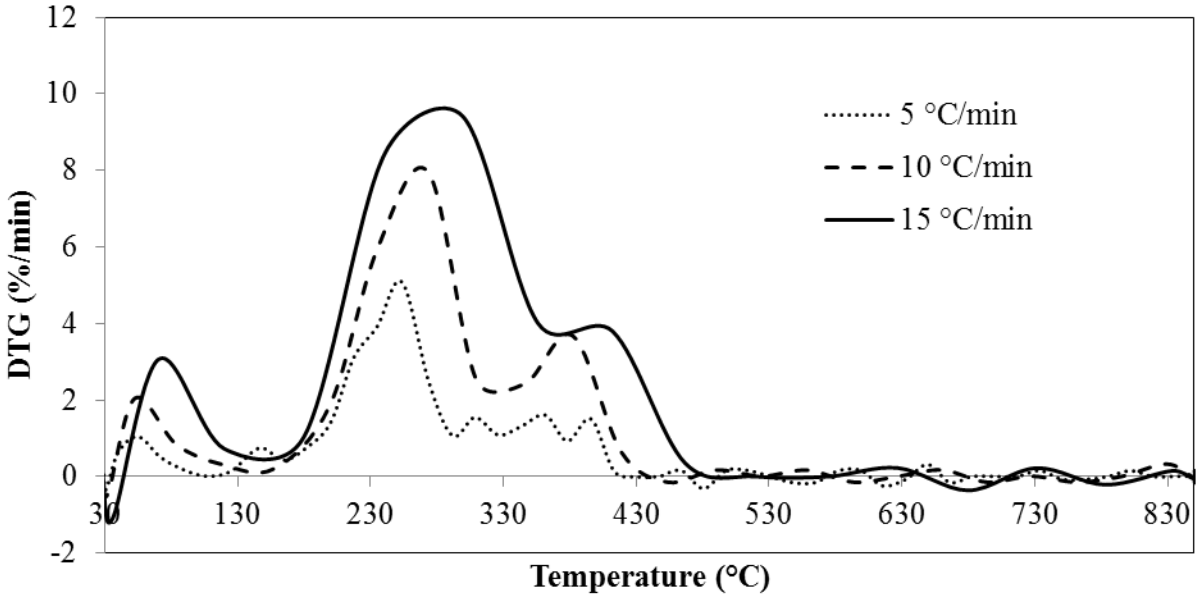

Figure 73: DTG curves of 4 year old raw bamboo at different heating rates

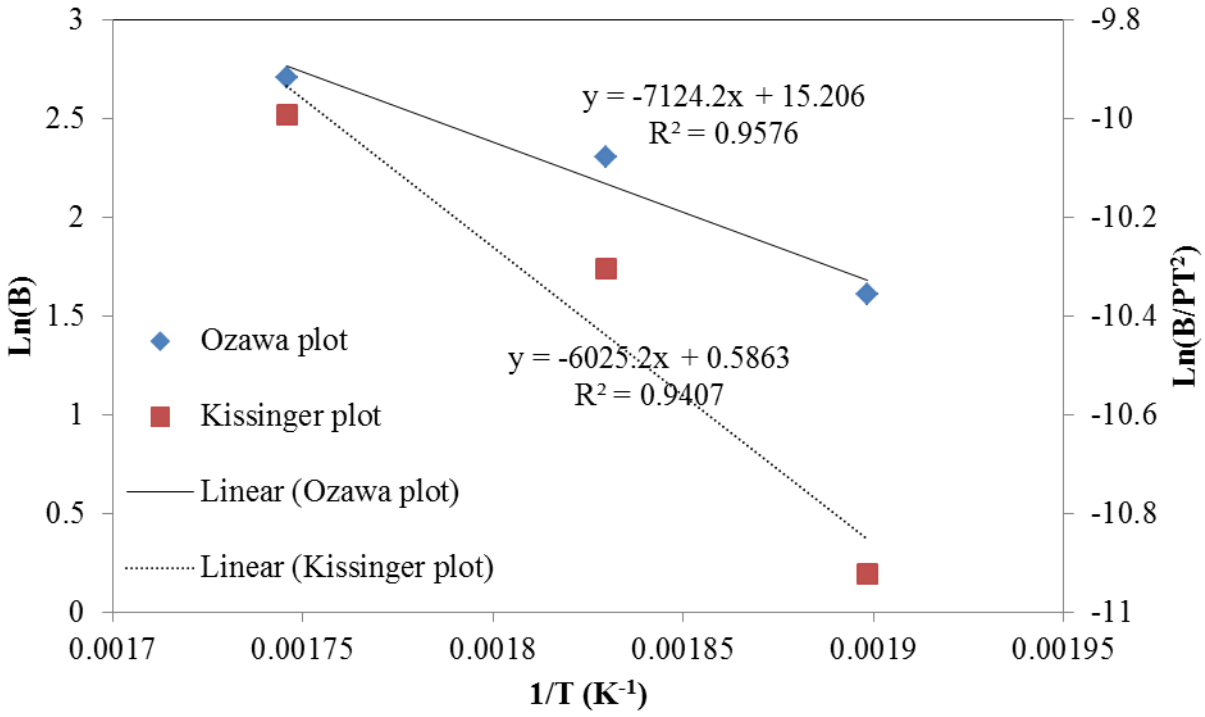

Figure 74: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 4 year old raw bamboo

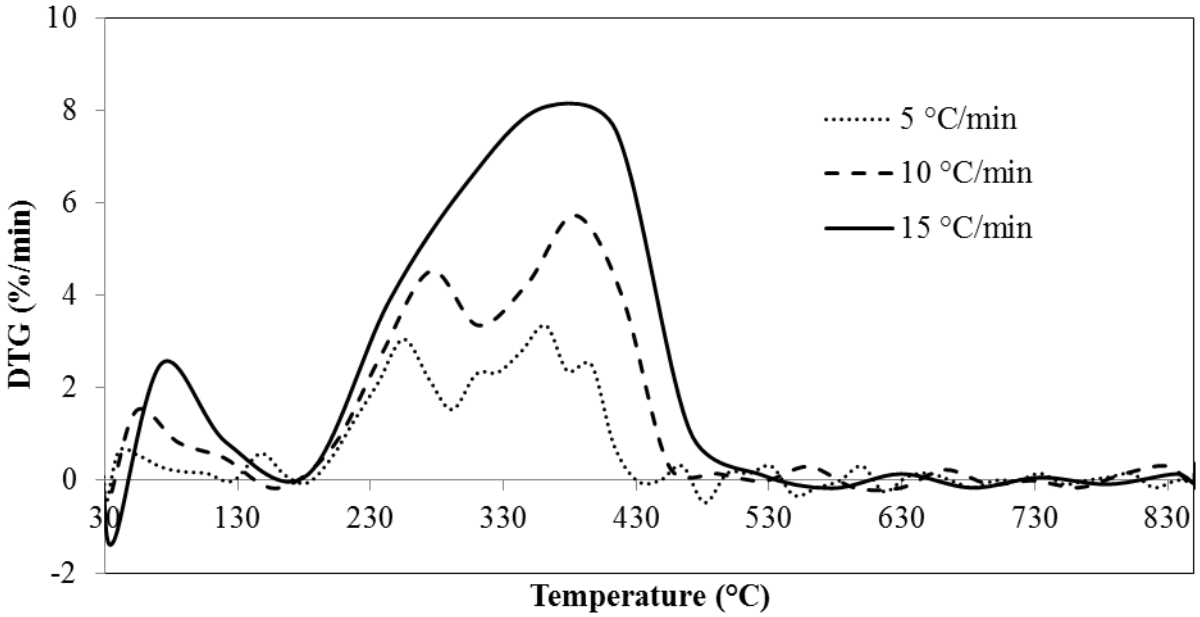

Figure 75: DTG curves of 4 year old T250 bamboo at different heating rates

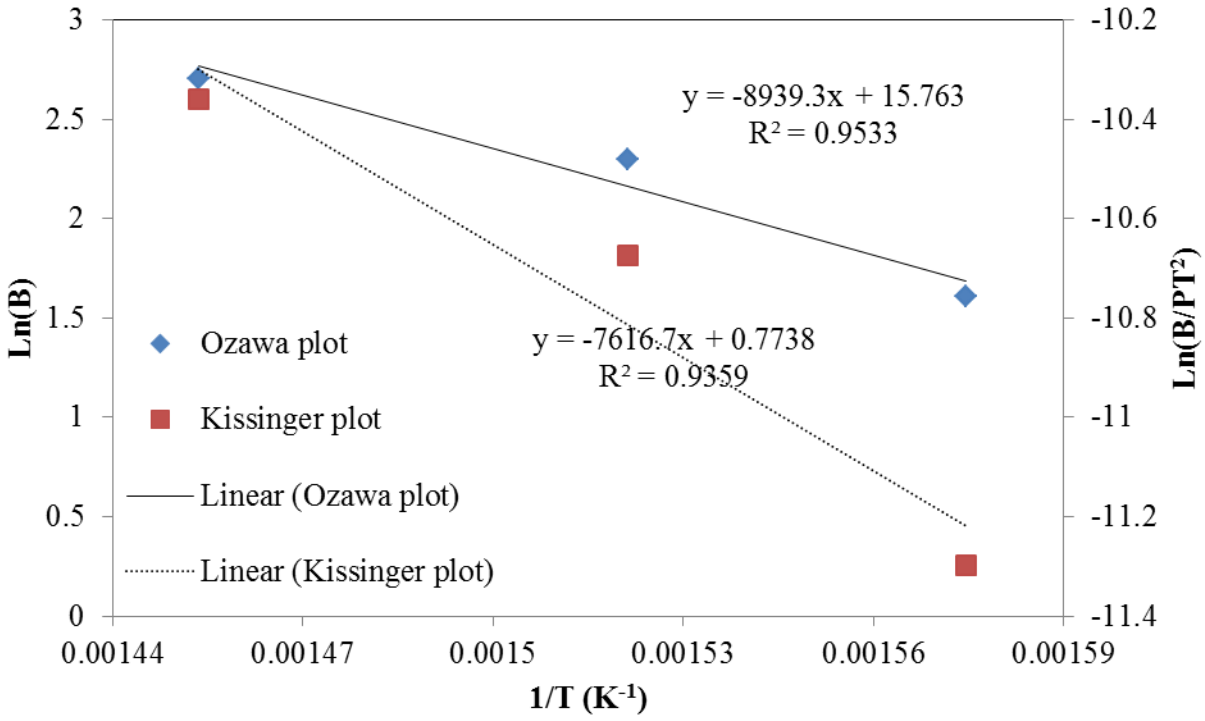

Figure 76: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 4 year old T250 bamboo

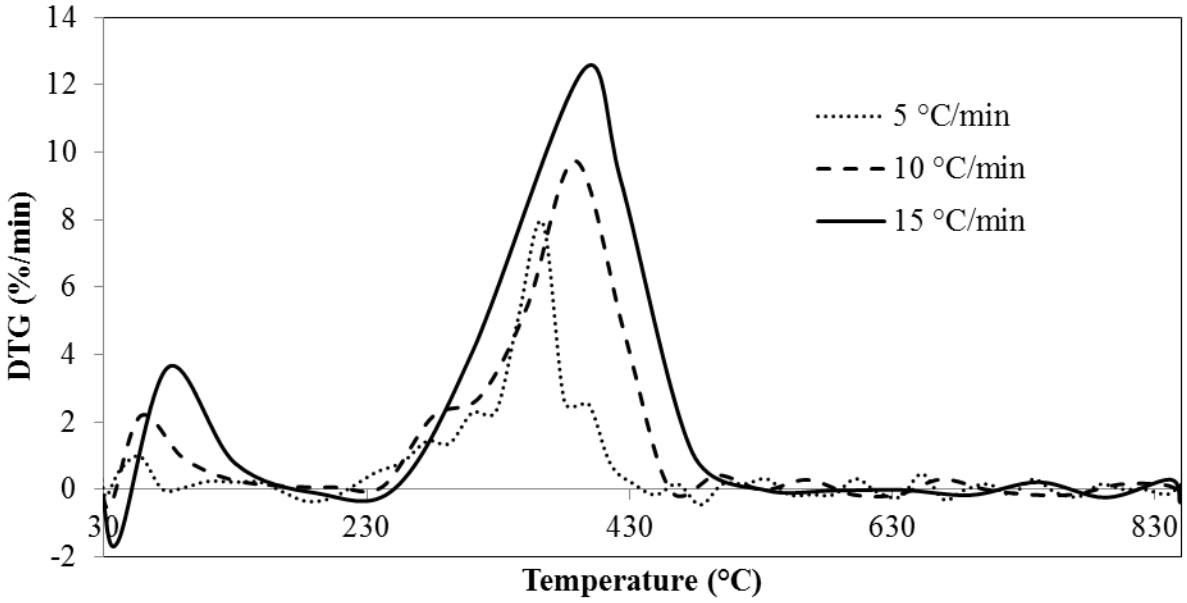

Figure 77: DTG curves of 4 year old C400 bamboo at different heating rates

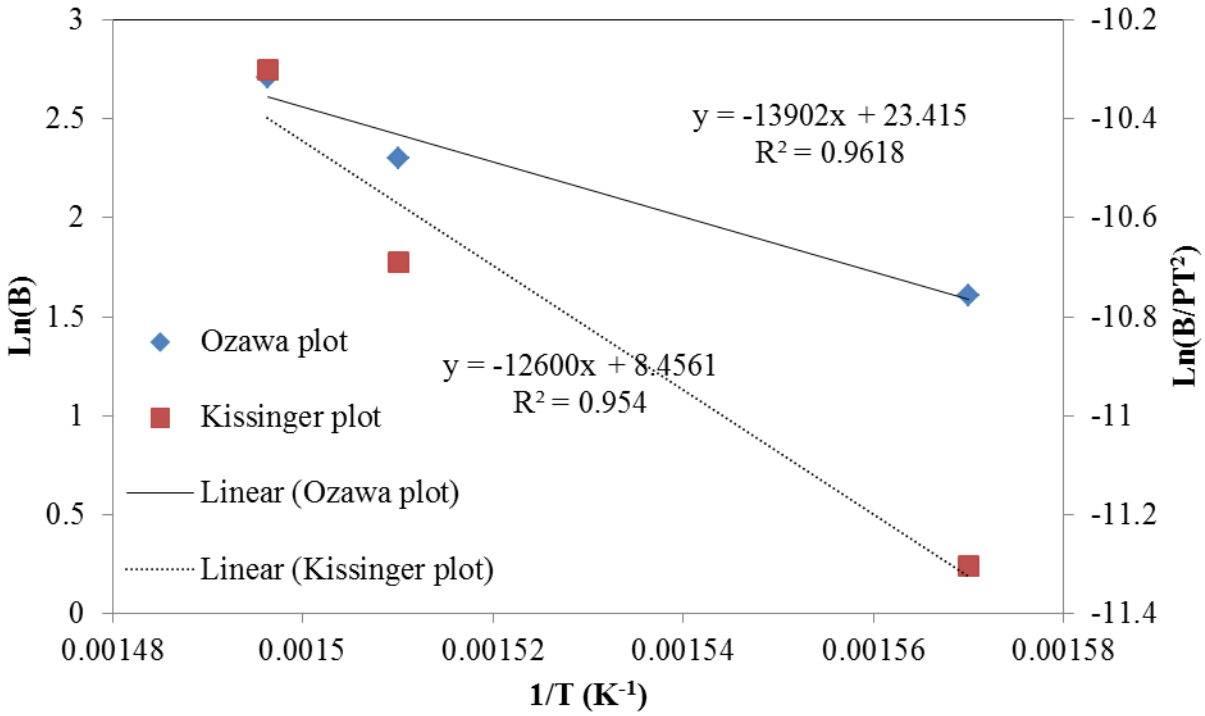

Figure 78: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of 4 year old C400 bamboo

8.6. Differential thermogravimetric profiles for the co-combustion of 4 year old bamboo with coal at varying heating rates and kinetic plots (Ozawa and Kissinger plots).

8.6.1. Co-combustion of 4 year old raw bamboo with coal.

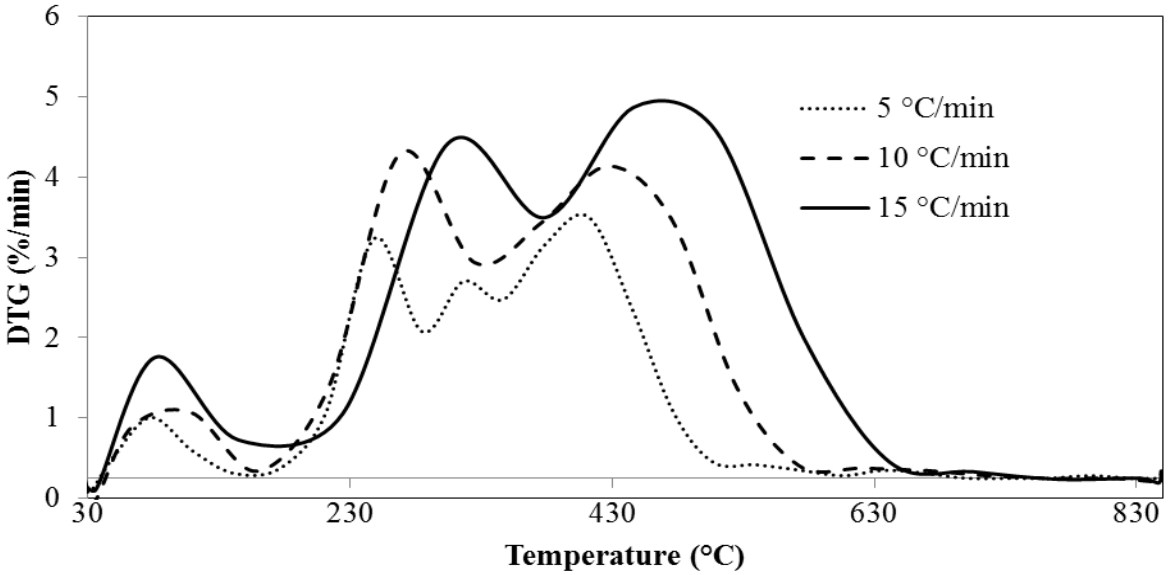

Figure 79: DTG curves of (25% 4 years raw + 75% coal) blend at different heating rates

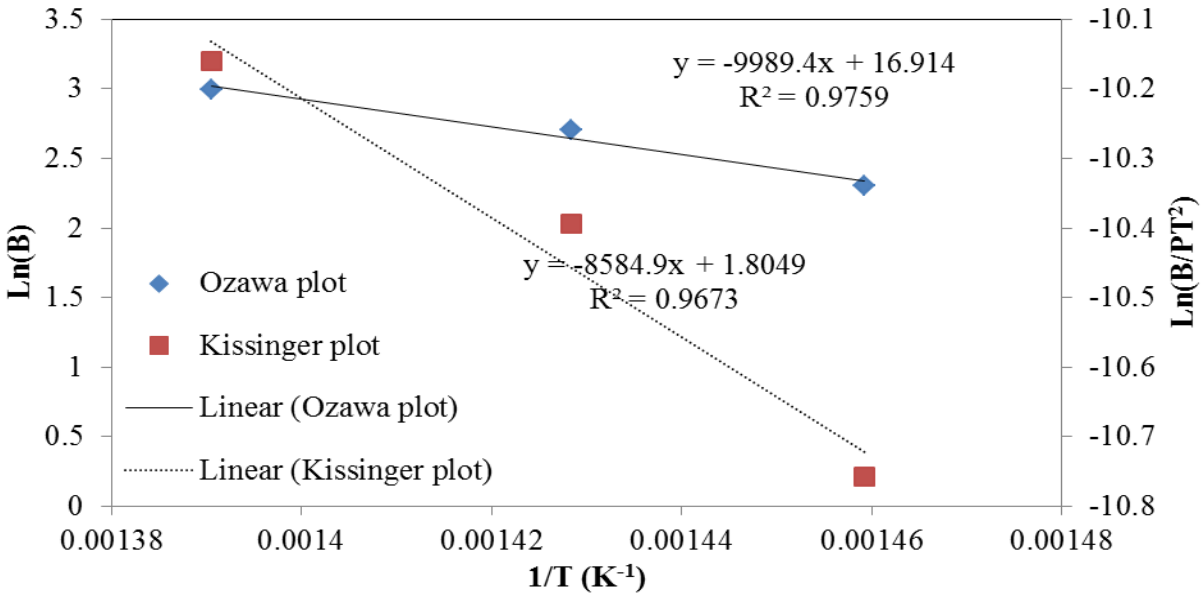

Figure 80: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (25% 4 years raw + 75% coal) blend

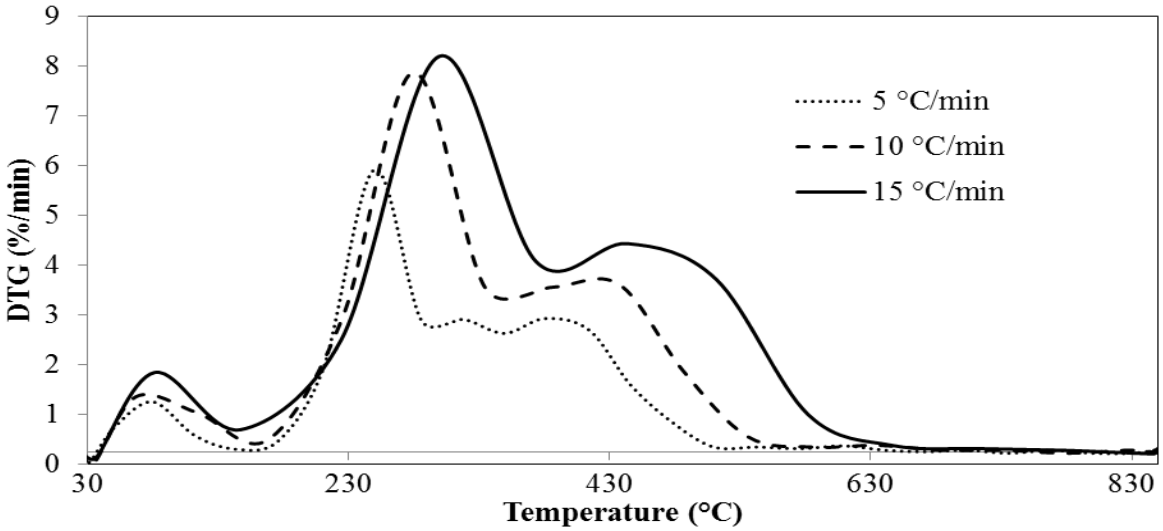

Figure 81: DTG curves of (50% 4 years raw + 50% coal) blend at different heating rates

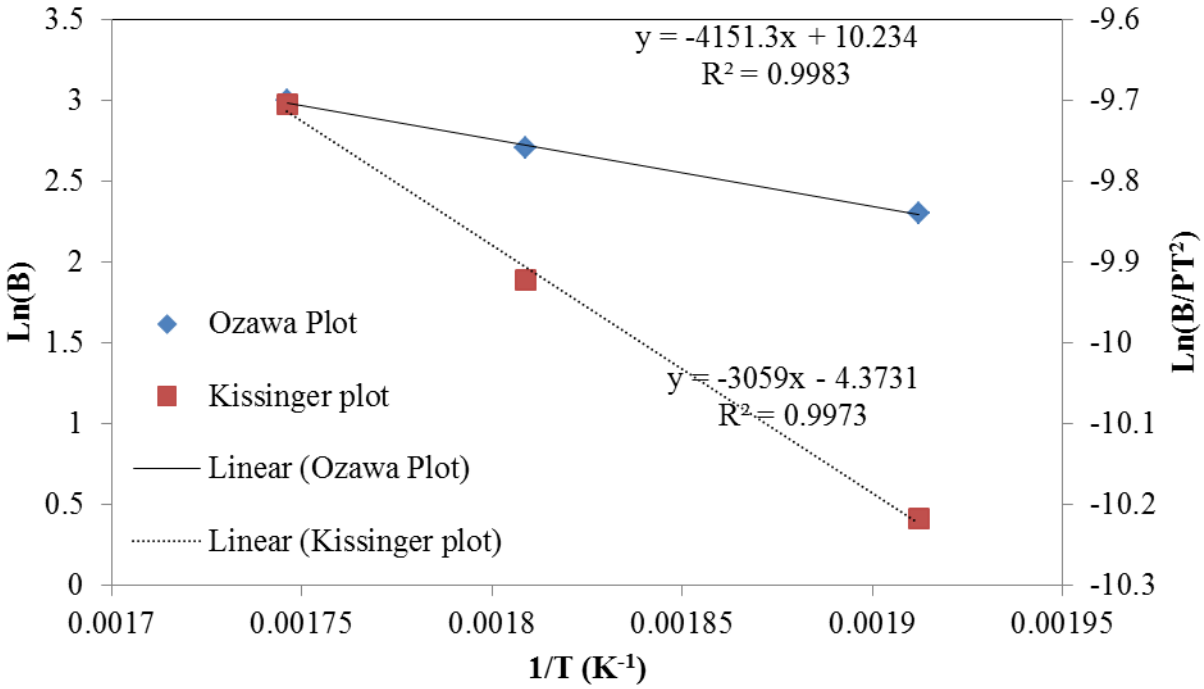

Figure 82: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (50% 4 years raw + 50% coal) blend

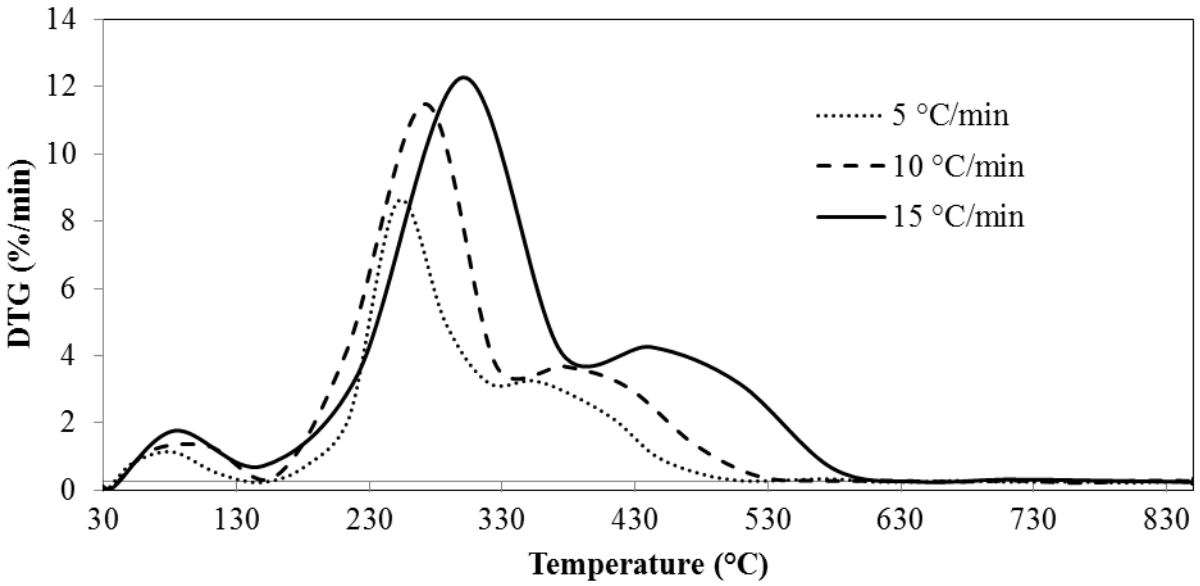

Figure 83: DTG curves of (75% 4 years raw + 25% coal) blend at different heating rates

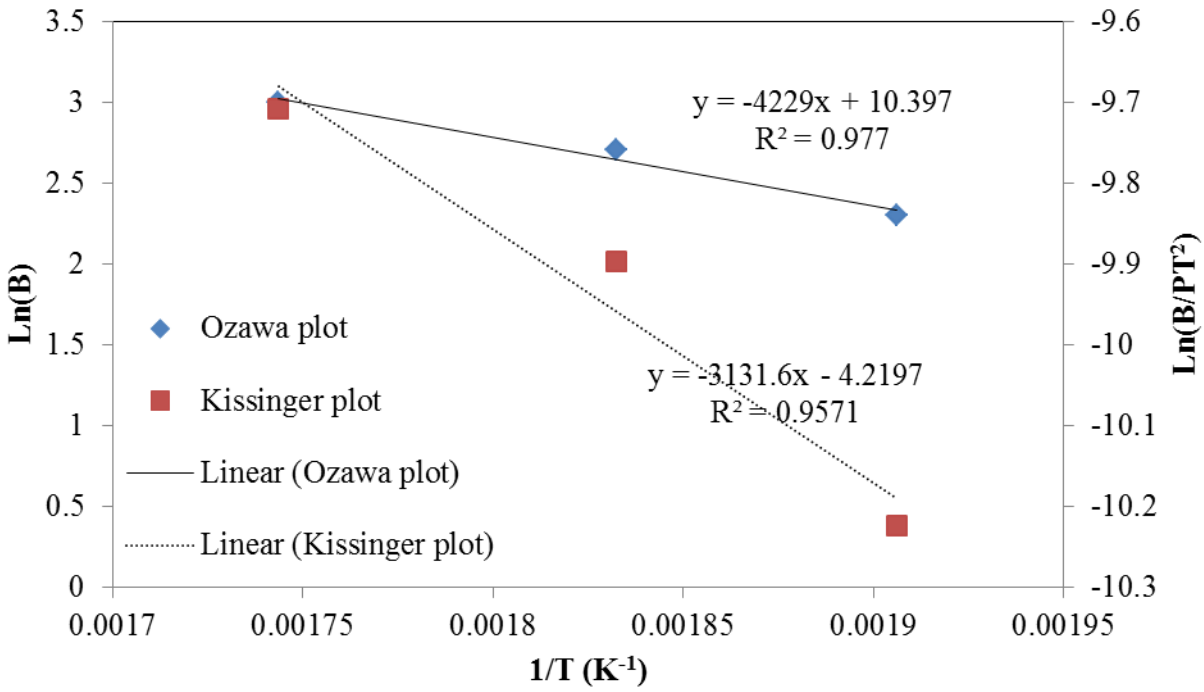

Figure 84: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (75% 4 years raw + 25% coal) blend

8.6.2. Co-combustion of 4 year old T250 bamboo with coal.

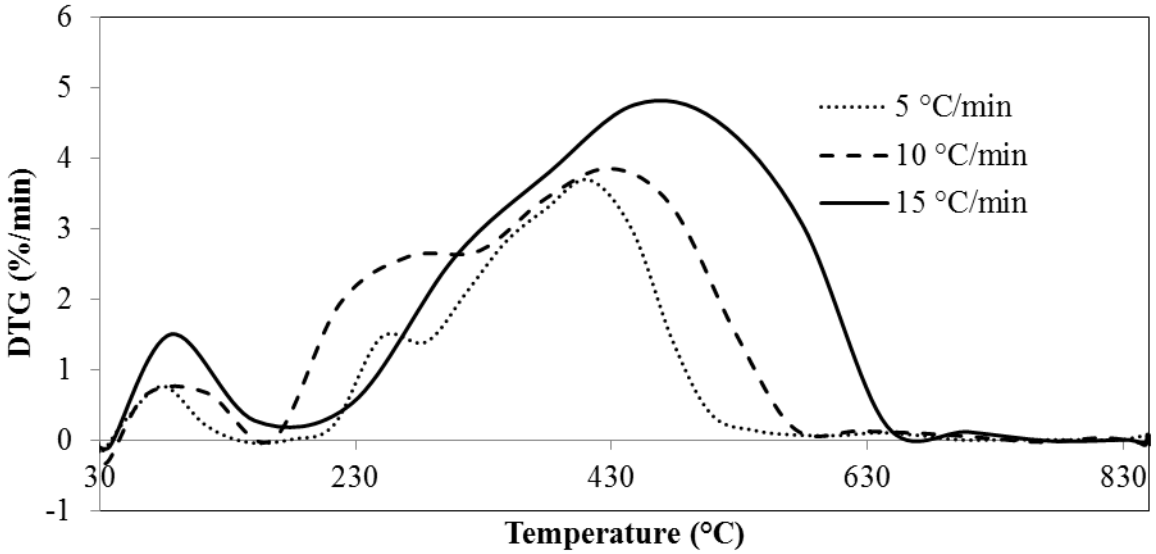

Figure 85: DTG curves of (25% 4 years T250 + 75% coal) blend at different heating rates

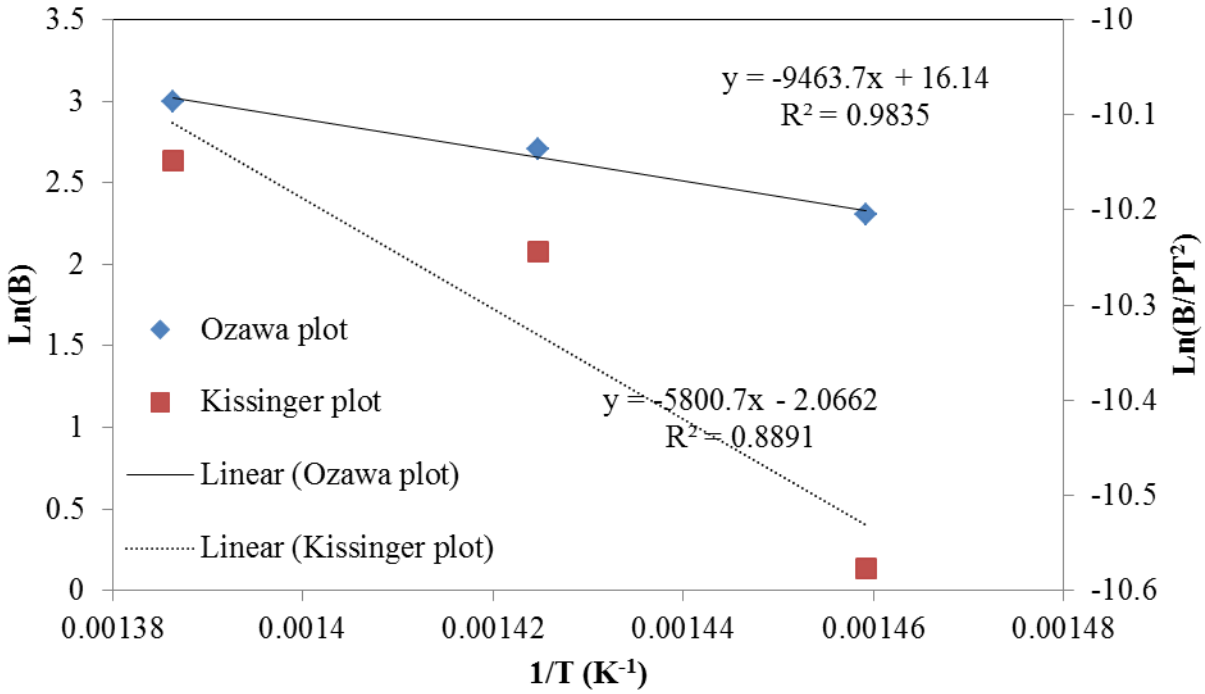

Figure 86: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (25% 4 years T250 + 75% coal) blend

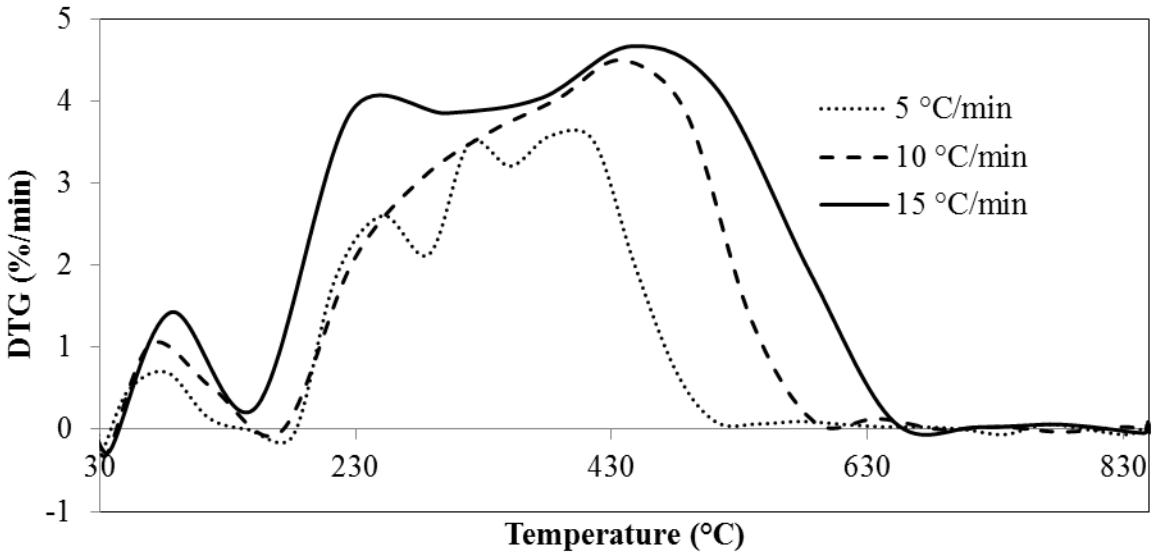

Figure 87: DTG curves of (50% 4 years T250 + 50% coal) blend at different heating rates

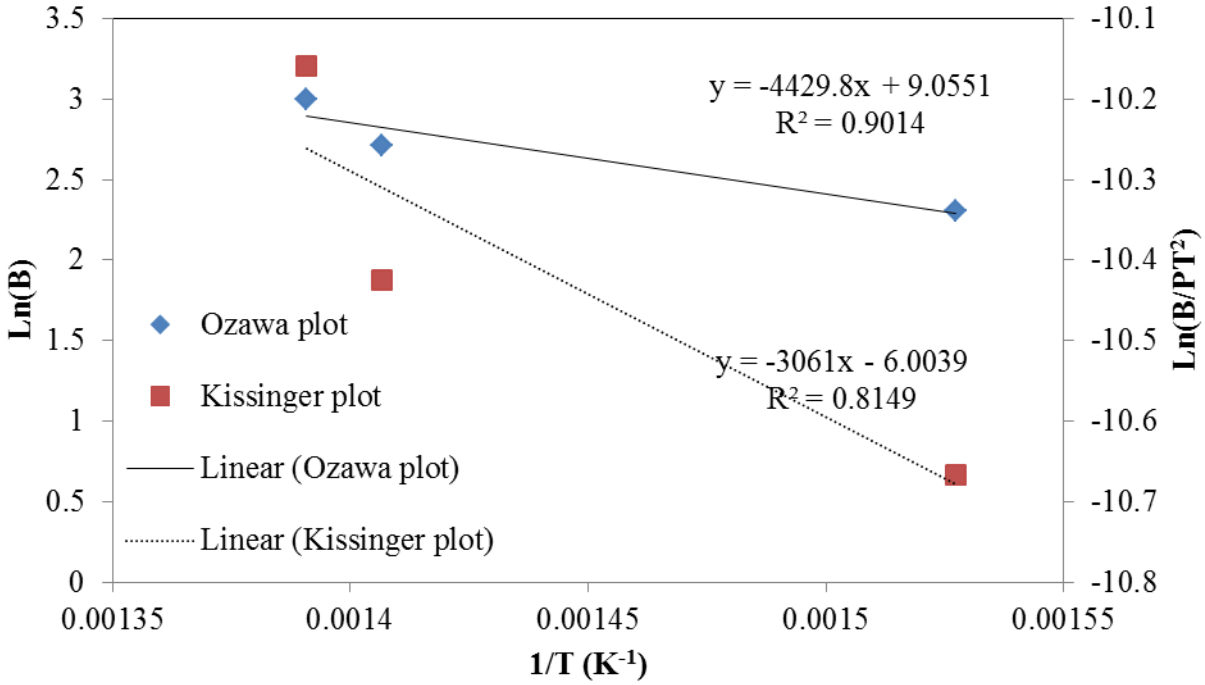

Figure 88: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (50% 4 years T250 + 50% coal) blend

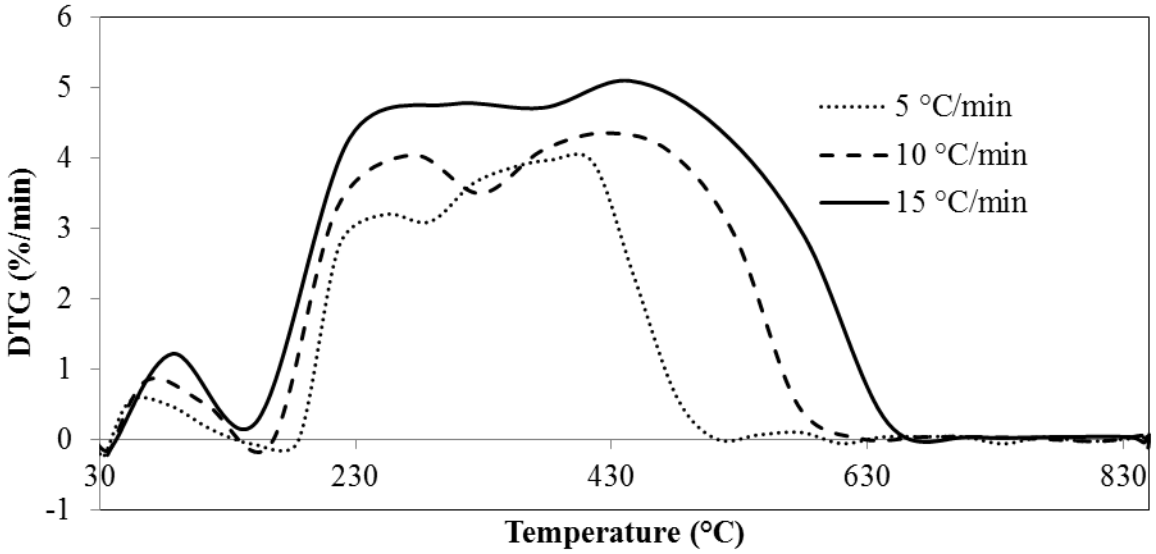

Figure 89: DTG curves of (75% 4 years T250 + 25% coal) blend at different heating rates

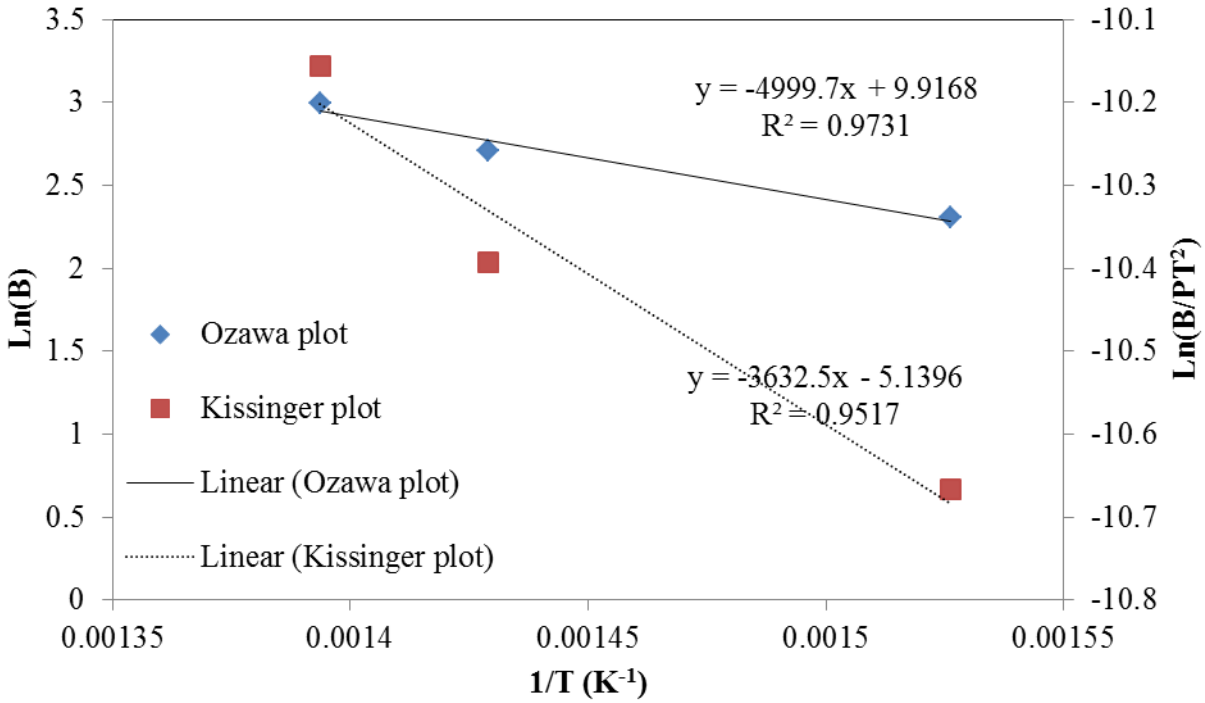

Figure 90: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (75% 4 years T250 + 25% coal) blend

8.6.3. Co-combustion of 4 years old T280 bamboo with coal.

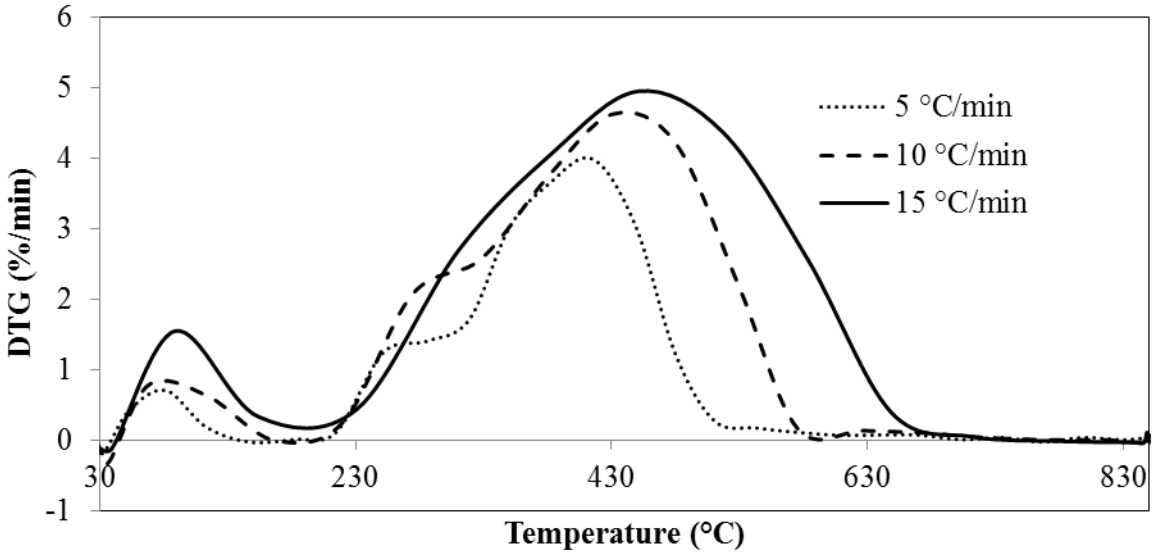

Figure 91: DTG curves of (25% 4 years T280 + 75% coal) blend at different heating rates

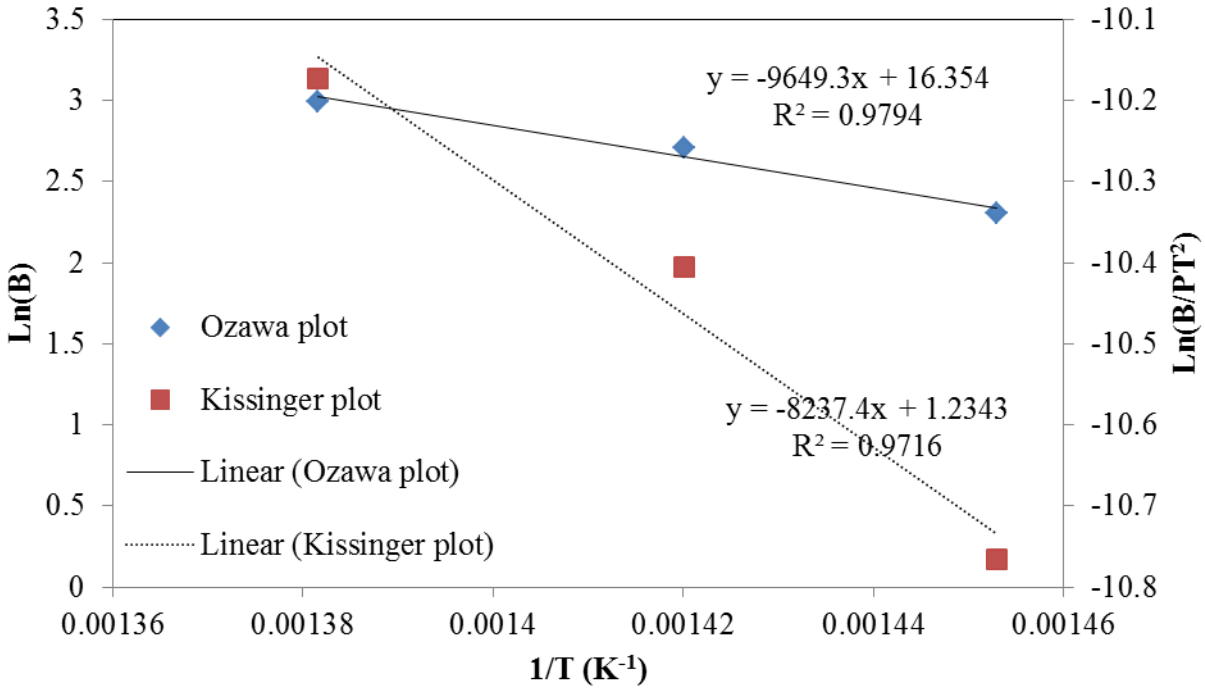

Figure 92: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (25% 4 years T280 + 75% coal) blend

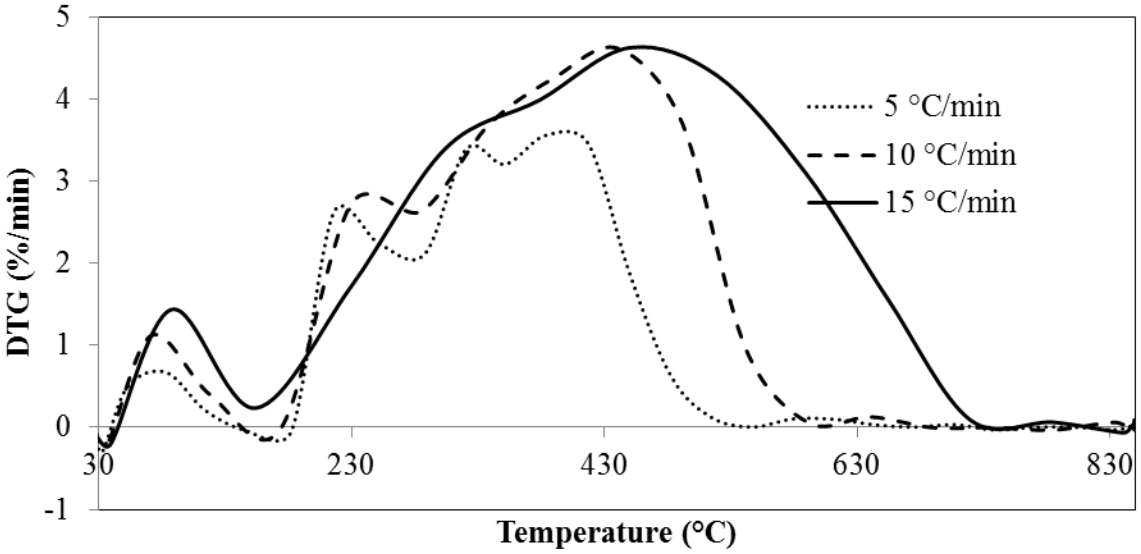

Figure 93: DTG curves of (50% 4 years T280 + 50% coal) blend at different heating rates

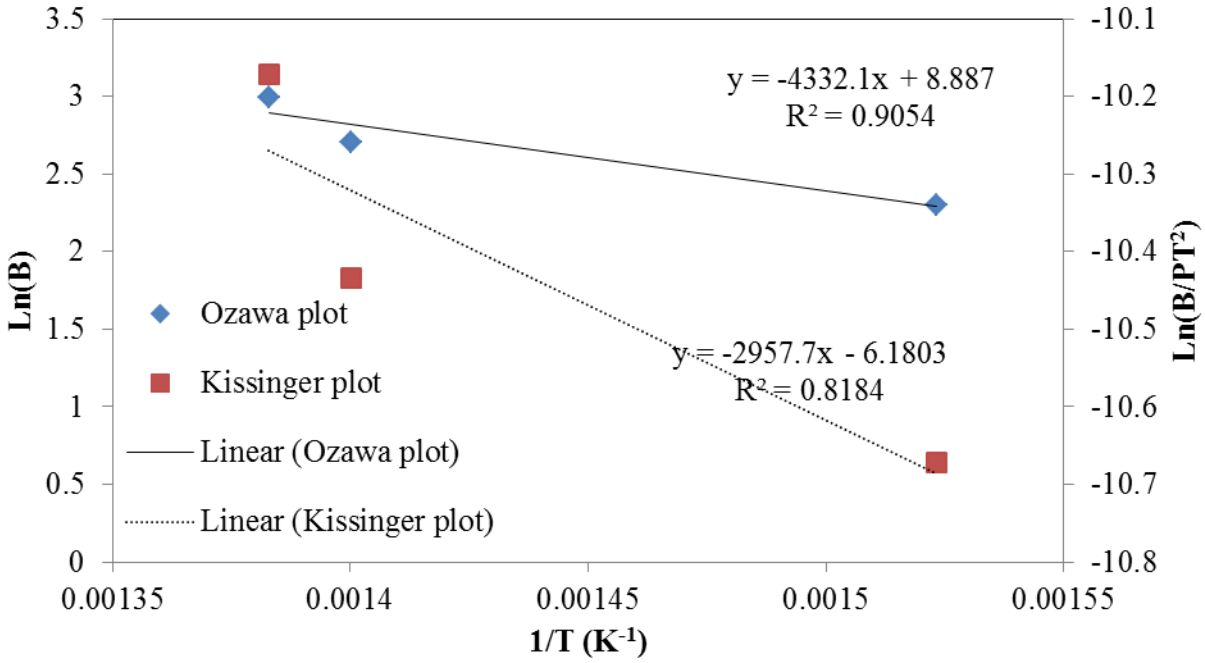

Figure 94: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (50% 4 years T280 + 50% coal) blend

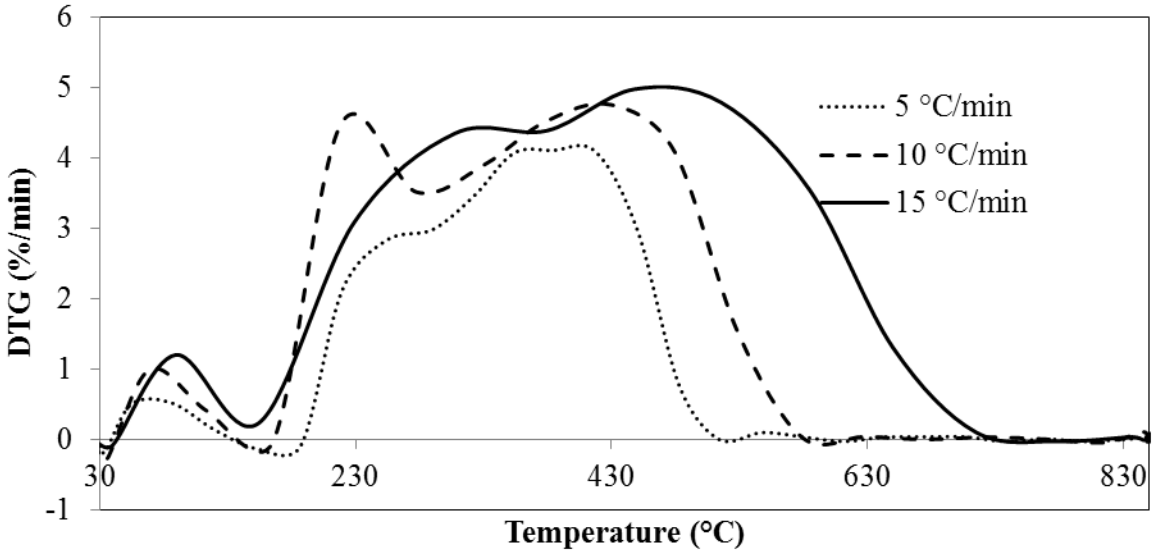

Figure 95: DTG curves of (75% 4 years T280 + 25% coal) blend at different heating rates

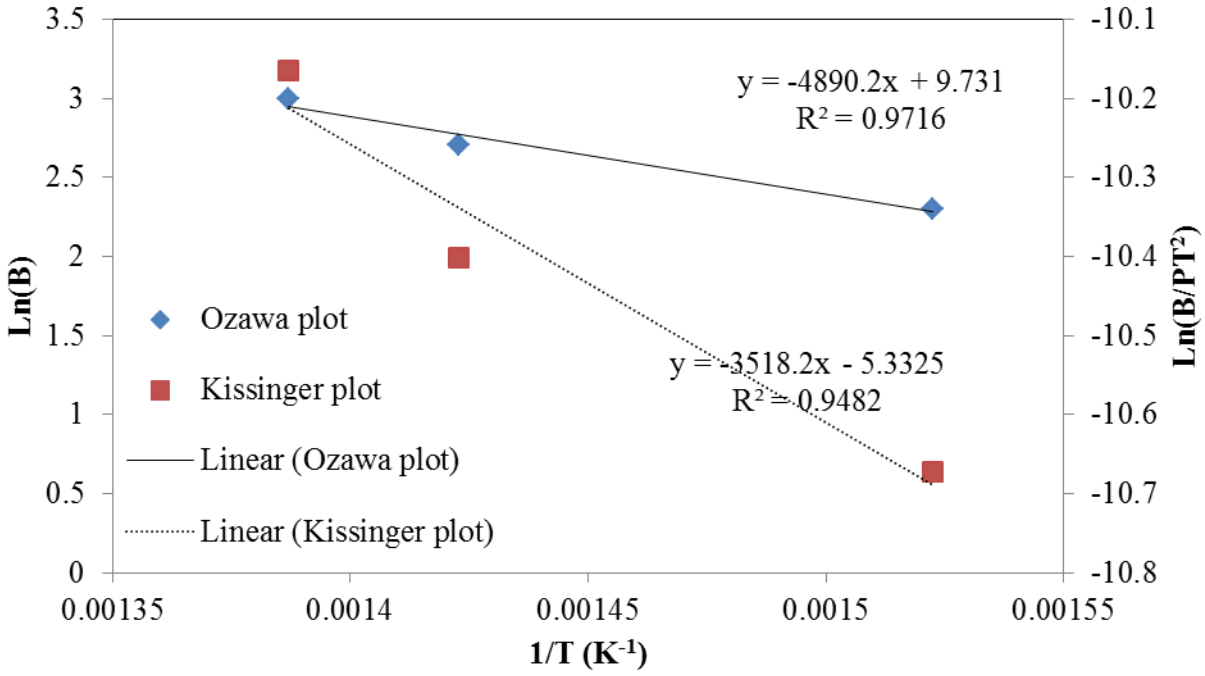

Figure 96: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (75% 4 years T280 + 25% coal) blend

8.6.4. Co-combustion of 4 year old C350 bamboo with coal.

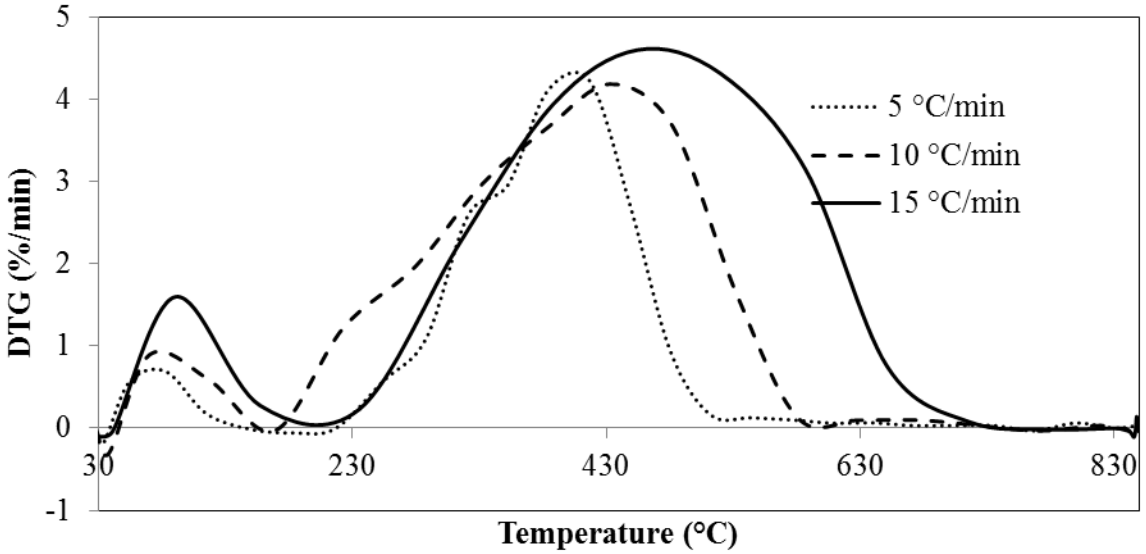

Figure 97: DTG curves of (25% 4 years C350 + 75% coal) blend at different heating rates

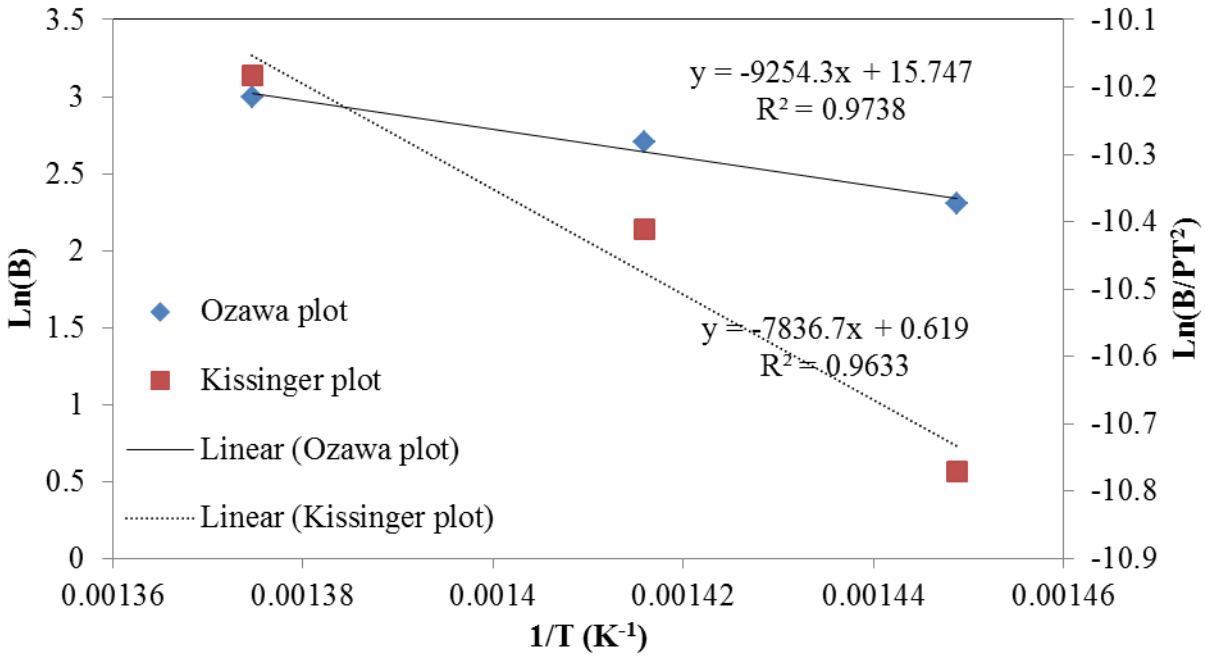

Figure 98: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (25% 4 years C350 + 75% coal) blend

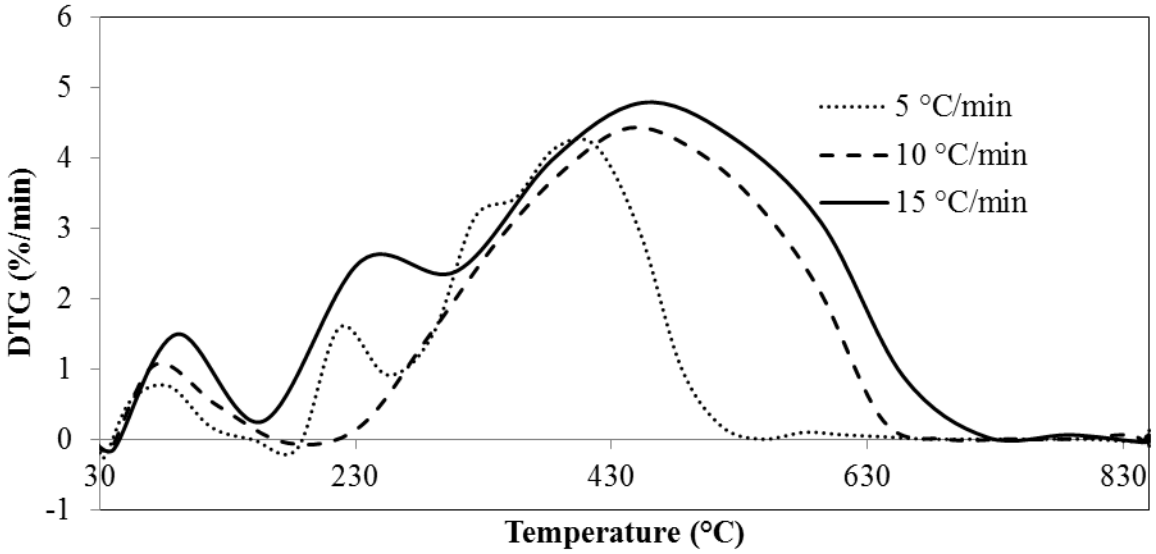

Figure 99: DTG curves of (50% 4 years C350 + 50% coal) blend at different heating rates

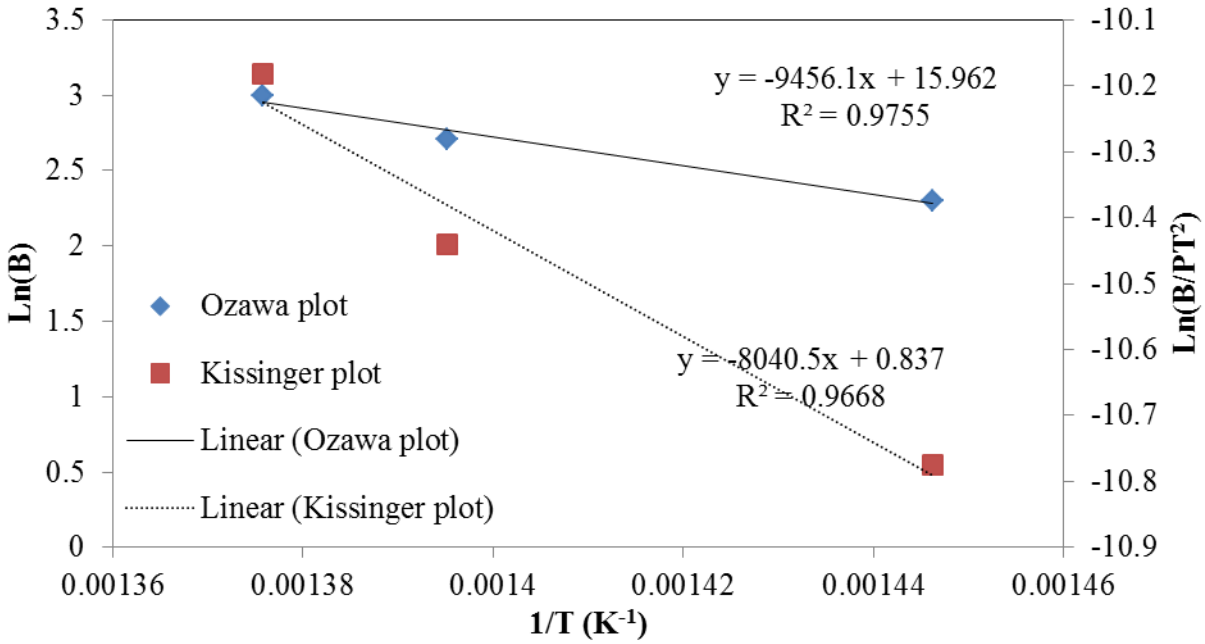

Figure 100: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (50% 4 years C350 + 50% coal) blend

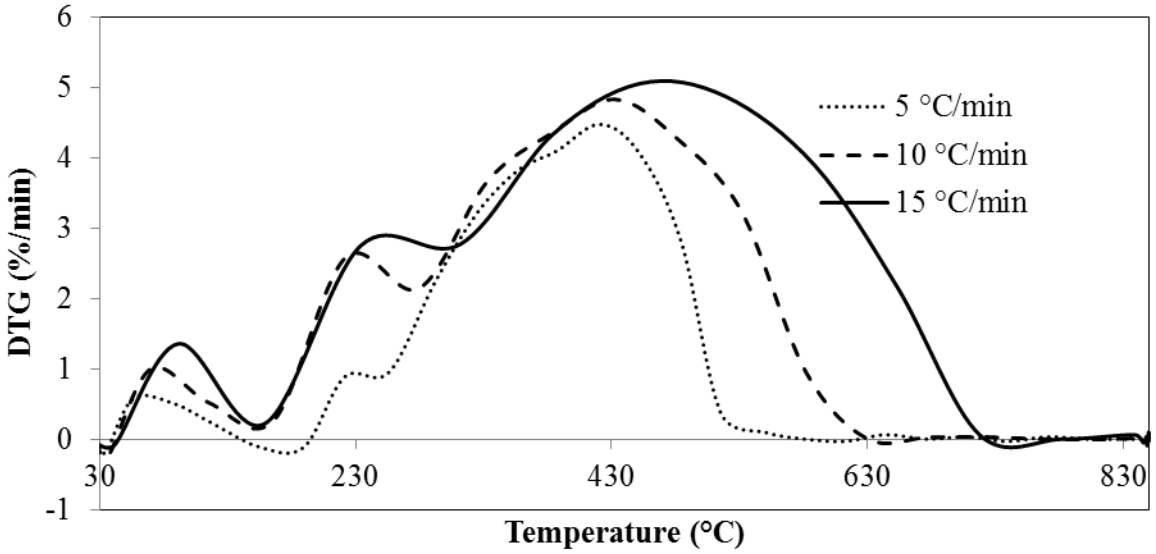

Figure 101: DTG curves of (75% 4 years C350 + 25% coal) blend at different heating rates

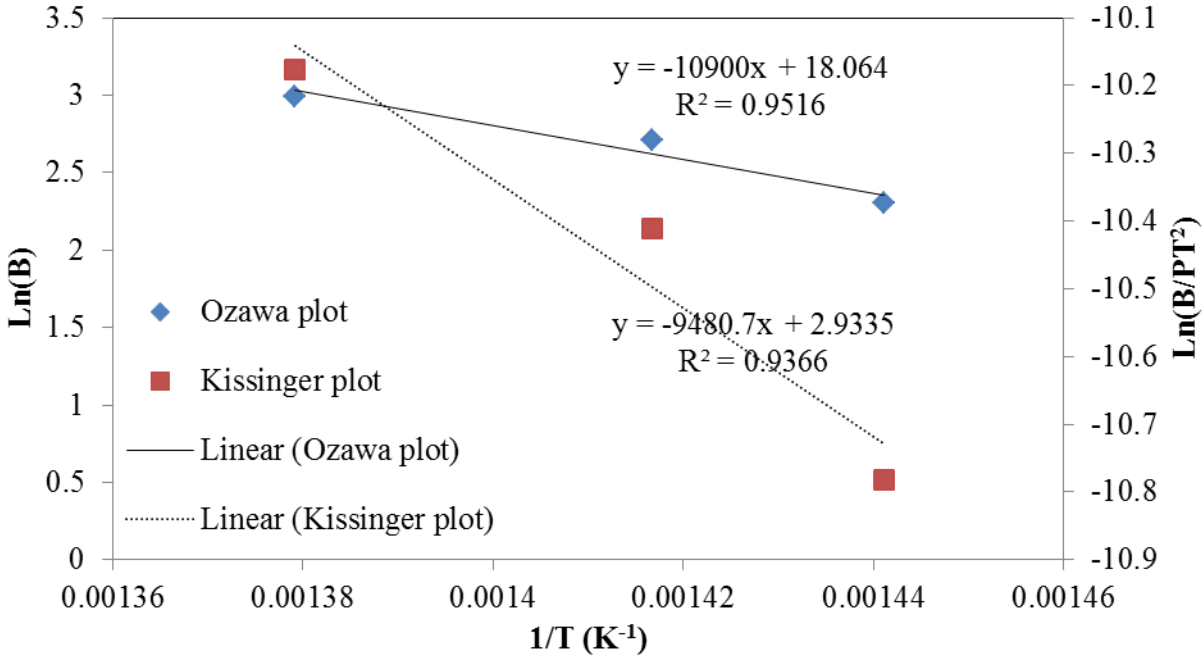

Figure 102: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (75% 4 years C350 + 25% coal) blend

8.6.5. Co-combustion of 4 year old C400 bamboo with coal.

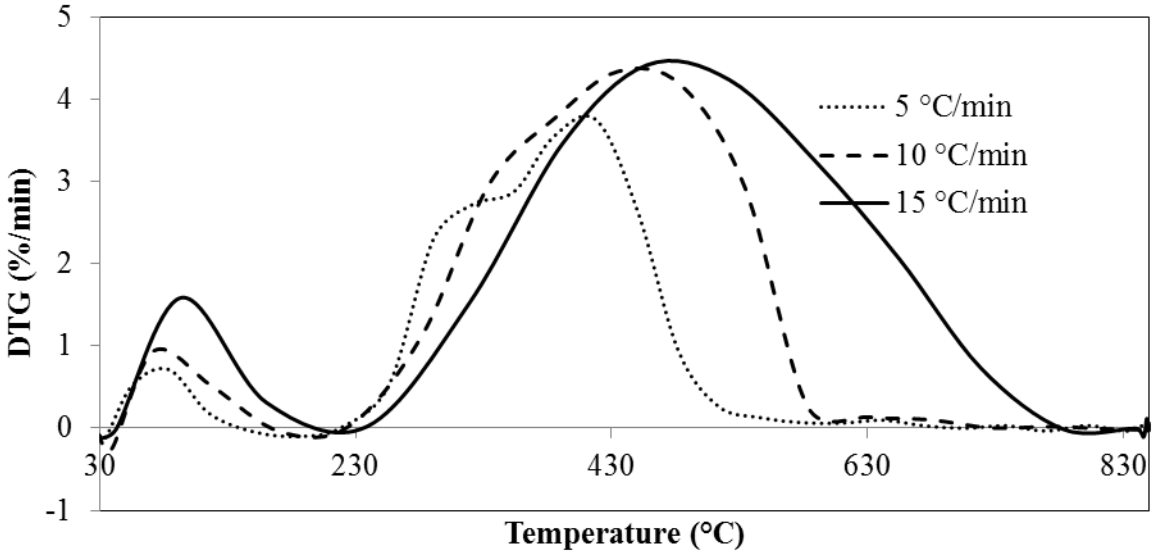

Figure 103: DTG curves of (25% 4 years C400 + 75% coal) blend at different heating rates

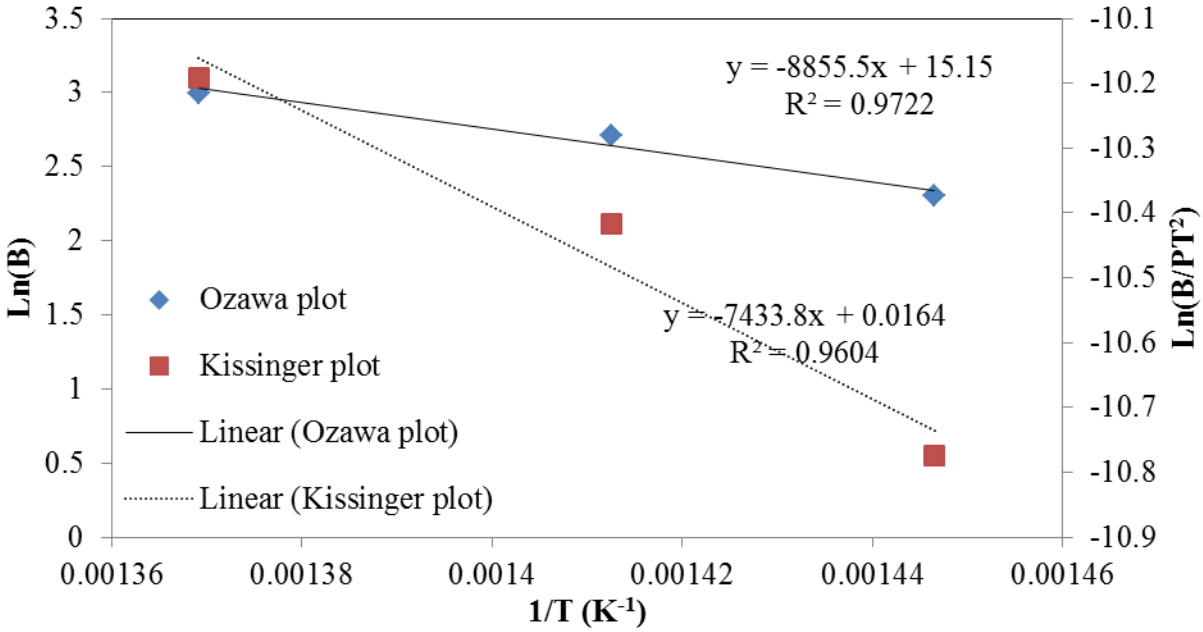

Figure 104: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (25% 4 years C400 + 75% coal) blend

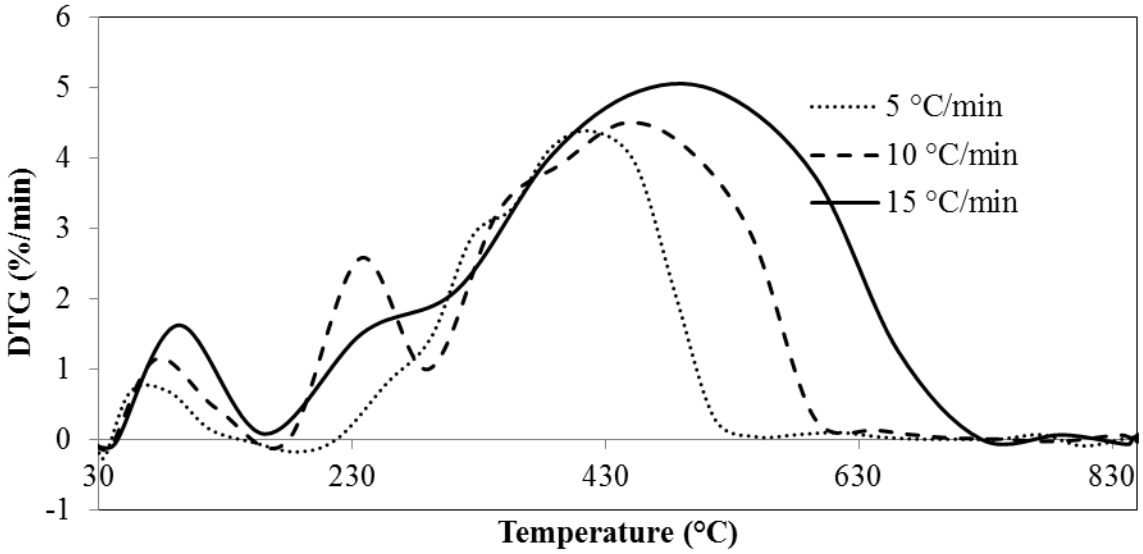

Figure 105: DTG curves of (50% 4 years C400 + 50% coal) blend at different heating rates

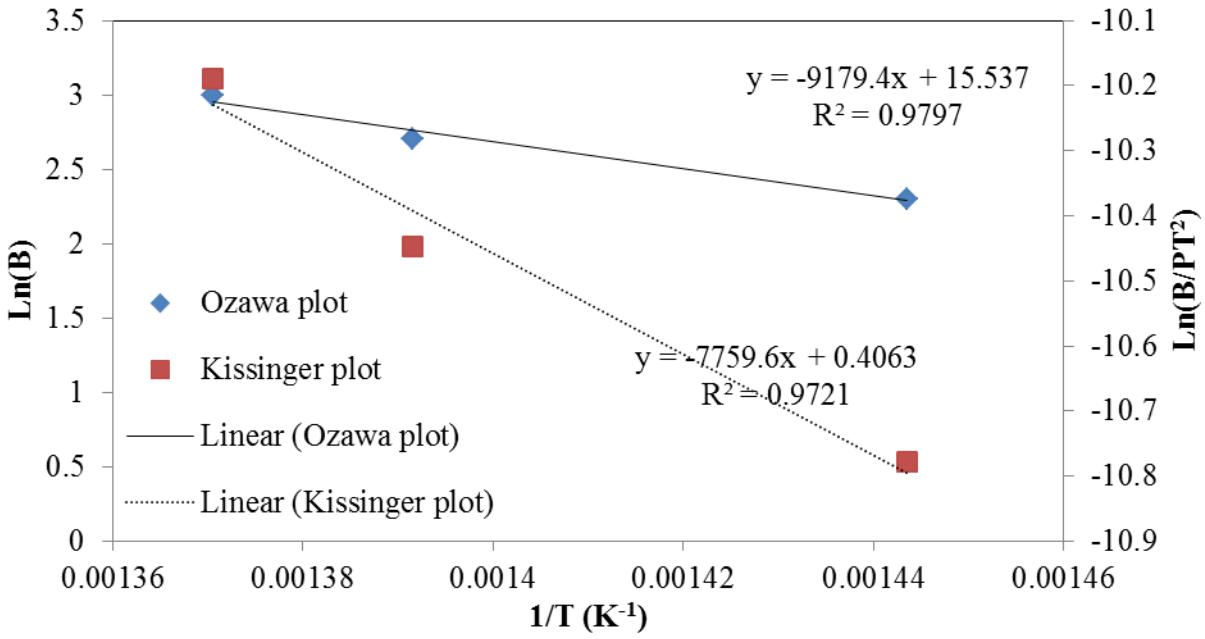

Figure 106: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (50% 4 years C400 + 50% coal) blend

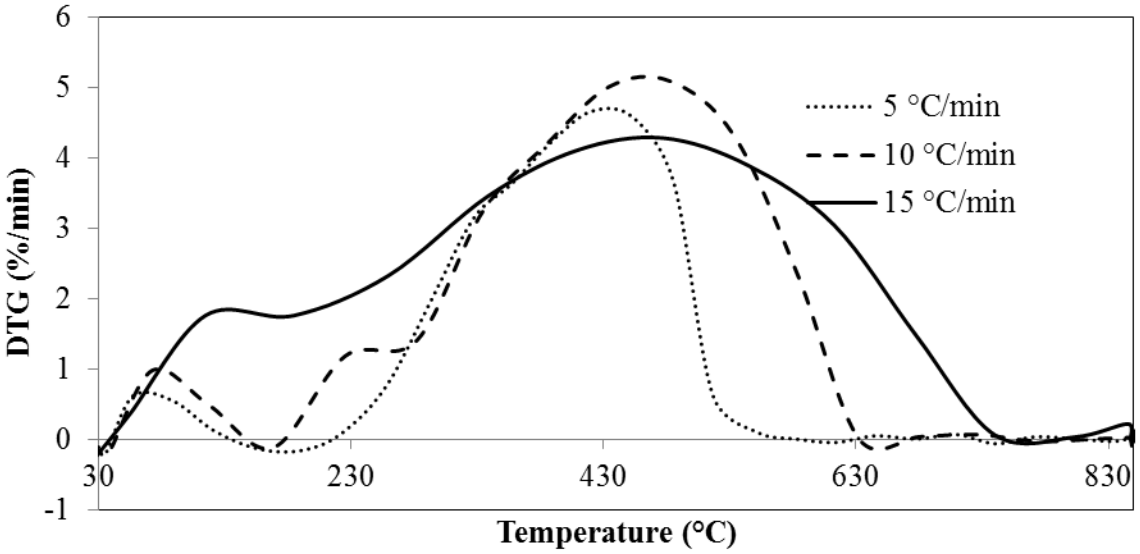

Figure 107: DTG curves of (75% 4 years C400 + 25% coal) blend at different heating rates

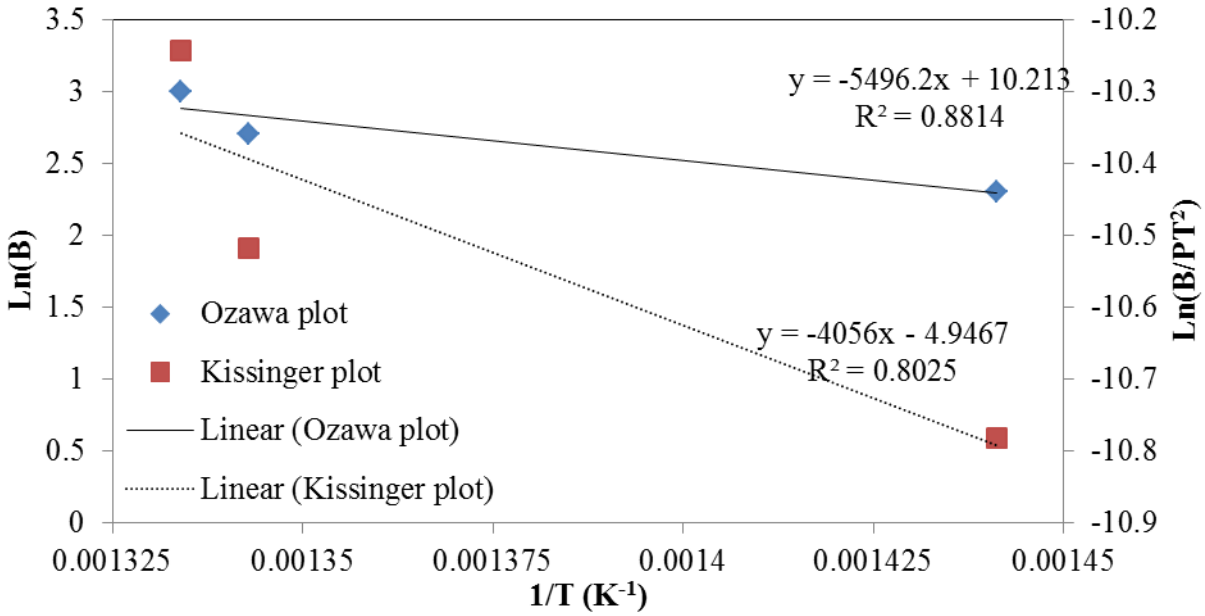

Figure 108: Model free kinetics: Ozawa plot and Kissinger plot for the combustion of (75% 4 years C400 + 25% coal) blend