



Analysis Of Tar Formation During Gasification And Its Thermochemical Characterization

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*“Taller mountains are harder to climb,
But the view from the top is always worth it”*

- *Anonymous*

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Abstract

The search for a sustainable alternative source from fossil fuels has been ongoing for quite a long time. Due to the dwindling world reserve of petroleum global warming and other associated inconveniences this search is becoming more urgent. The use of biomass is getting more attention as a renewable energy source. Currently bioenergy's share of the world energy mix is around 14% of the total 18% for renewable energy. One of the major pathways for conversion of biomass to energy is gasification and a significant problem it has is the unacceptable level of tar contained in the producer gas. The Tars are required to be removed before the producer gas can be used. So, it is important to control the amount of tar formed for biomass conversion to energy technologies.

In this project, the formation and characteristics of tars produced during the direct (air) gasification of biomass in a pilot-scale bubbling fluidized-bed gasifier was studied. The tars collected from the gasification were studied by thermogravimetric analysis with simultaneous differential scanning calorimetry to further the understanding of the thermochemical characteristics of these compounds and their reactivity under gasification conditions with different gaseous atmospheres. An initial kinetic study of the biomass sample at different temperature using thermochemical conversion was also carried out.

The data obtained allowed the analysis of mass degradation of biomass sample from the TGA, and further the understanding of the behavior of the biomass when char was added. The behavior was studied using a pseudo-component approach and assuming first-order kinetic. Also, tar gasification in air and in CO₂ were compared to see the effect of each of the gasifying agents. With CO₂ the tars degrade at a higher temperature (> 700 ° C) that, nevertheless, falls well within the gasification temperature range of the gasifier. The kinetic parameters of the samples were also estimated.

Resumo

A procura de fontes de energia sustentáveis alternativas aos combustíveis fósseis está em curso à muito tempo. Tendo em conta a escassez das reservas mundiais de petróleo, o aquecimento global e outros inconvenientes associados esta tarefa torna-se mais importante. A utilização de biomassa está a ganhar mais atenção como fonte de energia renovável. Atualmente a quota de bioenergia na produção mundial de energia é cerca de 14 %, dos 18 % que correspondem ao total das energias renováveis. Uma das vias mais importantes na conversão de biomassa em energia é a gasificação e um dos problemas que lhe estão associados é o teor inaceitável de alcatrões no gás produzido. Estes alcatrões devem ser removidos antes de o gás produzido poder ser utilizado. Assim, é muito importante controlar a quantidade de alcatrão formado em todos os processos de conversão de biomassa em energia.

Neste projeto estudou-se formação e características do alcatrão produzido durante a gasificação direta (com ar) de biomassa num gasificador piloto de leito fluidizado borbulhante. Os alcatrões recolhidos durante a gasificação foram estudados por análise termogravimétrica com calorimetria diferencial de varrimento simultânea para melhorar a compreensão das características termoquímicas destes compostos e a sua reatividade em diferentes condições de gasificação, com diferentes atmosferas. Um estudo cinético inicial foi também realizado com a biomassa em condições de transformação termoquímica a várias temperaturas.

Os dados permitiram analisar a perda de massa das amostras de biomassa em condições de termo-análise e aumentar a compreensão do comportamento da biomassa quando lhe foi adicionado *char*. O comportamento foi estudado utilizando uma abordagem de pseudo-componentes assumindo cinética de primeira ordem. Também foram comparadas a gasificação do alcatrão e *char* e em CO_2 para se compreender o efeito de cada um destes agentes de gasificação. Com CO_2 os alcatrões degradam a temperaturas superiores ($> 700^\circ\text{C}$) que, no entanto, ainda estão bem dentro da gama de temperaturas vigente no gasificador. Os parâmetros cinéticos para estas transformações foram também estimados.

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List of Abbreviations

Acronym	Meaning
CSBR	Conical spouted bed reactors
ER	Equivalence ratio
Ea	Activation energy
ECN	Energy research Centre of Netherlands
MAS	Microwave assisted reactors
KAS	Kissinger Akahira Sunose
PSW	Plastic solid waste
STP	Standard temperature and pressure
TGA	Thermogravimetric analysis

1. INTRODUCTION

1.1. Overview

There are a lot of industries that uses biomass as their main feedstocks, one of this is a paper production company that uses woody biomass from Eucalyptus to produce pulp that is then used in the production of paper. Usually there are waste biomass from this process and as a move towards sustainable economy, zero waste and waste to energy train of thoughts, the company has decided that such waste biomass should be put to good use by producing electricity from it. The best way to go about that is the gasification of the biomass to generate producer gas which would be used to produce the electricity. Gasification of biomass does involve some difficulties like the undesirable formation of tars.

1.2. Objectives

The goal of this thesis is to study the formation and characteristics of tars produced during the direct (air) gasification of biomass in a pilot-scale bubbling fluidized-bed gasifier.

For that purpose, tar samples were collected in the raw produced gas exiting the gasifier during the operation with different biomass feedstocks and operating conditions. The tars collected were studied by thermogravimetric analysis with simultaneous differential scanning calorimetry to further the understanding of the thermal characteristics of these compounds and their reactivity under gasification conditions with different gaseous atmospheres. The collected information about thermochemical behaviour of the tars will be analysed under different atmospheres and the information obtained would help in the design parameters of a gasifier considering possible modifications to generally reduce tar formation.

An initial kinetic study of the biomass sample at different temperature using thermochemical conversion will also be carried out.

1.3. Problem statement

The search for a sustainable alternative source from fossil fuels has been ongoing for quite a long time, due to the dwindling world reserve of petroleum global warming and other associated inconveniences. According to BP's annual report in 2018 on proved global oil reserves, our world had nearly 1.696 trillion barrels of crude as at the end of 2017, which will likely last 47.3 years at current consumption rate [1].

We never seem to run out of options for possible alternatives. Wind energy, solar energy, biofuels from first generation to fourth generation biofuels are typically the most widely named top contenders to replace Petroleum based vehicle engines and coal fired power plants.

The use of biomass is getting more attention as a renewable energy source. Currently bioenergy's share of the world energy mix is around 14% of the total 18% for renewable energy, with the consumption pattern varying from region to region. Used mainly as biofuels in the Americas, solid fuels and charcoal in Asia and Africa, heat and electricity in Europe [2] .

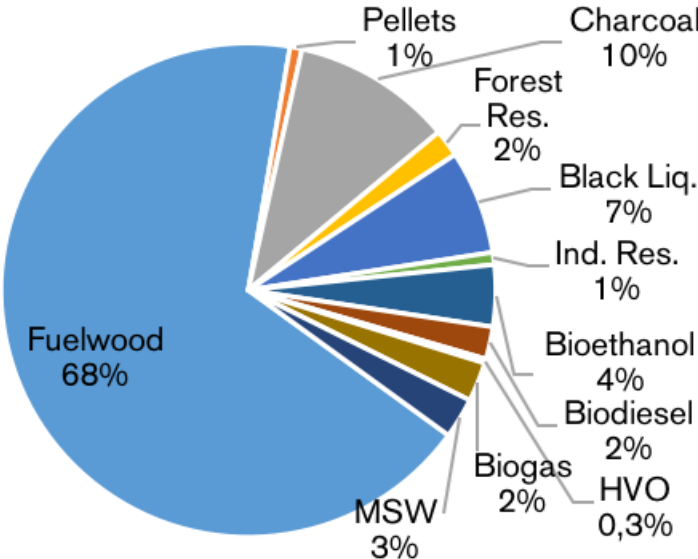


Figure 1 primary energy supply of biomass resources globally 2013 [2]

Biomass materials can be converted using either the thermal physical or biological methods. This investigation will be based on the thermochemical conversion mainly gasification. Biomass gasification is getting more attention as a pathway for conversion of biomass to energy. One of the most significant problems is the unacceptable level of tar contained in the producer gas which can lead to several complications in downstream operating process, blocking out pipes in cooling and condensation units and other channels. The Tars are required to be removed before the producer gas can be used. So, it is important to control the amount of tar formed and control it for biomass conversion to energy technologies.

2. LITERATURE REVIEW

2.1. State of Energy

The amount of energy a society has access to reflects its economic development as energy is a main enabler of economic growth. And it has been a proven fact that energy generation activities have impact on the surrounding environment, so it becomes imperative to devise an energy system that grows the economy and preserve the environment.

It is quite hard to take in that over 1.4 billion people don't have access to electricity and 85% of them reside in the rural areas and as such rely on rather traditional use of biomass to get their energy and these numbers are still going up from 2.7 billion today to 2,8 billion in 2030 [3].

While the Major dominance of fossil fuel in the energy industry and the huge increase in the population has increased the energy demand globally, CO₂ emissions have also increased rapidly [4]. A dramatic and yet significant climate change has become one of the biggest global challenge, and its impact can still be mitigated with the transformation of current energy systems. Renewable energy will play a key role in mitigating this climate changes by reducing greenhouse gas emissions [5].

There has been an ongoing fundamental structural change in the energy sector often referred to as energy transition occurring all over the globe, the aim and intentions behind this movement may vary, but it all boils down to the energy trilemma. The energy security, production using the least cost approach, and the environmental protection. The many different conventional, new and novel technologies now used in the energy sector.

Table 1: Renewable Energy Sources and usage option [6]

Energy sources	Energy conversion and usage options
Hydropower	Power generation
Modern biomass	Heat and power generation, pyrolysis, gasification, digestion
Geothermal	Urban heating, power generation, hydrothermal hot dry rock
Solar	Solar home systems, solar dryers, solar cookers
Direct solar	Photovoltaic, thermal power generation, water heaters
Wind	Power generation, wind generators, windmills, water pump
Wave and tide	Numerous designs, barrage, tidal stream

Gasification technologies are expected to play a big role in the use of biomass as a renewable energy source. the producer gas or syngas produced when solid biomass is processed in a gasifier is the reason for this. As the gas produced could be used to produce heat and electricity in a co-fired power plant or the gas can be used to produce liquid fuels using the Fischer-Tropsch process.

2.2. Biomass

Biomass can be considered as the organic matter derived from trees, plants and animals, agricultural and urban waste. When biomass is in combustion, oxygen combines with the carbon and hydrogen in the biomass to give CO₂ and water. That's the reason that biomass is considered as a carbon neutral because CO₂ released replaces the ones taken to produce the biomass. Bioenergy is energy derived from biological renewable origin: - examples include wood, grass and bagasse. The most important property of these biomass feedstocks is their moisture content as it influences the energy content. Fresh wood typically has around 55% moisture content with lower heating value of around 7MJ/kg and after drying in air the water content drops to around 20% and the LHV increases to around 15 MJ/kg [7].

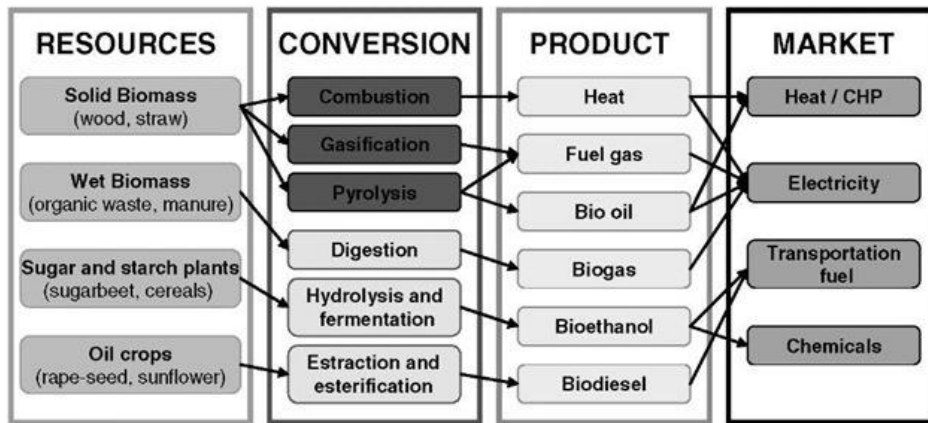


Figure 2: Processes to convert biomass into useful energy [7].

The practical issues with using biomass range from its bulk volume which makes transportation quite difficult to its water content which could lead to biodegradation. The moisture content also affects the efficiency of processing systems. Although these listed problems can be solved by standardization and densification. Standardization involves the processing of the original biomass to obtain fuels with standard size and heating properties while the latter involves compressing the materials.

Eucalyptus: In Europe, Spain and Portugal are big producers of eucalyptus with total of 1.4 million ha of cultivated land. It is a major source of wood fibers to produce wood pulp for paper making. Other products from the tree include charcoal biochar, eucalyptus oil, and dyes [8].

There are three main thermal/thermochemical ways of conversion of biomass to get energy. We have combustion, pyrolysis and gasification. Among the by-products of the processes are tars which are our indirect purpose by trying to investigate the thermal properties of tars produced during one of these conversion processes, gasification. We will start with a brief description of these processes.

2.2.1. Combustion

Combustion is in fact the oldest form of energy technology used by man, direct burning of wood and solid biomass for heat. Now commercial combustion technology is available in most developed and developing countries, although there are still the environmental issues to resolve and the need to improve the efficiency of the whole process.

Using biomass combustion devices ranges from small things like stove (1-10Kw) for small heating to huge boiler used in power plants (>5MW). In between these ranges we have the small boilers used for house heating, small family houses use around (10-50kW) while municipal housing and large houses use bigger boilers (50- 150kW) and district heating use even bigger ones (over 1MW) [7].

Biomass could be used alone as a fuel or as a supplement to fossil fuels used in boilers. The second option is becoming quite popular as the fastest and cheapest way of decreasing carbon emission from existing fossil fueled power plant [9], often called co-combustion or co-firing which is the combustion of two (or more) type of materials at the same with the added advantage that an existing could be used to burn a new fuel, which may be cheaper or more environmentally friendly.

2.2.2. Pyrolysis.

Pyrolysis is defined as the thermal decomposition of organic materials in the absence of oxygen [10]. It is an irreversible process that involves the change in physical phase and chemical composition simultaneously. The process could go with or without a catalyst, subjecting large molecules of biomass to high temperature, which leads to breaking of the chemical bonds [11]. This bond-breaking process is usually known as cracking. Depending on the raw material and the process conditions, different decomposition pathways dominate. The complexity of the reactions taking place during the pyrolysis of polymers represents one of the main difficulties to its complete understanding. This is especially the case in the treatment of mixed feed streams. As a result, the product distribution in pyrolysis processes can vary strongly when changing single process parameters [12].

In general, pyrolysis products can be classified into three fractions: a pyrolysis gas, a liquid pyrolytic oil and a solid char [13]. In its application in plastic solid waste (PSW) recycling, usually the gasoline range hydrocarbons within the liquid fraction are the desired products. In literature it is reported that volatile matter and ash content are the factors that most influence their production. Accordingly, high volatile matter contents favor high yields of liquid pyrolysis oils [14].

However, also the other products can be of use. The non-condensable fraction of the gases obtains a high calorific value and can be burned to compensate the energy requirements of the pyrolysis plant [15]. Pyrolysis process units principally include a feeding section, a reactor unit assembly and product collectors.

The reactors can be of several construction types. In literature, designs ranging from bubbling fluidized bed and stirred tank reactors to screw or auger reactors have been reported. Fixed bed reactors including kettle type units have also been used. Batch and semi-batch reactors are typical for lab-scale projects. More sophisticated ones include conical spouted bed reactors (CSBR) and microwave assisted reactors (MAS) [12], [15].

Fluidized bed reactors have shown to be a promising option for biomass pyrolysis. Due to the improved heat and mass transfer reached inside the reactor, higher conversion rates and more uniform products can be yielded. For the fluidizing gas, nitrogen, steam or a recycle gas may be used. Economic and technical reasons make steam to the preferred option in most cases [16].

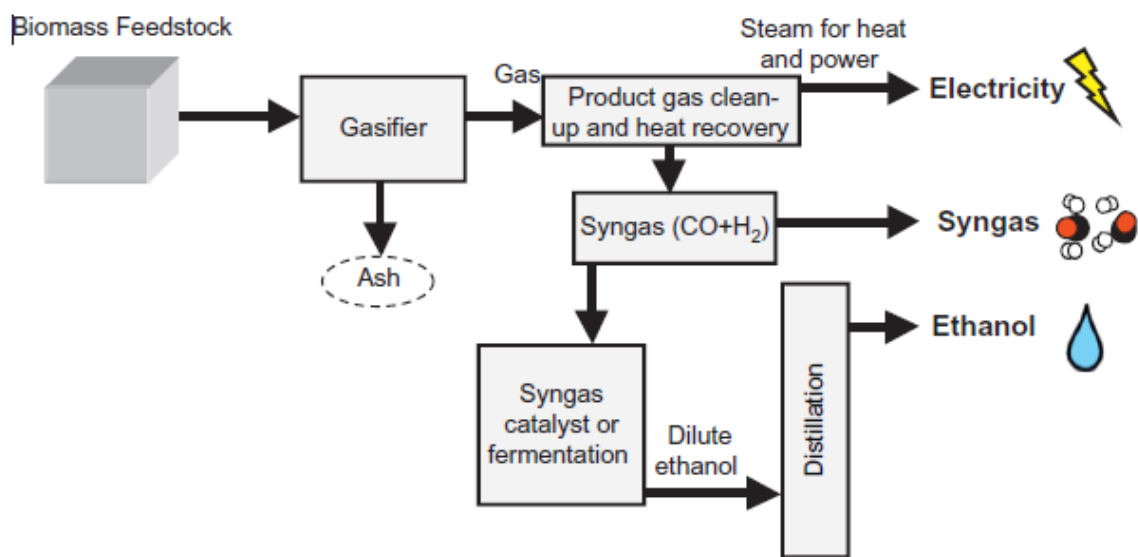


Figure 3: Biomass conversion flow chart

2.2.3. Gasification

Gasification converts solid, liquid or gaseous fuels into useful gases and chemicals, the fuels could be fossil or non-fossil. Usually it involves the use of a medium for the reaction, it could be air, oxygen subcritical steam or a mixture of these. For now, gasification of fossil fuel is more in use than that of non-fossil fuel like biomass. It potentially converts fuels from one form to another. It's a chemical process that uses non-stoichiometric amount of oxidant to convert carbon materials and carbonaceous waste into syngas gas at high temperature around 700-1500 °C. The main advantages of gasification include:

- Increasing the heating value of fuels by rejecting the non-combustible fractions like nitrogen and water

- Striping the fuel of Sulphur preventing its release to the atmosphere
- Increase the H/C mass ratio of fuels
- And reduce oxygen content of fuels

Gasification of biomass basically increases the energy density of the fuel by reduction to negligible the initial amount of oxygen which is around 40% in biomass [9].

Usually the gasification process can be broken down into four stages, happening in their respective zones: drying, pyrolysis, oxidation and reduction zones.

Drying: Dehydration occurs in this zone. The moisture content of the feedstock is evaporated at the temperature range of 150-200 °C. typically, the resulting steam move down and mix with vapor from the oxidation zone.

Pyrolysis: Takes place below the drying zone at temperatures from 400 to 650 °C. as mentioned earlier pyrolysis involves the degradation and breakdown of macromolecules like cellulose hemicellulose and lignin in the biomass into smaller chains hydrocarbons and char. Further breakdown and combustion of these pyrolysis product occurs as they move towards hotter areas of the gasifier to give H₂, CO, CH₄, C₂H₆, C₂H₄ [17].

Oxidation: In this zone the air injected into the gasifier oxidizes the biomass in the following reaction



These are exothermic reactions releasing large amounts of heat that raises the temperature within the gasifier above 900 to 1200 °C.

Reduction: These endothermic reactions use the energy released in the oxidation zone for their processes. The final producer gas is formed in this zone. The gases leaving the gasifier are at a temperature of around 250 – 500 °C and can then be either sent for additional cleaning or sent to burners



2.3. Gasification Technologies

The main gasification technologies commercially in use are fixed bed, entrained flow and fluidized bed gasifiers. But when it comes to biomass gasification the main ones are the fixed bed and the fluidized bed gasifiers.

In a broader sense these are:

- Updraft Fixed bed
- Downdraft Fixed bed
- Bubbling fluidized bed
- Circulating fluidized bed [18].

Table 2: Gasifier Types

Gasifier Type	Flow direction		Support	Heat source
	fuel	oxidant		
Updraft Fixed bed	↓	↑	Grate	Combustion of char
Downdraft Fixed bed	↓	↓	Grate	Partial combustion of volatiles
Bubbling fluidized bed	↑	↑	–	Partial combustion of volatiles and char
Circulating fluidized bed	↑	↑	–	Partial combustion of volatiles and char

2.3.1. Updraft fixed bed

The updraft fixed bed gasifier also called counter-current is the oldest and simplest gasifier configuration design in use. The feed is introduced from the top of the reactor and while the gasification medium (air, oxygen and steam) flows in the counter direction, flowing in from below the grates and passing through the bed to meet the biomass and char. with the ash removed either dry or as slag. It has high thermal efficiency as the gases exit the reactor at relatively low temperatures. This means tars and methane are significantly produced at typical operating conditions and the producer gas produced needs additional cleaning. That is during complete combustion of char and biomass above the bed, carbon dioxide and steam are produced around a temperature above 1000 °C which are then reduced to carbon-monoxide and hydrogen and cooled to 750 °C as they move

upward in the bed upward. The still hot gasses pyrolyze the descending biomass and dry wet biomass before leaving the reactor at a temperature around 500 °C [19].

Advantages [20]

- Simplicity and ability to gasify wet fuels
- High charcoal conversion and internal heat exchange
- Proven and matured technology

Disadvantages:

The primary disadvantages are the relatively large amount of tars in the syn-gas or producer-gas, requiring additional clean-up.

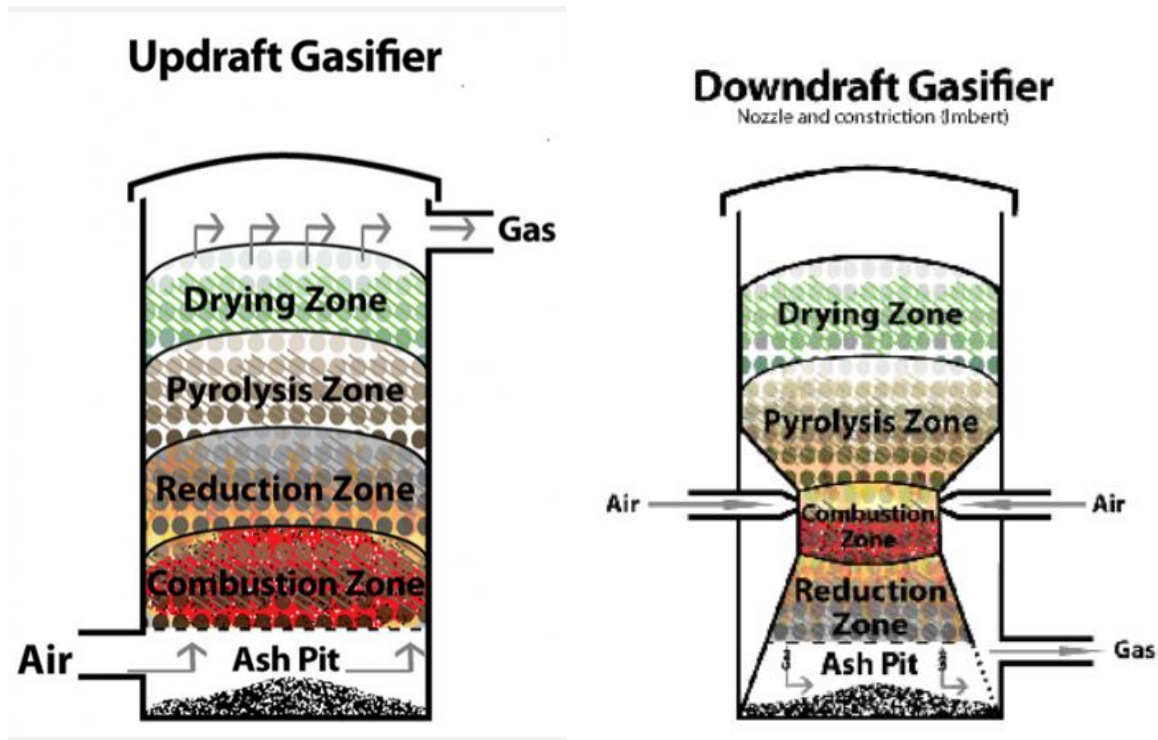


Figure 4: Updraft and Downdraft Gasifiers [21]

2.3.2. Downdraft fixed bed

Unlike updraft, downdraft gasifiers can combust 99,9% of the tars formed during the process. In this configuration the gasifying medium and the biomass flow in the same direction down the reactor. The biomass, usually with a low moisture content less than 20% and the gasifying medium are ignited in

the reaction zone at the top of the reactor. The heat for the drying pyrolysis and gasification is generated at the combustion zone, and the hot combustion gases and chars move to the reduction zone. Here gases react with char at 800 -1200 ° C. The ash and char left unconverted are disposed from the bottom of the grate [18].

Advantages

- Simplicity and low cost
- High level of tar removal, therefore minimal tar clean-up

Disadvantages

- Cannot work with feed with high moisture content. Requires drying first
- Requires secondary heat recovery system due to high exit temperature
- Relatively high unconverted carbon

2.3.3. Fluidized beds

Fluidized bed designs overcome the commonly encountered problems of fixed bed gasifiers whether the updraft or downdraft. Issues like lack of bunker flow pressure drop over the gasifier and slagging.

Fluidization technique employs the suspension of small solid particles in a vertical rising stream of fluid, mostly a gas, so that the fluid and solid intimately mix. So basically, air (or other suitable carrier gas) is blown through the bed at a sufficient velocity for the particles to float. Usually the bed is heated till it reaches a sufficiently high temperature before introducing the feed. The feed goes in at the bottom of the reactor and it is pyrolyzed very fast, resulting in a component mix of gaseous materials. The main setback of fluidized bed is the high tar content and incomplete carbon conversion.

2.3.4. Bubbling fluidized bed

As shown in the schematic diagram of BFB shown in figure 5 below. The air (or other suitable gas) flows in from the bottom and feedstock fed from the top. The bed is mostly made from sand, but some other materials can be used. The biomass undergoes successive reaction processes described as unique zones within the reactor, this is because of the heat and mass transfer between the fuel particles and the gasifier environment. It has been shown that the thermo-chemical conversion of the biomass is strongly related to its size and shapes and dimensions [22]. The heat required for the drying, pyrolysis, and gasification stages is derived from the heat and product gases from the combustion of the biomass. In a BFB the upward velocity of the air is around 1-3 m/s and the

expansion of the inner bed regards only the lowest part of the gasifier. The low velocity prevents the sand bed and char from coming out of the reactor.

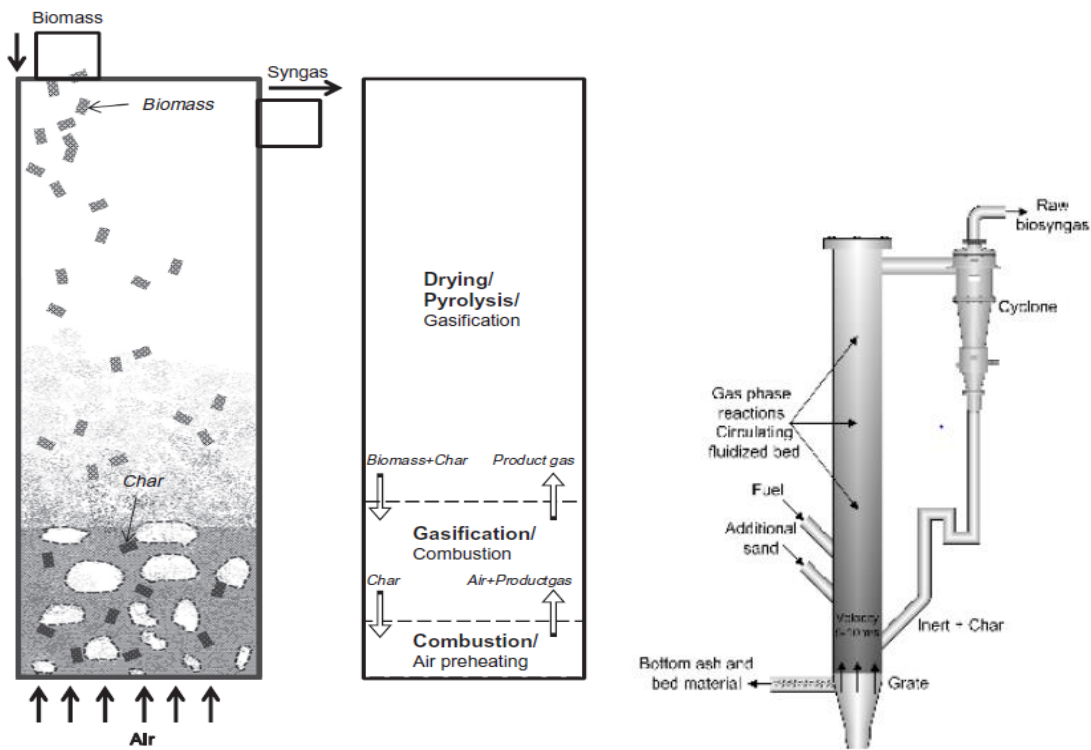


Figure 5: BFB and CFB Gasifiers [22]

The gasifier yields uniform product gas and almost uniform temperature distribution throughout the reactor, providing a high rate of heat transfer between the fuel gas and inerts. It can also accept a wide range of fuel particle sizes including fines. Its major drawback is that large bubbles may result in gas bypass through the bed [18].

2.3.5. Circulating fluidized bed gasifier.

Circulating fluidized bed operates at higher velocities than the minimum fluidization velocity thereby allowing some of the bed particles to be entrained and carried out of the gasifier. These entrained particles are separated using a cyclone and transferred back into the reactor. The gas velocity is around 5-10 m/s.

2.4. Macroscopic kinetic modelling

Chemical kinetics when used with transport phenomena should be able to predict conversion time and product distribution while varying operating conditions. We do have two main descriptions for these kinds of processes. A one stage reaction process that describes the decomposition in a simple way, mostly used for isothermal condition and fast heating rates, with the weight loss curve being used to describe the yields of the three products to evaluate the formation rates. The second which is a multi-stage reaction considers several pseudo-components in the measured curves of weight loss. These kinetic models can be based on Arrhenius dependence on temperature with parameters activation and pre-exponential factor, and a linear dependence on component mass fraction which may lead to additional parameters [23].

2.4.1. One step global model.

These were first used on experiments detailing biomass pyrolysis. In the model a first order reaction is assumed to detail the decomposition of solid biomass into volatiles and chars. Over the years several scientists have tried to use these models to describe decomposition of the biomass, Volvelle in his research concluded on two main component 50% each while later Varhagi propose something in same direction but using two first order reaction to model hemicellulose and cellulose. Their findings cumulated to a refined description that lignocellulosic biomass is constituted by three main components lignin cellulose, hemicellulose that decomposes independently [24].

This analysis is widely used to depict biomass devolatilization in terms of three concurrent first order reactions. It is quite suitable for comparing kinetic data from the decomposition of different type of biomass under the same or similar condition [24], [25].

2.4.2. Multiple step models

Being unable to compare kinetic data from biomass under different condition has drove a lot of researcher into developing complex multiple step models that solves their problem. Rigorous kinetic treatment of the pyrolysis data should give the formation rates of the individual product species and the heat and mass transfer. Pyrolysis of cellulose can be adequately described using three consecutive first order reactions. With the first reaction describing devolatilization which is around 30% and the last would be 70% representing the volatile materials. The middle reaction only represents the rearrangement of the solids and release no volatile matter [26]. Although there are other mechanisms, but they all seem to have drawbacks, either by having more than 3 reactions or having

three reactions with order higher than one. For example, Dieblod proposed a seven-stage kinetic model for cellulose pyrolysis which gave very good prediction for both fast and slow pyrolysis. Heating rates, pressure residence time were all accounted for in this model [27]. Where as in their own research Vargas and Perimutter [28], they provided that the during coal isothermal pyrolysis its kinetics shows that the process can be described using ten consecutive iso-thermal step, each associated with a specific pseudo-component of coal's degradation. And there is more, Mangut et al trying to outshine the others revealed that pyrolysis of food waste in tomato productions kinetics can be modelled using 10 consecutive reactions identified from the DTG curve[29]. It should be noted that despite its usefulness in several applications multistage models have limitations based on the several reactions used, subtle errors present in the kinetic parameters in the first-rate equation are multiplied and carried over in successive multiple stage [30].

2.4.3. Macroscopic kinetic models for mass loss simulation

The two main models use for mass loss simulation are the model-fitting method and the Isoconversional methods. The aim is always to simulate and determine to a satisfactory extent the activation energy E_a , rate constant K values and a final reaction model for future predictions.

2.4.3.1. *Model fitting method*

The model fitting methods are widely used in researches. This approach assumes a value for $f(\alpha)$ and modifies the function in lieu with the experimental data using the nonlinear least squares fitting to get the kinetic parameter [31]. Thermal decomposition of the biomass is taken to be the sum of the degradation of the components: hemicellulose, cellulose and lignin.

In the ICTAC kinetics committee recommendations, many practical advice and general guiding principle were proposed like to never conduct kinetic measurements on random or arbitrarily chosen Conditions and sample weight, therefore before an experiment one must invest time and effort in ensuring the accuracy of the data by performing exploratory runs to reveal the effect of the samples and the repeatability of the measurements. The purpose is to pick out samples and conditions so that their effect is minimized [32].

2.4.3.2. *Isoconversional method*

These methods are quite reliable among the kinetic method used nowadays for the analysis of thermal data.[32], [33]. The Isoconversional methods was first used by Kujirai and Akahira on their work with TG data to investigate the decomposition of some insulating materials under isothermal conditions. Its main advantage is that it provides a way to get the kinetic data while ignoring the reaction mechanism completely. Another advantage is that errors due to kinetic analysis of using the Arrhenius equation is eliminated [34]. Isoconversional models have two approaches, the differential

and the integral approach to treatment of TGA data. The differential method is described by the Friedman equation expressed in general terms as shown below [24], [35]:

$$\frac{d\alpha}{dt} = \beta \left(\frac{d\alpha}{dT} \right) = A e^{\left(\frac{-Ea}{RT} \right)} f(\alpha) \quad (9)$$

Taking Log of both side from equation yields

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln \left(\beta \left(\frac{d\alpha}{dT} \right) \right) = \ln(Af(\alpha)) - \frac{Ea}{RT} \quad (10)$$

The conversion function $f(\alpha)$ is assumed to be constant which means the biomass degradation only depends on the rate of mass loss and independent of the temperature. When $\ln \left(\frac{d\alpha}{dt} \right)$ is plotted against $1/T$, a straight line is obtained, and the slope corresponds to $-\frac{Ea}{RT}$.

The Flynn-Wall-Ozawa method is an integral approach that assumes the activation energy remains throughout the duration of the reaction. The fact that in the differential approach, large amount of data produces high level of noise when differentiated is among the drive that led to the proposal of the integral method which doesn't have this problem.

$$g(\alpha) = \int_0^\alpha \left(\frac{d\alpha}{f(\alpha)} \right) = \frac{A}{\beta} \int_0^{T_\alpha} \exp \left(-\frac{Ea}{RT} \right) dT \quad (11)$$

Where T_α is equal to the temperature at conversion α . If $x = \frac{AEa}{\beta R}$, equation becomes:

$$g(\alpha) = \frac{AEa}{\beta R} \int_\alpha^\infty \left(\frac{\exp^{-x}}{x^2} \right) = \frac{AEa}{\beta R} p(x) \quad (12)$$

Another widely used integral approach is the Kissinger-Akahira-Sunose (KAS) method. The equation is shown below.

$$\log \left(\frac{\beta}{T_m^2} \right) = -\frac{Ea}{R} \left(\frac{1}{T_m} \right) - \ln \left[\left(\frac{Ea}{AR} \right) \left(\int_0^\alpha \left(\frac{d\delta}{f(\alpha)} \right) \right) \right] \quad (13)$$

Where T_m is the temperature difference at the maximum reaction rate. At constant value of α Ea can be determined from the slope of a plot of $\log \left(\frac{\beta}{T_m^2} \right)$ against $1/T_m$.

The merits of the integral approach over the differential are tempered by some weaknesses like the need for Picard iteration for the temperature, ill-defined boundary conditions for the temperature integral and error accretion during successive approximations [24].

2.5. Tars

Tars are a complex mixture that include phenols, polycyclic aromatic compounds (PAHs) and heterocyclic compounds [22]. According to the ECN definition, tar comprises all organic components having a higher molecular weight than benzene. Benzene is not considered to be a tar. ECN uses a tar classification system comprising six classes (see Table 3). This classification system is developed to simplify the general composition of tar. Trends are easier recognized based on these classes. However, for more specific problems or issues the detailed data will remain necessary [36].

Table 3: Tar types and components

Class	Types	Examples
1	GC undetectable tars	Biomass fragments, heaviest tars
2	Heterocyclic compounds	
3	Aromatic components	Toluene, Xylenes, Ethylbenzene (excluding benzene)
4	Light polyaromatic Hydrocarbon (2-3 rings PAHs)	Naphthalene, indene, binaphyl, Anthracene
5	Heavy poly aromatic hydrocarbons (4 rings and more)	Fluoranthene, Pyrene, Crysene
6	GC detectable, not identified compounds	Unknowns

2.6. Tar reduction methods

Tars are generally a problem in gasification processes and because of the importance of this technologies for power generation a lot of research has been done on ways to mitigate the formation of tars. The methods used are classified as primary and secondary methods.

- 1). Primary methods that works mainly to reduce the formation of tars by self-modification either in terms of operation parameters or reactor design. Tars are formed from the incomplete conversion of the liquid products in the gasification step.
- 2). Secondary methods which mainly deal with post gasification removal of tar, these are Physical methods, thermal cracking, catalyst cracking and plasma method [37].

2.6.1. Primary Methods

An ideal primary method eliminates the need for secondary treatment. Mainly operating conditions and reactor design. A brief insight to these primary methods is given below.

2.6.1.1. Operating conditions

Operating conditions play a vital role during biomass gasification. It influences the carbon conversion, product gas composition and tar formation. The main parameters usually considered are temperature, pressure, gasification agent, additives and the mass ratio between fuel feed and gasifying agent.

Based on several researches that had evaluated the effect of temperature on tar content in the product gas, it has been shown that the decreasing the temperature leads to formation of more tars in the product gas. When pressure is increased from 8.0 to 2.4 bar, the phenols were completely eliminated leading to a reduction in tars but increasing pressure increases the PAH formation [38].

Similarly, the tar content is affected by the gasification agent used (air, steam or an oxygen-steam mix), with a higher tar content when steam is used and lowest when air is used [39]. This is due to the reduction in gasification temperature by the injection of steam, especially if it is saturated. The mass ratio between fuel and gasifying agent which is called equivalence ratio ER when air is the gasifying agent and steam-biomass ration when steam is used, influences the quality of the tar content.

2.6.1.2. Gasifier design

The gasifier design is an important aspect to consider on tar content in biomass gasification product gas. Modifications on gasifiers allows an efficient production of clean product gases. Pan et al. reported achieving 88.7% in total tar content reduction by injecting air above biomass feeding point within the gasification temperature range (840 -880 ° C) [40]. A two-stage gasifier design is also a good strategy for production of clean product gases, the idea is to separate the pyrolysis zone and the reduction zone. This way the tars produced during the pyrolysis (first stage) are reduced in the reduction zone (second stage) [41].

2.6.2. Secondary Methods

2.6.2.1. Physical cleaning methods

The physical methods to clean tars from effluent involve, for example the use of mechanical purifiers like the ESP electrostatic precipitator, filter, scrubber cyclones etc. these installations are popular in the power generation industry to remove particulate matter from flue gases. The removal sequence

is not limited to particulate matter as these devices has been shown through several experiments to have acceptable removal efficiency for tars. Instead of simple cooling, tars are more easily removed using physical agglomeration, biomass-based tars are even harder to agglomerate requiring complex systems to achieve high efficiency of removal. Tar levels of 20-40 ng/m³ are obtainable using such systems, a saturator and scrubber [42].

Hasler [43], reported in an assessment of gas cleaning systems for internal combustion engine that even with the state-of-the-art cleaning techniques it is difficult to attain more than 90% tar removal efficiency. And the investment cost of this systems is high.

At the Energy Research Centre of Netherlands (ECN) test were run using a rotating particle separator RPS with three GASREIP configurations which stands for gas cleaning (tar and ammonia) and power production. Results shows that tar concentration was considerably reduced, from 8 to 4.5 mg/m³, but tar droplets remained downstream which almost blocked the bottom channels of the RPS. It was concluded that tar, dust and water are not a good mixture and that if a proper liquid more compatible with tar, that absorb tar from producer gas and does not allow the tar to condense in the downstream of the equipment. This led to the development of the OLGAs technology that uses oil as the scrubbing medium [44]. The Olga technology has several advantages over conventional tar removal methods like no condensation of tar in the system and increased system reliability and availability [36].

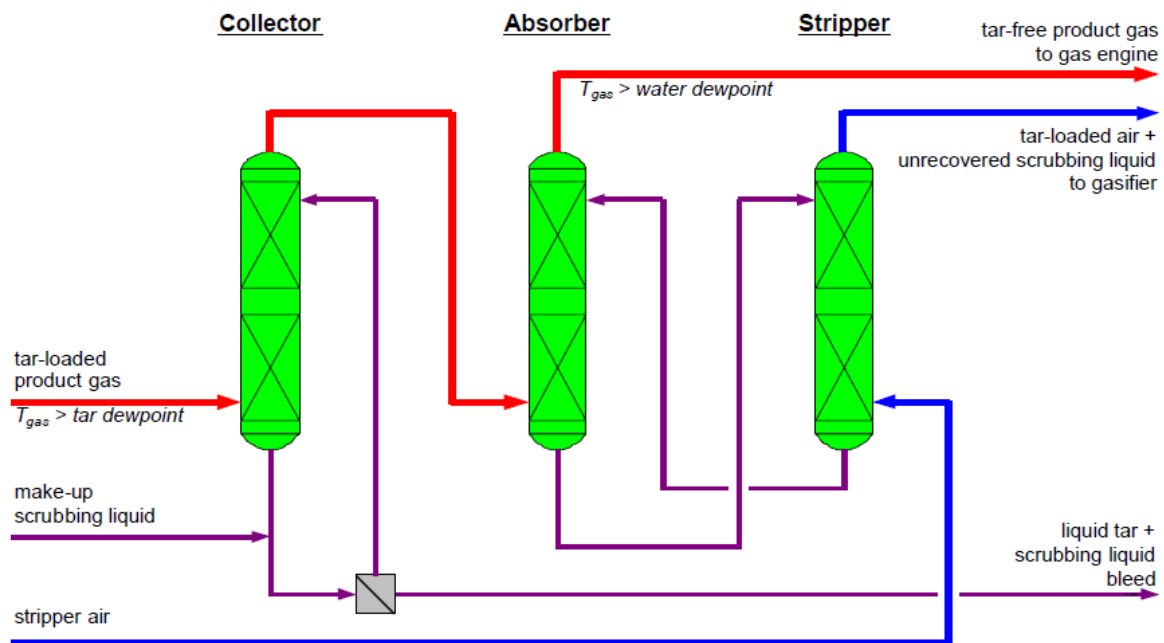


Figure 6: Schematic diagram of the OLGAs system [36]

Wet electrostatic precipitators have been shown to have very good efficiency for removing dust and tars from biomass product gas, with more than 99% efficiency for dust and reduction of the dew point of tars from 130 to 21 °C which makes it usable in IC engines [45].

Wenbin Zhang et al [46], in their own strategy decided to use a mop fan in combination with electrostatic precipitator (ESP) , even though more research is required the results shows that the combination has great potential for removing particle tars and other contaminants. In the end we could say the best strategies to use for gas cleaning depends on the requirements of the end users.

A summary of the major mechanical cleaning systems for particle and tar are presented in Table 4 below as show by Hasler [37], [43].

Table 4:Efficiency of mechanical cleaning systems

	Particle Reduction (%)	Tar Reduction (%)
Sand Bed Filter	70-99	50-97
Wash Tower	60-98	10-25
Fabric Filter	70-95	0-50
Rotational Particle Separator	85-90	30-70
Fixed Bed Tar Adsorber		50
Wet Electrostatic Precipitator	>99	0-60
Venturi Scrubber		50-90

2.6.2.2. Thermal cracking

Tar concentrations are a function of temperature and has been shown to decrease with temperature increase. And thermal is basically heating the tar to a high temperature were it is broken down to lighter gases at a particular residence time [47]. There are several ways of achieving this like 1). Increasing residence time after initial gasification which is only partially effective. 2). Contacting with a separately heated surface; this cost more energy, it seems to be less efficient and only partially effective. 3). Partial oxidation achieved by oxygen gasification.it can be very effective but increases CO2 levels and implies a higher cost when pure oxygen is used [42].

In a work done by Brandt [48] on the decomposition of tars using updraft gasifier, with a set up that uses contaminated gases for four experiments, three of which were based on gases from pyrolysis and the last from an updraft gasifier. The cracking temperatures were at 1200, 1250 and 1290 C at a residence time of 0.5 second. The results obtained showed that the cracking must be done at a temperature of at least 1250 ° C to achieve good tar cleaning, at 1290 ° C the tar content was as low

as 15 mg/Nm³. Despite these findings there is a drawback of high cost to achieve that temperature and the formation of heavier products and soot.

2.6.2.3. Plasma

Plasma technology is getting more popularity as a viable alternative to catalytic and thermal cracking of tar. The technology can remove dust tar and particulates in a single equipment [49].

Plasma constituted by highly charged atoms and molecule, ion, electrons and so on and can be divided into thermal (Equilibrium) and non-thermal plasmas (or non-equilibrium plasma). The thermal plasmas like gliding arc discharge has a typical gas temperature higher than 1,730 ° C and all the charged and neutral species are in thermal equilibrium [41]. As for the non-thermal plasma like the corona discharge, the electron temperatures can go as high as 10⁴ -10⁵ ° C while the gas is at normal room temperature [50].

In a demonstration to showcase a pulsed corona reactor. A wood gasifier of 100 KWh capacity with operating conditions of gas temperature of 200 ° C, a pressure of 1 bar and a pulse source of output energy 1J/pulse. The corona energy density varied from 150-160 J/L, STP. The results show that the conversion of heavy tars to lighter fractions as seen in Table (5) the results were considered favorable.

Table 5: Pulse Plasma tar removal results- Almelo pilot scale tests-1999 [49], [51]

Tars	Inlet (mg/Nm ³)	Outlet (mg/Nm ³)	Conversion (%)	Energy density (J/L)
Total	717	434	39	148
Heavy	603	232	62	
Light	114	202	-77	
Total	1928	1400	27	161
Heavy	1263	404	68	
light	665	996	-50	

Nair went further and compared the results with that of a thermal plasma reactor, based on a gliding-arc reactor tested for tar removal with a biomass gasifier at the Energy center of the Netherlands (ECN). The temperature was varied from 400 to 800 ° C, and energy density from 0-1900 kJ/m³. The results showed that tar conversion increasing with energy density and reactor temperature, but the degree of the conversion 40% at 800 ° C and 1600 J/L was lower than the desired conversion and there was also undesirable conversion of other hydrocarbons like ethene and ethane [52]. The comparison shows that the corona plasma is a better option than the gliding -arc for tar removal.

Non-thermal plasma techniques are very good for tar removal but suffer from some drawbacks such as the high cost and high energy demands of the whole process as well as short lifespan of the pulsed power devices [47].

2.6.2.4. Catalytic method

The catalytic tar processing for tar elimination and mitigation can be simplified into two types 1). one that involves the action happening within the reactor by mixing catalyst with the bed of feed to influence the gasification, this is a primary method as the whole process happens inside the reactor, and the corresponding catalyst is referred to as primary catalysts 2). The second type involves treating the producer gas in the downstream of the reactor and its one of the secondary methods and the catalysts are secondary catalyst.

The criteria for selecting the catalyst were summarized by David as [43] The catalyst must be ;1). Effective in removing tar 2). Capable of reforming methane if syngas is the desired product 3). Provide a suitable syngas ratio for the intended process 4). Resistant to deactivation from fouling and sintering 5). strong and inexpensive 6). Easily regenerated [41].

3. EXPERIMENTS

The series of experiments involved in this project were divided into 3; the thermogravimetric analysis (TGA) of the biomass samples, the gasification of the biomass, and the TGA of the tar obtained from the product gas from the gasification.

The main biomass used were Eucalyptus woody biomass (EA) obtained from paper production technologies to produce pulp. Simply known as “Estilho de Eucalyptus” Eucalyptus. The thermochemical behavior of this sample was studied using the TGA.

3.1. TGA Analysis of biomass

The experiments were done using a PerkinElmer STA6000 simultaneous thermal analyzer with an alumina crucible of melting point of around 2000. The highest temperature for the experiments was 800, so its conveniently within the safe range of use of the crucible.

The thermogravimetric analyzer is usually used to check the degradation of materials exposed to different heating conditions. The samples are subjected to a controlled heating program and the mass loss and rate of heat flow data are obtained.

At the beginning, a control experiment was made with the simple objective of direct combustion of the biomass at 800 °C. after the sample has been placed in the TGA a short program was written to instruct the TGA.

- First step is holding the sample at a temperature of 30 °C for 10mins to stabilize the system
- Followed by heating the sample in air from 30 °C at a rate of 10 C per minute until the temperature gets to 800 °C
- The system is held isothermal for another 10 minutes
- And finally, it is cooled at a rate of 50 °C per minute until the temperature gets to 30 °C.

After this more experiments were made in non-oxidative environment, the sweep gas was nitrogen to obtain char. Since in the gasifier experiments the objective was to maximize tar formation so that it could be more easily analyzed, a mixture of fresh biomass and char was also analyzed. For this purpose, the char obtained was added to fresh biomass at a ratio of 1:5 to 1:8 for char to biomass ratio and the mixture was then tested on under an oxidative environment with air as the sweep gas. The chars were obtained at four different temperatures (400, 500, 600 and 700 °C). The program for the pyrolysis (non-oxidative) for obtaining the chars is as follows:

- Holding the sample at a temperature of 30 °C for 10 mins
- Heating in Nitrogen atmosphere from 30 °C to T (where T = 400, 500, 600, 700).
- The sample is then held at that temperature for 60 mins
- The it is cooled at a rate 50 °C per mins until the temperature drops to 30 °C

After which more biomass is added and undergoes combustion in an oxidative environment as explained earlier.

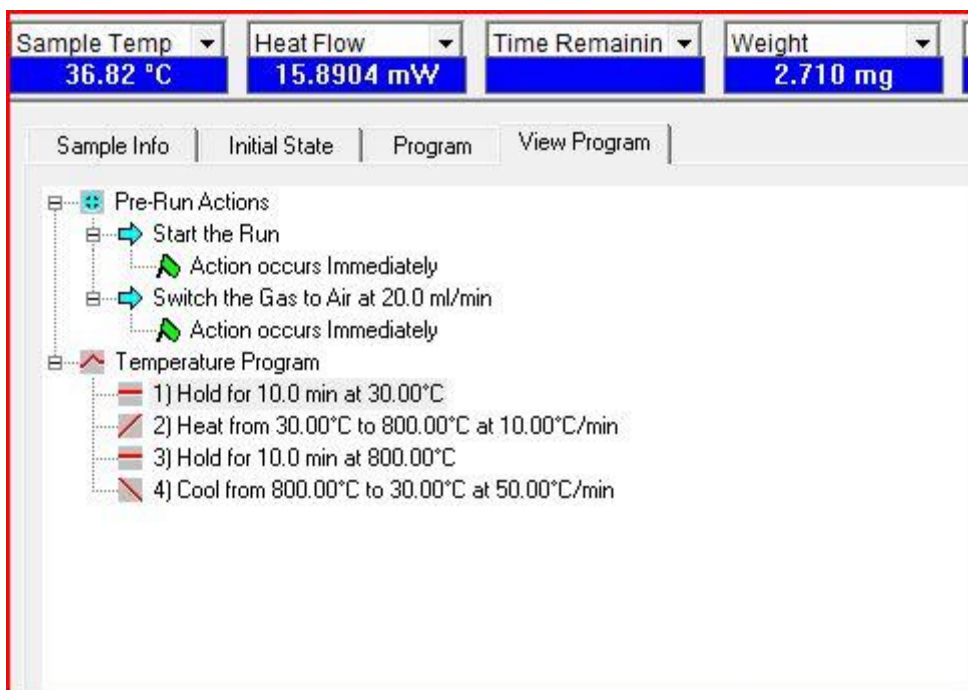


Figure 7-A view of the program on the TGA

Data analysis

The results obtained from the TGA were converted to an excel spreadsheet and from there a plot of the weight against temperature is obtained. This shows how weight is lost as the temperature of the samples increases. Then the heat-flow plot against temperature is also obtained as well as a differential weight against temperature. All these is to analyze the sample and find out what are its constituents in terms of water cellulose hemicellulose lignin and ash since we are working with biomass.

A kinetic model was also produce based on these data. It is assumed that the reaction follows a simple first order reaction and the kinetic model made is based on the Arrhenius equation. The summary of obtaining the kinetic parameters is as follows

- From the results obtained from the TGA after conversion into excel, a weight loss and heat flow graph are produced. Using weight against program temperature and heat flow against program temperature respectively.
- A kinetic model was then produced to simulate the weight loss. While assuming first order of reaction the kinetic expression used to get the kinetics of each component is

$$- \frac{dW_{comp\ x,n}}{dt} = k(T) W_{comp\ x,n} \quad (14)$$

Where

$k(T)$ = reaction constant from Arrhenius equation

$W_{comp\ x, n}$ = change in mass fraction of each component

And the value of $W_{comp\ x, n}$ was calculated using the Euler's method:

$$W_{comp\ x,n} = W_{comp\ x,(n-1)} + \frac{dW_{comp\ x,(n-1)}}{dt} \Delta t \quad (15)$$

- Then the total of the modelled mass loss was calculated by summing up all the components mass loss:

$$W_{model,n} = \sum W_{comp\ x,n} \quad (16)$$

- The activation energy, exponential constant and the initial mass fraction of the components were first assumed then estimated using the least-square approach and resorting to the Generalized Reduced Gradient (GRG) algorithm for non-linear optimization using Microsoft Excel's solver tool.

$$f(W) = \sum (W_{exp,n} - W_{model,n})^2 \quad (17)$$

3.2. Gasification

3.2.1. Gasifier

The experimental facility is located at the university of Aveiro Portugal, it consists of a pilot scale 80 kW_{th} bubbling fluidized bed reactor (BFB) made of AISI 310 SS with a reaction chamber of 0.25 m internal diameter and 2.3 m height. The bottom bed height of 0.23 m consists of sand particles with sizes not above 1mm, the bed contains 20 kg of sand. The oxidizing agent was dry atmospheric air fed through the distributor plate. A screw feeder is used to feed the biomass into the reactor onto the bed surface ,0.3 meters above the distributor plate, as seen from the pictures of the reactor is shown fig 8.

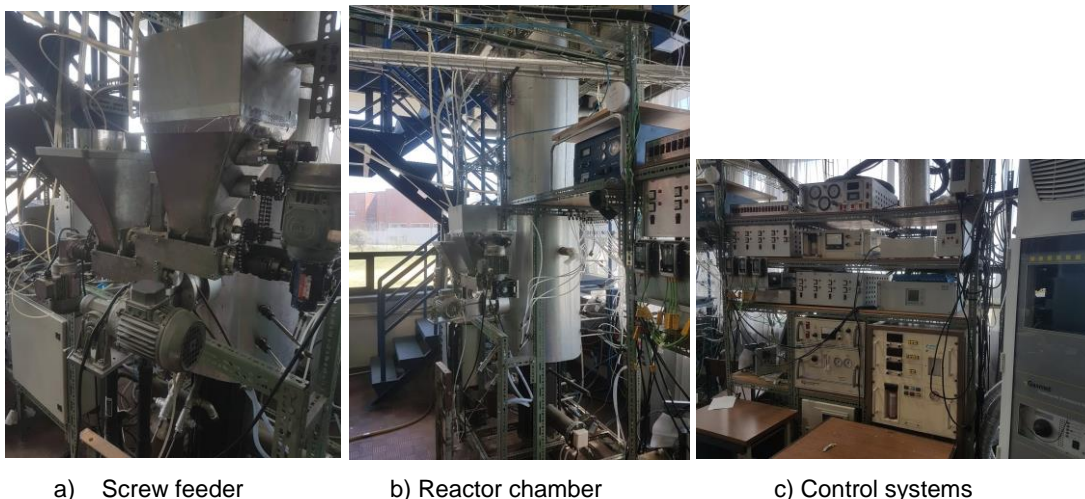


Figure 8: Direct Pictures of the Gasifier

3.2.2. Feeder and feedstocks

The gasifier uses a screw-type feeder, which can feed a uniform amount of feedstock to the gasifier continuously. The feed rate can be controlled and was calibrated a day before the experiments to determine the amount of biomass to be supplied by the feeder. Usually given in RPM (revolution per minute). The proximate analysis of the Eucalyptus biomass used is given in Table 6 The bio-chars mixed with the biomass were sourced from a neighboring pyrolysis plant that pyrolyzes woody biomass for chars. the biomass and chars to be used in the experiment were mixed and prepared earlier into 100% biomass, 95% biomass with 5% char, 90% biomass with 10% char and 80% biomass with 20 % char.

Table 6: Proximate and Ultimate Analysis of the Biomass (DRY BASIS)

Feedstock	
Proximate analysis	
Moisture	11.8
Volatiles	80.5
Fixed carbon	16.7
Ash	5
Ultimate analysis	
C	48.2
H	6.2
N	0.2
S	0.03
O	42.7
Cl	0.05

As shown in the table 6 above, the biomass consists of volatiles, fixed carbon and ashes. The volatile and fixed carbon content were 80.5 and 16.7% respectively.

3.2.3. Experimental method

Initial start-up of and raising of the bed temperature to around 500 ° C was done with a propane burner (F in fig 9) and by pre-heating the primary air. On getting to a bed temperature of 500 ° C the gas burner and the primary air are switched off while the biomass feeding starts. The biomass feeding allows the generation of enough heat to continue raising the temperature of the gasifier to the required operating bed temperature levels.

The temperature of the bed during gasification sometimes drops due to the presence of slightly wet biomass in the feed, the gasification had to be paused while pelletized biomass was combusted to raise the temperature of the bed and then the gasification was continued. So, the direct gasifier was operated under autothermal condition without need for auxiliary heating systems.

The fluidized bed was operated in a bubbling regime at atmospheric pressure with gas velocity around 0.3 m/s with average bed temperature around 731 ° C. The bed was kept at the desired temperature range by the insertion and regulation of eight water cooled probes at the bed level.

The raw gas produced is highly combustible when mixed with air in an atmospheric burner downstream of the reactor (O in Fig 9). The gas produced was continuously burned throughout the run of the reactor.

The feed rate, air feed rate, equivalence ratio, temperature and pressure of the reactor were used to characterize the operating conditions of the reactor.

The biomass feed was from residual forest biomass (RFB) derived from eucalyptus (Estilho de Eucalyptus). it was mainly from industrial operations to produce pulp and paper. The eucalyptus chips were dried in sunlight. The char samples used in the gasification experiment were obtained from a pyrolysis plant. The raw gas from the exit were sampled using an electrically heated sampling line at 350 ° C and then cooled by passing it through a series of impingers submerged in an ice bath.

The samples collected were from the exhaust(char) at point N and the air burner (tar) at point O of the reactor.

3.3. TGA of char and tar samples from the gasification

Although obtaining tar samples proved challenging during the gasification, two samples (char and tar) were obtained at different points downstream of the gasifier. Thermogravimetric analysis of the samples was carried out as follows:

- Straight combustion under air until 900 °C
- Pyrolysis under nitrogen also up to 900 °C – if there was still char in the pan after the pyrolysis, then a second run under air to characterize the remaining material.
- CO₂ gasification, by heating the material under pure CO₂ atmosphere up to 900 °C. and the remaining material was oxidized under air.

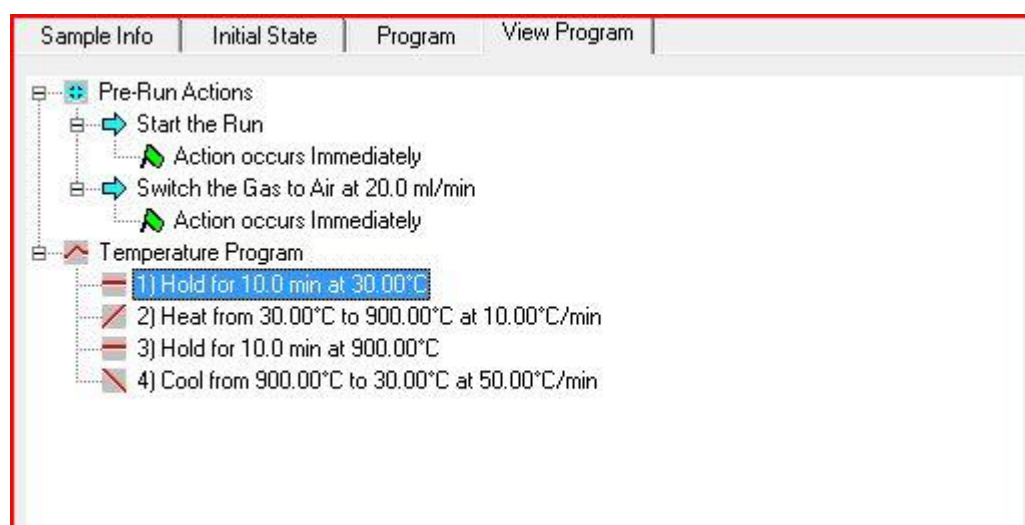


Figure 10-A view of the program at 900 °C in the TGA

4. RESULTS AND DISCUSSION OF RESULTS

4.1. Combustion

The initial combustion of the Eucalyptus biomass sample to a final temperature of 800 °C gave the degradation profile shown below. The combustion was programmed to run with dry air at a rate of 20 ml/min, this rate was used for all the combustion in this experiment. The heating rate of the experiment was 10 °C/min. As seen from the graph, the first thing to happen is moisture and some volatile components removal as depicted in fig 11 by the gradient drop and the small peak in the range of 30 -100 °C which is around 10% mass loss.

The second stage starting around 200-520 °C shows the thermal decomposition of the biomass, this is the main combustion process with up to 80% mass loss. The breakdown of the components of the sample occurs during this stage which could be further divided into two, first (100- 345 °C) and second (345- 520 °C) sub-stages with mass loss of around 50% and 40% respectively.

And in the last stage above 520 °C we have the oxidation of the residual char and there is practically nothing left, and the weight loss is also very low less than 1%.

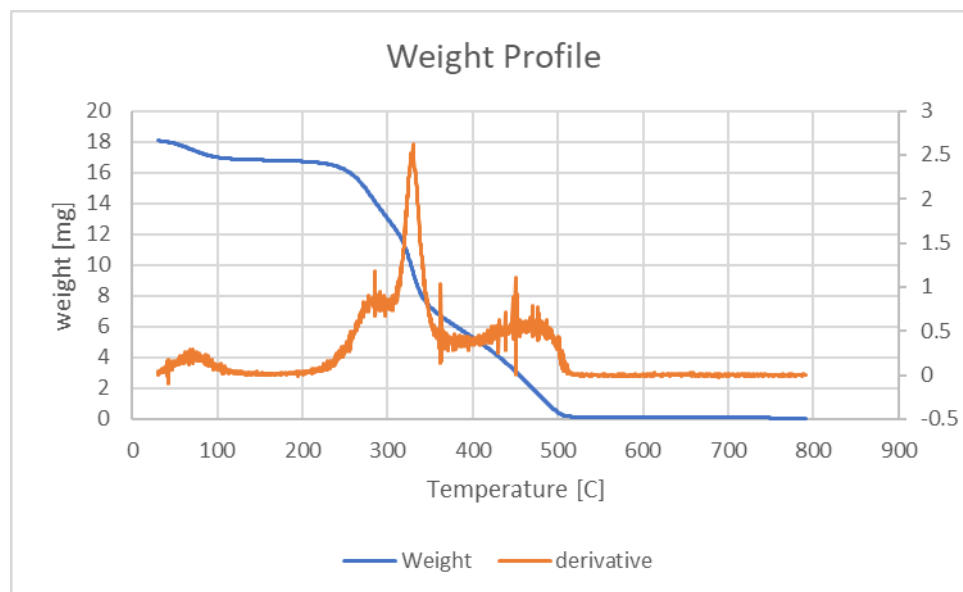


Figure 11:EA Combustion 800 C A) weight. B) derivative

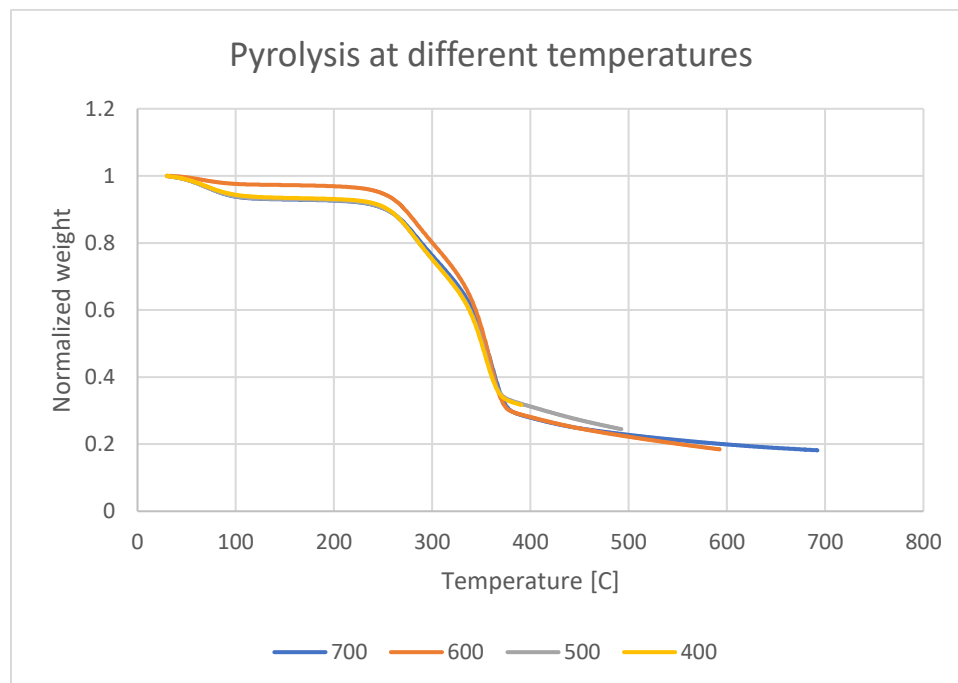
4.2. Pyrolysis

This was done to obtain the chars at different temperature 400, 500, 600, and 700 °C. the pyrolysis occurred in an atmosphere of nitrogen flowing at 20ml/min. at different final temperatures the pyrolysis

tends to have a similar degradation profile as shown in figure 6 below, which could also be breakdown into three stages depicting the loss of moisture, the volatilization and degradation of components while the third stage is carbonization of the volatiles and carbonaceous solids.

First stage: for the four cases the first stage is the same irrespective of the final temperature, a mass loss of less than 10% representing moisture and some volatile content from 30 – 125 °C.

Second stage: starting from around 135-690 °C, corresponding to the degradation of the heterogenous polysaccharides of hemicellulose, the glucose polymers of cellulose and the complex structure of lignin into condensable and non-condensable gases as well as chars. During the first sub-stage we have the first mass which happens around 210-340 °C estimated to be hemicellulose because it reacts at relatively lower temperatures [31] with a 30% mass loss at this sub-stage. the second sub-stage occurring around 332- 375 °C with a corresponding 28.8% weight loss which would be the cellulose. At the beginning of the third sub-stage starting around 375 °C and as we know one of the final temperatures is 400 °C, It should be pointed out that during the earlier substages, we also have the degradation of lignin as it happens throughout the process until a temperature of around 900 °C depending on the biomass sample in use . The mass loss in the third substage depending on the final temperature of the pyrolysis is shown below.



700 – biomass + char obtained at 700 °C. 600 – biomass + char obtained at 600 °C. 500 – biomass + char obtained at 500 °C. 400 – biomass + char obtained at 400 °C

Figure 12-Pyrolysis at 10 °C/min for different final temperatures

700 – biomass + char obtained at 700 °C. 600 – biomass + char obtained at 600 °C. 500 – biomass + char obtained at 500 °C. 400 – biomass + char obtained at 400 °C.

Table 7- Summary of pyrolysis data

Final T	Tstage1	Mass loss	T stage 2 Substage1	Mass loss	T stage 2 Substage2	Mass loss	Tstage 2 Substage3	Mass loss
400	30.0– 125.1	7.0	211.6-332.4	31.1	332.0- 372.8	39.6	375.7-390.7	0.4
500	30.1– 125.1	7.0	211.6-332.4	31.1	332- 375	30.8	375.7-491.1	7.5
600	30.1– 125.1	6.7	218.6-332.4	31.1	334.9-385.9	30.8	375.7-592.2	13.2
700	301.0– 125.1	7.0	211.6-332.4	31.1	332.0- 375.0	30.8	375.7-691.6	18.8

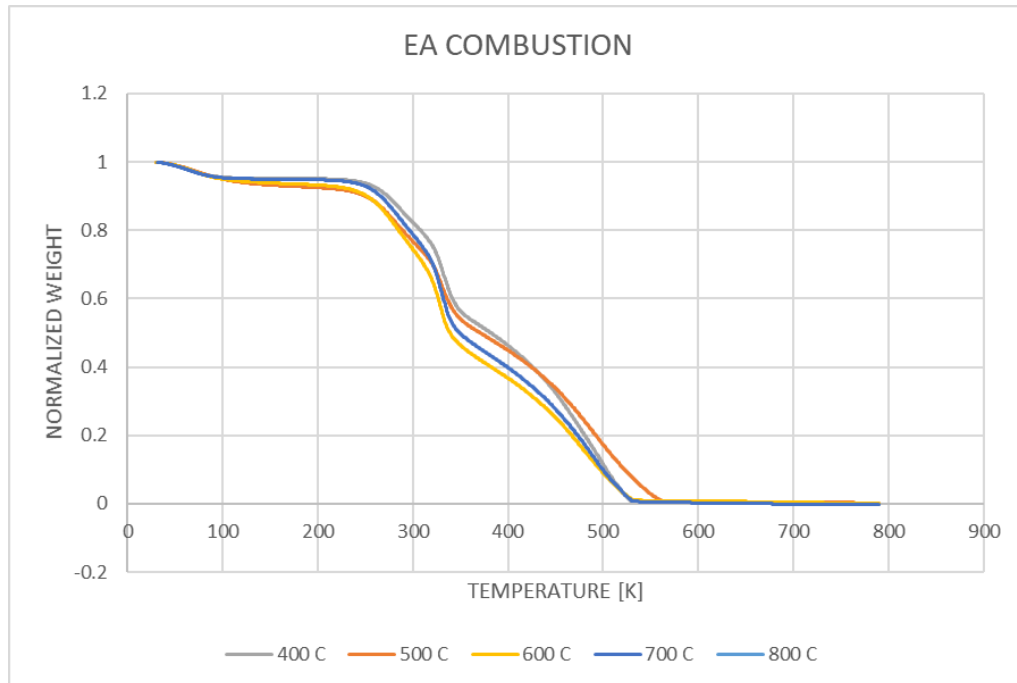
The final temperature of a pyrolysis reaction affects the product yields and the composition of the products. And in this case, we have four experiments with four final temperatures 400, 500, 600, 700 °C, and from the results obtained the lower final temperatures seems to have a higher percentage of char left after the procedure. Around 22% char for pyrolysis final temperature at 400 °C, 13 % for 500 °C and 9% for 600 °C. that also means the higher the final pyrolysis temperature the high the volatiles produced.

4.3. Combustion of biomass with chars

On combustion of the chars obtained with biomass the weight loss profile is show below. and as described earlier the first stage (30-110 °C) shows the loss of moisture and volatile components of the biomass, while the second stage (200- 560 °C) shows the combustion of the lignocelulosic materials, the third stage showing the oxidation of the residual chars. The relevant data showing the weight loss is shown below.

Table 8- Mass of samples for the combustion

	Total mass/mg	Char/ mg	% Char
Original	18.1	0	0
700	10.9	2.8	0.2
600	17.8	1.4	0.1
500	1.6	2.5	0.1
400	10.2	4.3	0.3



700 – biomass + char obtained at 700 °C. 600 – biomass + char obtained at 600 °C. 500 – biomass + char obtained at 500 °C. 400 – biomass + char obtained at 400 °C

Figure 13- EA biomass combustion with chars

It seems that when the char is obtained at a lower temperature 400 and 500 °C the combustion takes place at a higher temperature as compared to when the chars were obtained at a higher temperature 600 700 °C.

Table 9- Summary of mass loss during combustion

Samples	T-stage 1	Mass loss-stage 1	T-stage 2	Mass loss stage 2	T-stage 3	Mass loss stage 3
EA400	101.5	9.5	356.0	54.9	535.1	0.6
EA500	107.6	9.4	356.1	53.1	564.7	1.5
EA600	108.6	9.5	343.0	46.7	539.8	1.8
EA700		9.6	344.5	47.8	539.2	1.0

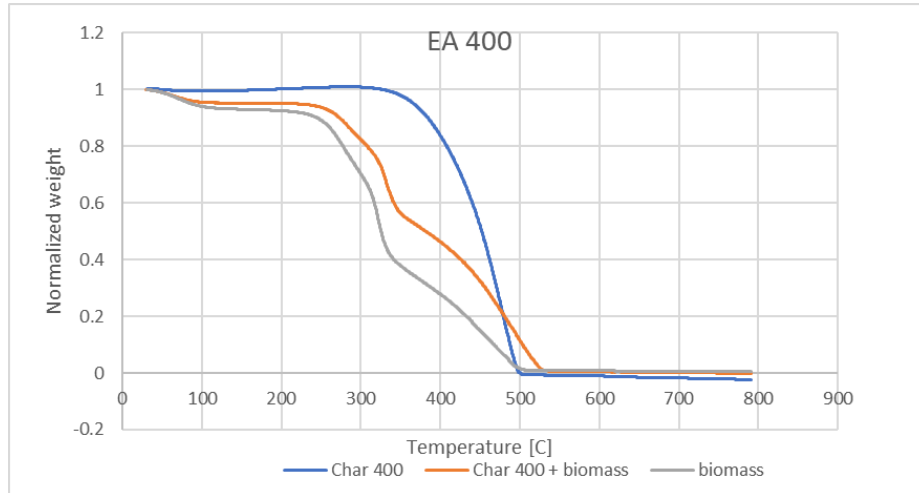


Figure 14- EA combustion at 400

The figure above shows that the char obtained at 400 ° C burn at a higher temperature when compared to the char with additional biomass. For more perspective, direct biomass combustion to final temperature of 800 ° C was included in the graph. The char also burns more uniformly. Using these two graphs together with the original combustion plot at 800 ° C we can compare using linear combination of the char and the original biomass curves. Which assumes the assumes the combustion of the char and biomass independently.

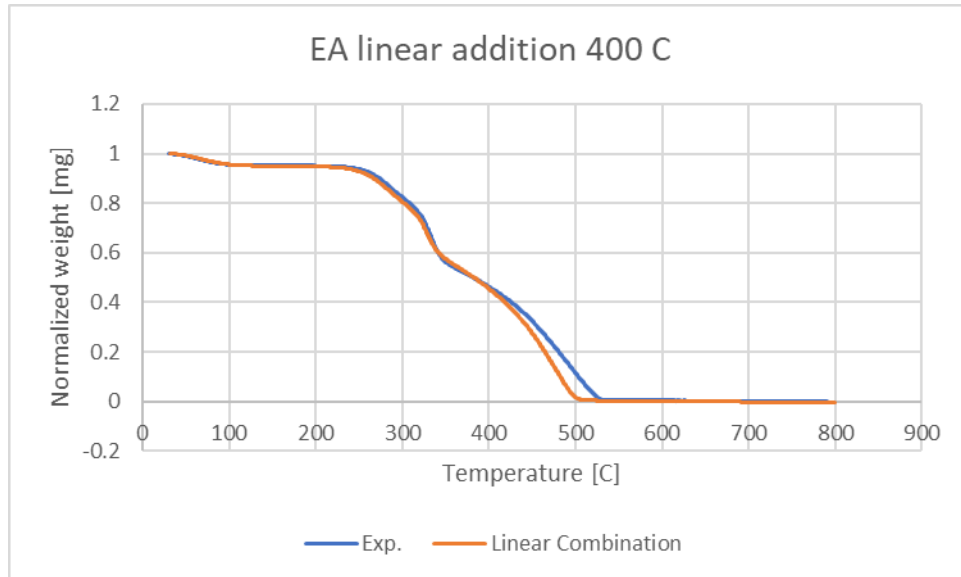


Figure 15- Comparison of linear addition of EA combustion data and experimental data

From figure 15 we can conclude that the combined incineration of the original biomass and the char increases the temperature of the final incineration step, which indicates a negative interaction of the previously produced char in the final combustion step.

4.4. Energy profile

The heat flow during the experiments show the energy profiles be it exothermic or endothermic or both as shown in the following figures 16 and 17 for both the combustion of the sample at 800 °C and also the combustion of the sample with chars obtained at different temperatures. The heating rate used was 10 °C/min.

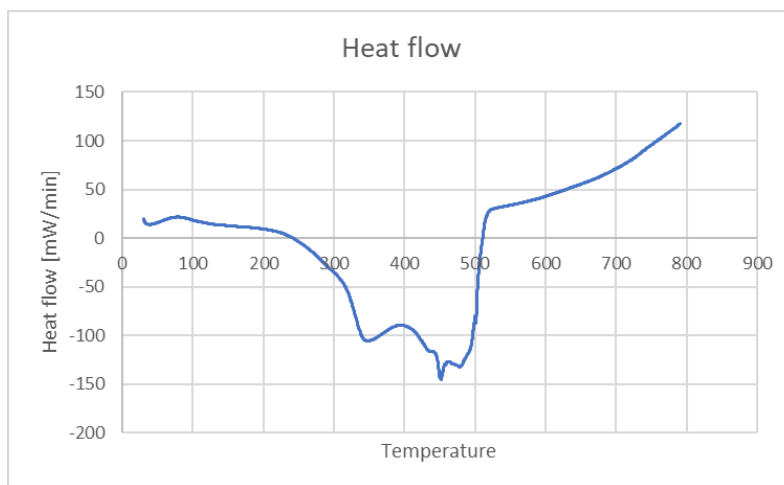


Figure 16-Heat flow EA 800 °C Combustion

As shown on the graph above for the combustion of the sample at 800 °C the reaction starts with the application of heat to increase the temperature of the biomass sample, then the reaction continues with an exothermic profile 248.11-509.6 °C which is related to the main combustion reactions, breakdown of the complex components and weight loss, and after this stage there is virtually no weight loss of the sample, marking the end of the combustion reaction.

In the combustion of the samples together with the chars, the first peak seemed to appear around the same temperature, and probably corresponds to the combustion of the original biomass, second peak varies widely depending on the char used and it is larger than the first peak. It should be noted that the direct combustion without any chars at 800 °C has the highest 1st peak and the smallest 2nd peak. Also, the combustion with chars obtained at lower temperature seems to be more exothermic.

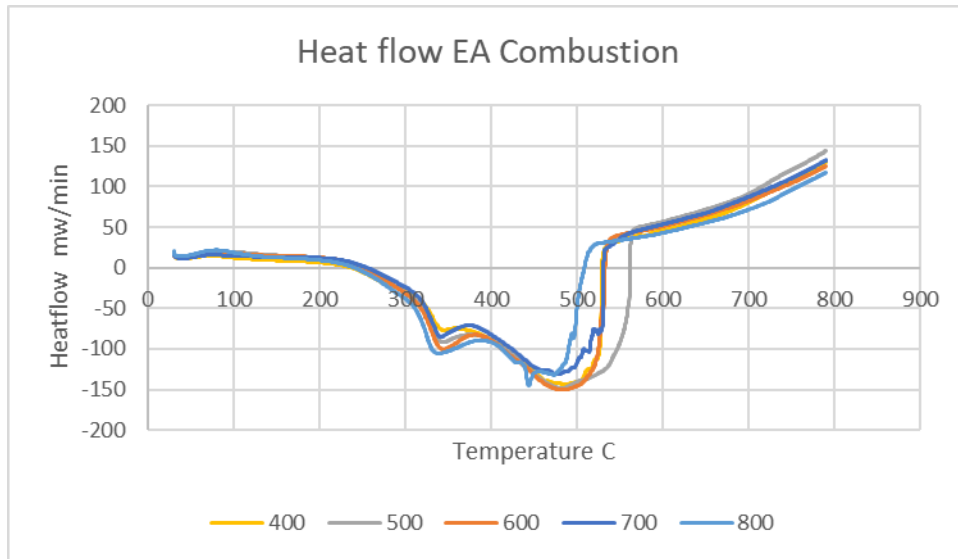


Figure 17- heat flow comparisons

700 – biomass + char obtained at 700 °C. 600 – biomass + char obtained at 600 °C. 500 – biomass + char obtained at 500 °C. 400 – biomass + char obtained at 400 °C

Table 10- Exothermic peaks of the samples at 100 C/min

Sample	Final Temperature	Peak (mW/min)	Temperature (°C)
400		-73.9	339.1
		-144.3	488.5
500		-86.8	356.2
		-148.4	483.2
600		-100.3	344.9
		-150.1	487.2
700		-85.1	342.6
		-131.3	478.7
800		-102.9	358.5
		-144.2	450.7
		-131.9	178.8

During the combustion of the EA Adding char to the biomass tends to be more exothermic than when the pyrolysis is followed directly with combustion as seen in the figure below.

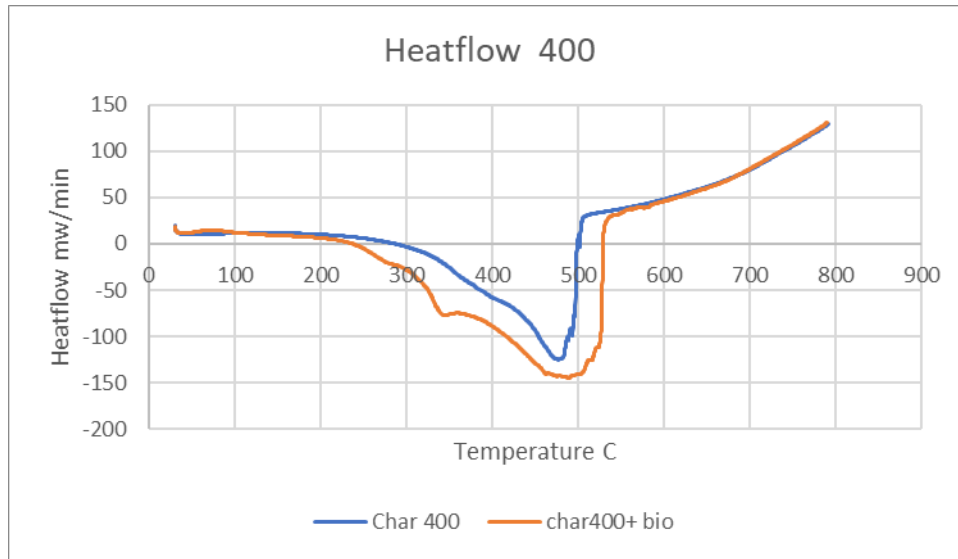


Figure 18- EA 400 Heat flow comparison

4.5. Gasification

The gasification experiments were carried out using three feeds. First was 100% Eucalyptus, followed by 90% Eucalyptus and 10% char and then 80% Eucalyptus and 20% char. The temperature profile of the bubbling fluidised bed reactor is shown below for each of these. The biomass feed rate was 10 kg/hr with the air feed rate of 200L NTP/min.

The gasifier was operated at steady-state conditions from the beginning of the feeding at a bed temperature of 500°C till the achievement of the gasification regime which took almost 2hrs. The typical temperature profiles at different points along the height of the reactor was analogous as shown below in fig 13.

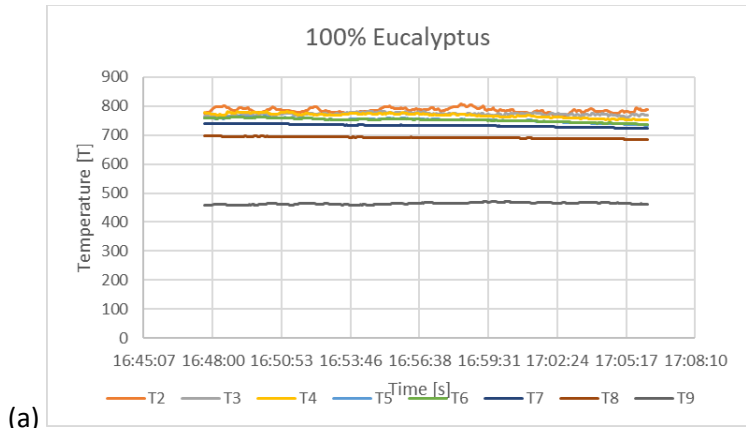
Table 11- Temperature probe distance in the reactor

	T2	T3	T4	T5	T6	T7	T8	T9
Distance to the reactor distributor plate [m]	0.2	0.3	0.4	0.6	0.8	1.2	1.7	2.9

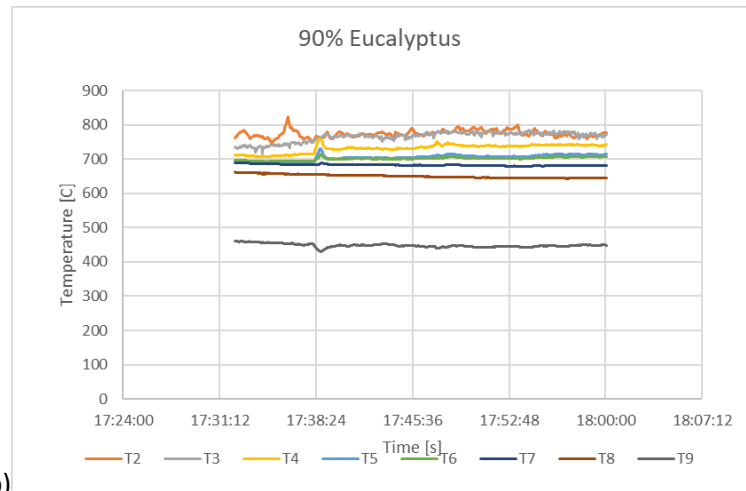
The position of the temperature probes is independent of the feed, these are default position of the gasifier design.

One of the goals of running the experiment is trying to show a steady state flow which is attributed to fluidized bed reactors in theory. From the temperature profiles obtained, it did really look an unsteady state profile from the beginning but when after some time running the reactor, it does achieve a steady

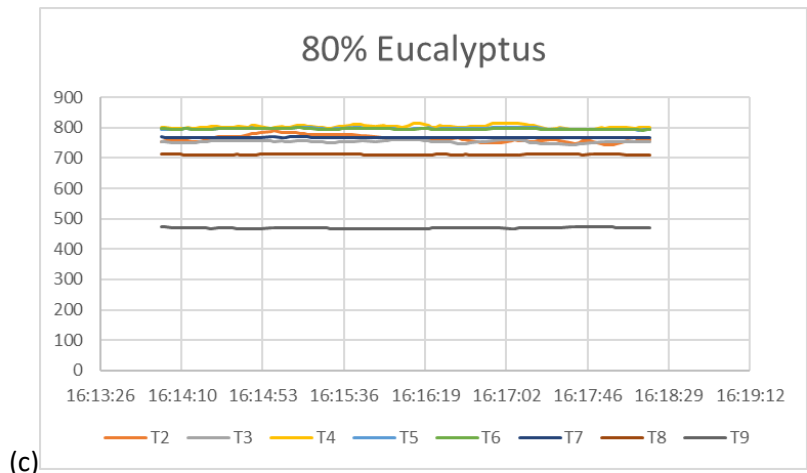
state for several minutes. This always changes whenever the feed composition is changed, for example when switching from 100% Eucalyptus biomass to 90% Eucalyptus biomass with 10% chars.



(a)



(b)



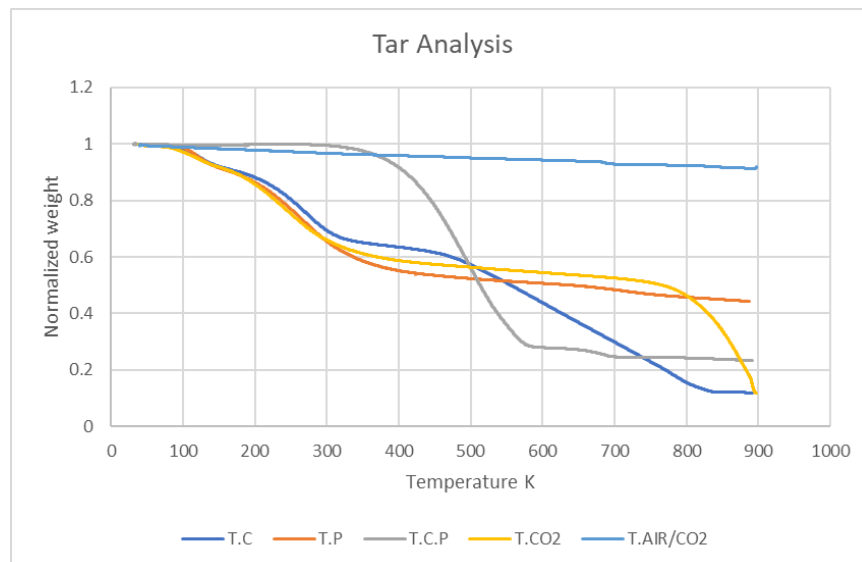
(c)

Figure 19- Gasification temperatures at different locations along the height of the reactor during gasification at: (a)100% Eucalyptus (b) 90% Eucalyptus and (c) 80% Eucalyptus

There were some noticeable changes in the temperature when different feed ratios were used. It seems from this that adding chars influence the temperature of the gasification reactions. Although the temperature profiles show a not so steady state behaviour which could be attributed to some fluctuations in the heat supplied to the reactor because of the presence of some slightly wet biomass in the feed. By analysing these temperature profiles, it could be concluded that addition of char to the biomass feed increases the gasification temperature which is in line with our initial observation while analysing the biomass using TGA.

4.6. Tar and char analysis

The results obtained from the TG analysis of the tar samples obtained is summarised in the graph below. Carrying out pyrolysis before combustion produces more ashes than direct combustion of the tar samples. And although gasification with CO₂ happens at a higher temperature it has almost the same mass loss compared to direct combustion with air. While burning after CO₂ gasification lead to very little mass loss.



T.C = Tar combustion, T.P = Tar pyrolysis, T.C.P = Tar combustion after pyrolysis, T.CO₂ = Tar gasification with CO₂, T.Air/CO₂ = Tar combustion after gasification with CO₂

Figure 20-Tar mass analysis

4.6.1. Tar gasification in air and CO₂

The samples obtained from the air injector burner at the downstream of the reactor when analysed with the TGA gave some interesting results as shown below. The thermal degradation in the presence of air and in the presence of CO₂ have a similar behaviour for temperatures lower than 200 °C. We

could assume the first stage of mass loss to be here and attribute it to volatile compounds in the tar samples and perhaps with some trapped moisture. From 200 °C upward, there is a gradual divergence in degradation, for the air combustion the weight loss process happens more rapidly and there is a second peak around 230-240 °C until around 360 °C this would be taken as the breakdown of one of the complex groups that make up tars. The third stage which is depicted by the steady mass loss from around 460 °C till 820 °C where what is left is the ash content of the tar. On the other hand, for the CO₂ the second stage also start around 230 to 360 °C, after which there was hardly any mass loss until a temperature of 780 °C then we have the final mass loss stage 3 which stopped at 884 °C. We can conclude from Figure 22 that CO₂ is only able to actively react with tar samples at very high temperature that are however well within the temperature range achieved in the gasifier (see figure20).

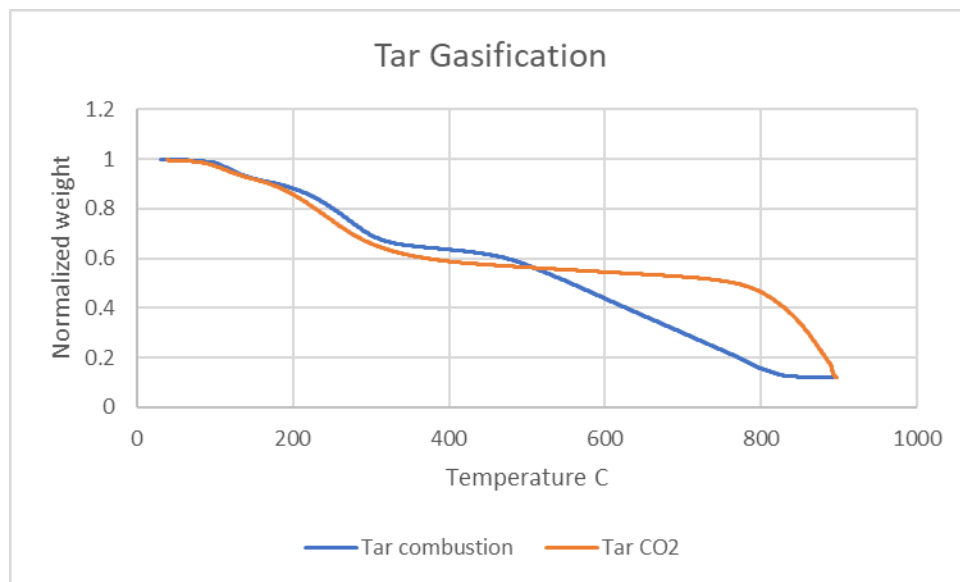


Figure 21- Tar Gasification Analysis

4.6.2. Tar pyrolysis and the corresponding combustion of the residue

Pyrolysis of the tar samples done by heating to a final temperature of 900 °C was carried out under the flow of dry nitrogen at 10 °C/min at normal temperature and pressure as shown in figure 16, there are two stages in the degradation of the tar sample. The first stage (100- 170 °C) depicts the loss of the volatiles with around 10% mass loss. The second stage starts around (220- 800 °C) with around 55% mass loss.

The residues considered as chars was then combusted in air to 900 °C also at 10 °C/min at normal temperature and pressure. As seen from the figure, there was not mass loss until the temperature got to 330 °C and mass loss was till 700 °C. all that's left is the ashes which is like 22% of the initial char mass and 9.24% of the initial tar sample.

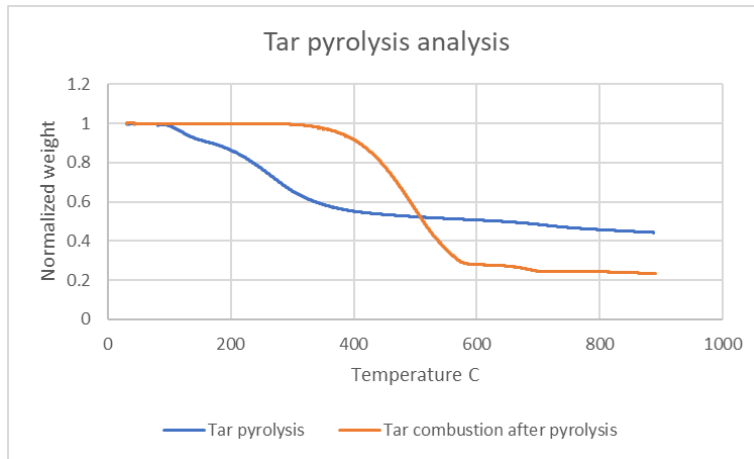


Figure 22- Tar Pyrolysis Analysis

4.6.3. Tar combustion under different atmospheric condition

To further understand the thermal reactivity of this tar. It was gasified at different atmospheric condition varying the percentage of CO₂ to air to form a mixture. 100% 75% 50% and 0% CO₂ were with a corresponding amount of air to make it to 100% in each case. It could be seen from figure 24 that at the beginning the curves all show a similar tendency which could be described as getting rid of whatever moisture content are in the samples, all these happening at temperatures below 100 ° C.

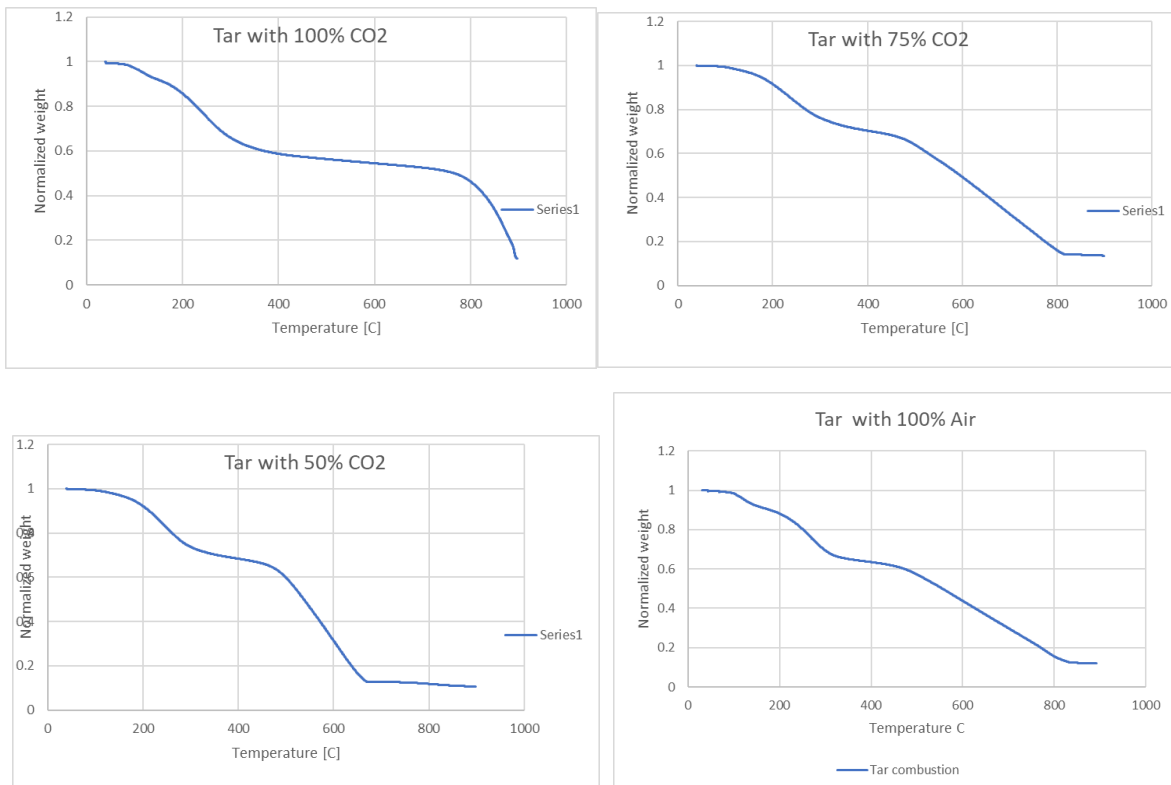
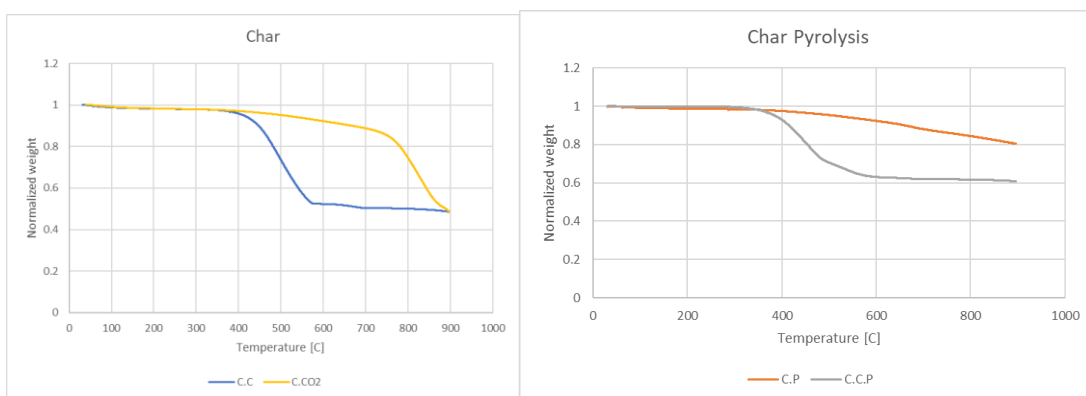


Figure 23: Tar combustion under different atmospheres

As the temperature continue to rise the curves begin to diverge from each other and it could be seen that the sample gasified using 100% air tend to degrade faster and as the percentage content of CO₂ start to increase the distance between the 2nd and 3rd peak begins to increase depicting and increase in the amount of energy required to break the bonds of the aromatic mixture making up those component of the tars.

4.6.4. Char gasification

The powder char samples obtained from the exhaust of the reactor at point N. The combustion with air was carried out at 10 °C/min at normal temperature and pressure. The figure below compares the decomposition of the char in air and the decomposition of the char in CO₂. One obvious thing from looking at the graph is that irrespective of the route the decomposition leaves almost 50% ashes after the process and using CO₂ the decomposition happens at higher temperature. The decomposition during the combustion with air has just one major stage of mass loss which starts around 400 °C to 588 °C a mass loss of 45% after the decomposition was happening at an extremely slow rate until the final temperature of 900°C was achieved. In the case of the CO₂ the decomposition start slowly from the beginning of the reaction picks ups a little bit around 400 °C, it was at 750 °C there was a sharp drop and a final mass loss of 35.1% to give the final ash content which is around 48.8% of the initial char mass.



C.C – Char combustion. C.CO₂ -Char combustion in CO₂ C.P.C – Char pyrolysis followed by combustion

Figure 24-Char mass analysis

4.6.5. Char Pyrolysis.

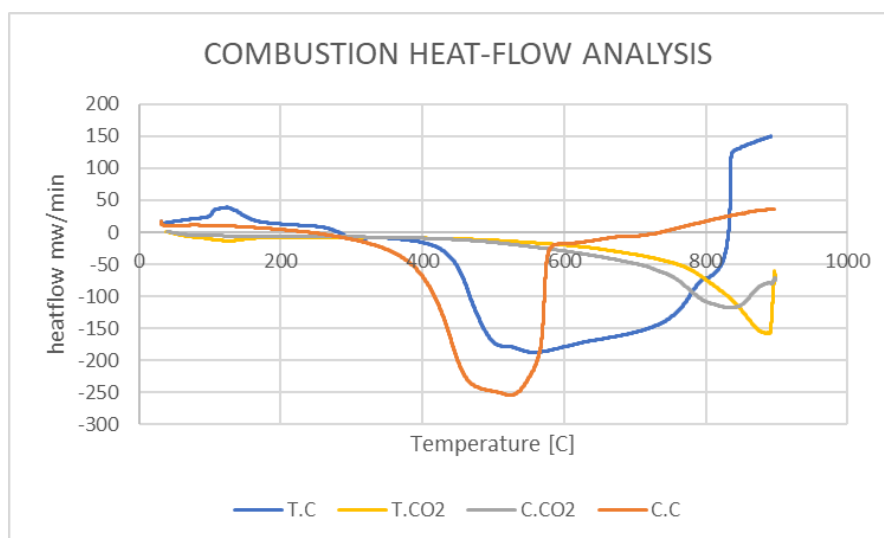
In the initial pyrolysis only 40% mass was lost as at the end of the final pyrolysis temperature of 900 °C and when the residue was burned in air to 900 °C there was only 20% mass loss of this residue

giving a total of 52% mass loss consistent with the initial observation when the char was decomposed in air and also in CO₂ giving approximately the same amount of char.

4.6.6. Energy Analysis

The following figure 26 obtained using the data of heat absorbed or released by the tar and char samples during combustion and gasification with CO₂ at a heating rate of 10 ° C/min was analyzed. CO₂ gasification although was carried out in a different TGA equipment but the results obtained is comparable to the STA6000 thermal analyzer.

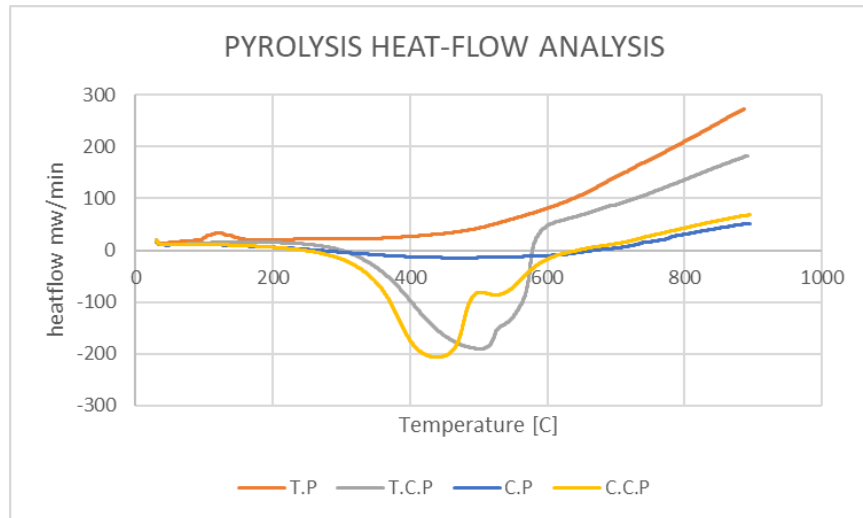
The thermal profile of tar combustion shows a highly exothermic thermic process between 400-830 ° C and then ended with an endothermic behavior at temperatures above 830 ° C. but the profile for char combustion although has a higher exothermic peak was in the exothermic region for a shorter temperature range from 300-590 ° C. In the case of CO₂ gasification both samples didn't decompose until a high temperature of 600 ° C.



T.C =Tar combustion, T.CO₂ = Tar gasification with CO₂, C.C = Char combustion, C. CO₂ = Char gasification with CO₂.

Figure 25- Combustion energy analysis

The thermal profile of the two samples char and tar when pyrolyzed in Nitrogen is completely endothermic. Although the char is considerably more endothermic than the tar, and there were no observable peaks in their pyrolysis thermal profile. On the other hand, the combustion of the residues left after the pyrolysis are mainly exothermic till the end of the process where we have virtually no weight loss. The char was exothermic for a wider range of temperature from around 250-600 ° C the tar residue combustion after pyrolysis was less exothermic between 311-566 ° C. There are two peaks overlapping and appearing almost as one in the combustion after pyrolysis profile, this could be assumed to be two substages in a single stage.



T.P. = Tar pyrolysis, T.C.P = Tar Pyrolysis followed by combustion, C.P = Char Pyrolysis, C. C. P = Char pyrolysis followed by combustion

Figure 26-Pyrolysis heatflow analysis

4.7. Kinetic model fitting.

4.7.1. EA Model fitting

This section of the report shows the model fitting for the combustion of the EA biomass with the biochars obtained at different temperatures at a rate of 10 °C/min. the graphs are represented below and the correlation coefficients are shown in table X . these models obtained are accurate and appropriately describes the the thermal behavior of the biomass sample.the approximate errors are shown in the form residual squares and a function based on the regression analysis.

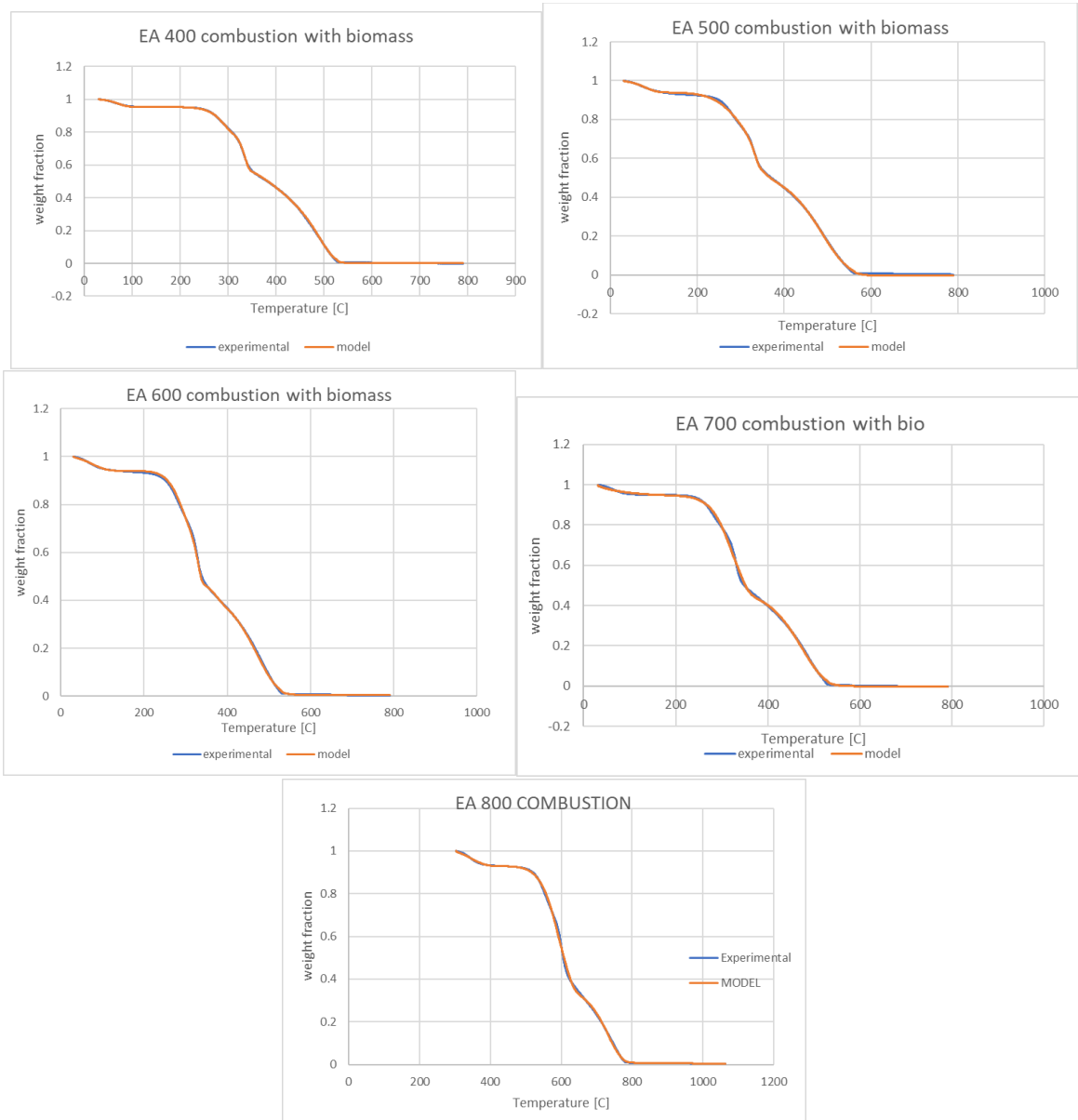


Figure 27: Model fitting for combustion of EA samples with biochar

So, the development of a simple model simulating the gasification of the biomass plus biochar shows a good result with good correlation ($r^2 > 0.99$) as further shown below.

Table 12: A table of the residual square

	r ²	F (w)
EA 400	0.99	0.014
EA 500	0.99	0.06
EA 600	0.99	0.06
EA 700	0.99	0.08
EA 800	0.99	0.09

A global fitting was made for all the above cases to fit them all using the same kinetic data in the form of apparent activation energy and apparent rate constant in other to get a single model describing the gasification of this specific Eucalyptus biomass with or without bio-char.

Kinetic parameters

The main kinetic parameters in analyzed in this work based on the multi-nonlinear regression are the apparent activation energy Ea, rate constant and the pseudo component of the biomass.

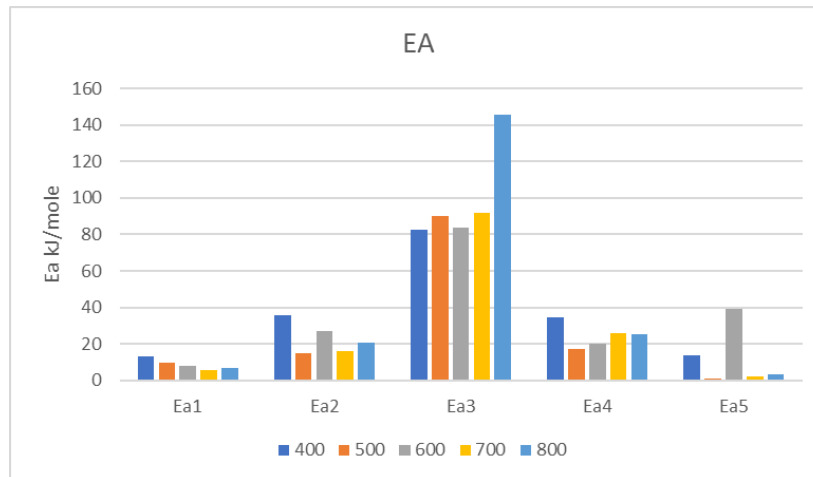


Figure 28: Apparent activation energy of the biomass samples

The figure above represents the apparent activation energy values obtained from the model fitting of the Eucalyptus and biochar gasification in air at 10 ° C/min. Ea1 up to Ea5 represents the pseudo components water, cellulose, hemicellulose and lignin. Usually the first component to be released is water followed hemicellulose, cellulose and lignin. The Ea5 is taken to be the remaining lignin that's degrading, as seen from the differential mass loss figure the decomposition of this biomass had 5 peaks. Representing each pseudo component's degradation.

Biomass composition

The model also provides an estimate of the fractions of the pseudo-components. These were based on the data obtained from the experiments. A summary of this pseudo components is shown in the table below.

Table 13: Pseudo-component weight

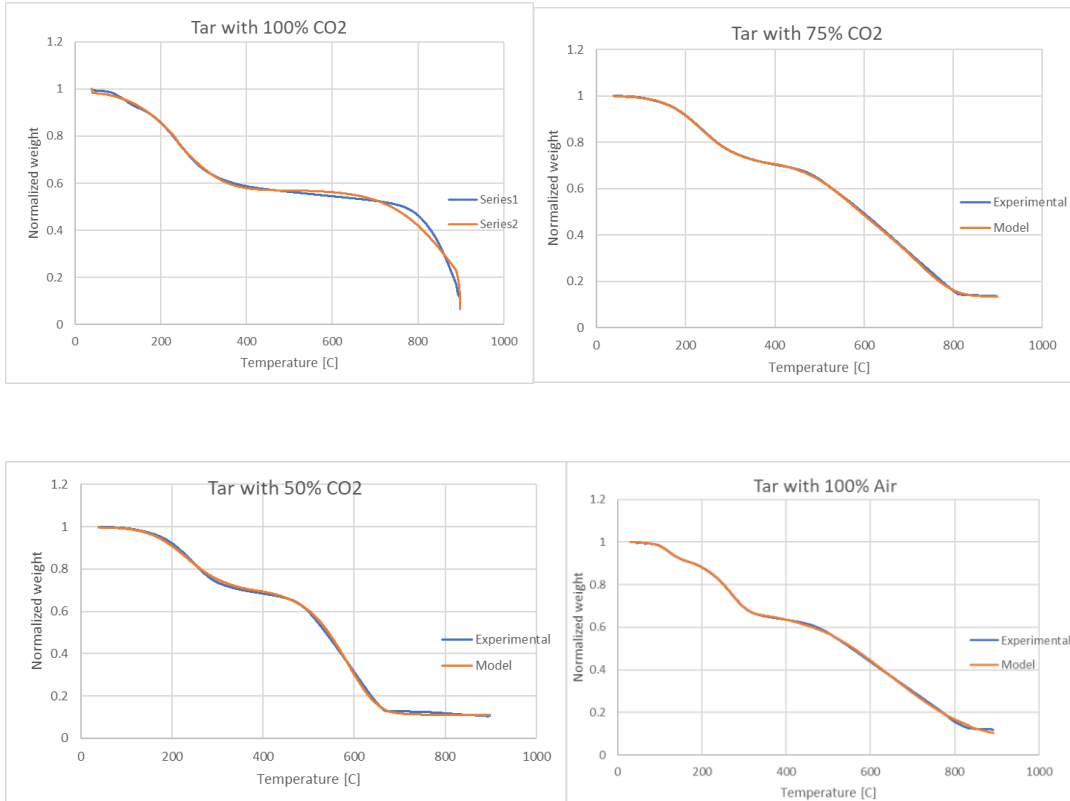
EA		W1(%)	W2 (%)	W3 (%)	W4 (%)	W5 (%)	ash
400	Individual	4.7	11.8	58.2	32.5	28.2	0
	Global	4.6	11.2	27.9	44.2	12	0
500	Individual	5.9	30.7	9.9	53	0.3	0
	Global	6.6	5.2	36.5	30.1	20.8	0
600	Individual	5.9	36.5	20	42.8	5.6	0
	Global	6	25.1	43.8	34.9	8.9	0
700	Individual	4.6	6	12.8	42.8	0.1	0
	Global	4.8	11.2	36	37.1	10.7	0
800	Individual	7.1	57.2	0.4	36.9	1.6	0
	Global	6.7	8.3	47.6	36.9	0	0

Just like with the activation energy W1, W2, W3, W4 and W5 represents the mass fraction of water, hemicellulose, cellulose, lignin and more lignin respectively. The table shows the mass fractions based on an individual model fitting for each, then a global model with all the samples using same kinetic parameters. In some cases, the global mass fractions are quite close to the normal model, and in others quite different. But if we look at all the values obtained for W1, the percentage of the water content is never up to 10% of the total mass of the biomass feed. And the biomass gasified without any biochar [800] has the highest amount of water, so we could say addition of biochar to the biomass reduces it's the total moisture content. considering that we are using the same biomass and only varying the final temperature we obtain our bio-char, the results should be relatively similar but with a higher carbon content. This could be reflected in the percentages of lignin present as depicted in W4 and W5. All the samples with biochar have a higher percentage of lignin [35%,53%,43%,43%] as compared to the control biomass that has no biochar [34%].

On the other hand, the control sample [sample] has a higher percentage of hemicellulose W2 as shown in the normal model fitting data. And based on the data we could say that addition of bio-char reduces the proportion of the hemicellulose and the higher the temperature this biochar was obtained, the closer the hemicellulose percentages are to the control sample. Because at 800 ° C which is the final temperature of the control sample the percentage of hemicellulose was 57% which is higher than for the samples with bio-char 30%, 24%, 30% and 12% for 700, 600, 500 and 400 ° C respectively.

4.7.2. Tar model fitting

The model fitting method was also used on the TGA results from the analysis of the tars samples obtained during the gasification. The focus was on the TGA gasification of the tars using different mixture on air and CO₂. The fittings are shown below.

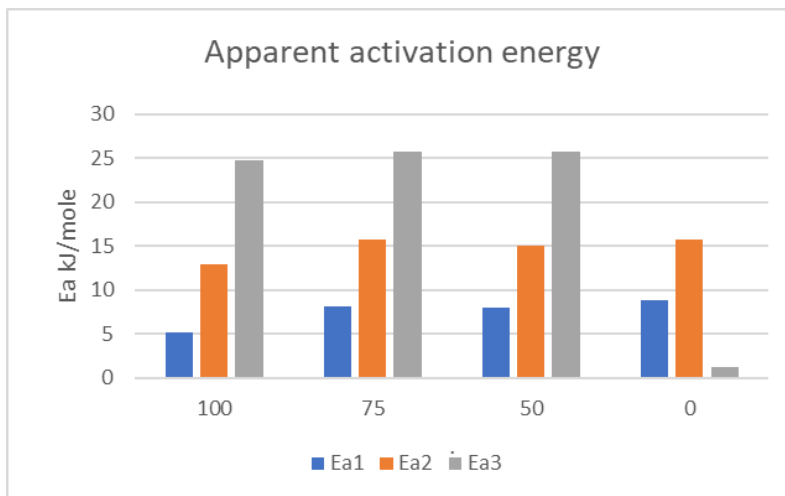


A global model was processed for this four separate model gasification at 100% 75% 50% 0% CO₂ respectively and it was quite difficult to obtain an acceptable global model that adequately describes the component models. Then the model 0% CO₂ -100% air was removed, and the global model was tried again. The result was not entirely impressive, but it was better.

Table 14: A table of the residual square for Tar models

	Individual model		Global model	
	r ²	F (w)	r ²	F (w)
100 % CO ₂	0.99	1.21	0.98	4.44
75 % CO ₂	0.99	0.044	0.99	3.23
50 % CO ₂	0.99	0.21	0.99	1
AIR	0.99	1.15		

The models coupled with the experimental results show that there are two main peaks in the mass loss of the tar degradation suggesting that the process follows two first order reactions each representing the pseudo-components present in tar structure. The r^2 for each graph is above 0.99 meaning it is satisfactorily acceptable. It should be pointed out the distance between these two peaks be a measure of its CO₂ proportion of the gasifying medium as the distance gets wider the higher the percentage of CO₂ in the mix.



From the apparent activation energies obtained from the model, while focusing on the main peaks shows that the activation energy for samples gasified in a CO₂ mix tends to have similar activation energies.

5. CONCLUSION

In this chapter, the themes that have been developed in line with the thesis objectives based on the experiments will be briefly summarized.

The main objective of this thesis was to study the thermal characteristics of the tars produced during direct gasification of Eucalyptus woody biomass EA, and the thermal characteristics of the feed biomass itself mixed with some bio-char. The tars were analyzed under different gasifying mediums.

The project sought to get the kinetic parameters mainly from the combustion reactions of the tars and biomass, effect of adding biochar to the biomass as well as the observable differences of changing the gasifying medium for the tars.

A preliminary observation that combined incineration of biomass and chars increases the temperature of the final incineration step was made after the biomass TGA. This was later confirmed while analyzing temperature profile data from the gasification experiment that the presence of char increases the final temperature of the gasification experiments.

The kinetic parameters were obtained using model fitting method to get mass loss as a function of temperature using least-squares approach, also the solver too in excel was used for the generalized reduced gradient for non-linear optimization.

On the part of the biomass, its mass loss profile shows that it undergoes thermal decomposition which can be sufficiently described by three first order reactions that corresponds to its main components according to literature. The hemicellulose cellulose and lignin, which is the same for all lignocellulosic materials. So basically, the development of a simple model simulating the gasification of the biomass plus biochar shows a good result with good correlation ($r^2 > 0.99$).

Addition of bio-char to the biomass tends to influence the percentage of the pseudo components. Like generally it increases the amount of lignin and some other less reactive components present during the mass loss degradation. And when was investigated further the final temperature of pyrolysis during the production of the bio-chars also have a lingering effect on the components like having a reduced amount of hemicellulose, which is more obvious the lower the final temperature of obtaining the bio-char. Lowest used for this experiment was 400 °C.

There are some slight discrepancies in the kinetic parameter measurement in term of the apparent activation energy EA which could be due to sensitivity of the model around the pseudo-components overlapping each other. Although the peaks obtained for each sample already describe a similar degradation profile. The results also show that the cellulose have the highest activation energy of the trio (82kJ/mole -145 kJ/mole) for all the samples followed by hemicellulose before the lignin

Concerning the tars, simulating the gasification of the tars under varying gasifying medium in terms of mixture of air and CO₂. It was concluded that CO₂ is only able to actively react with the tar samples at very high temperatures (> 700 ° C) that are however well within the temperature range achieved in the gasifier.

There are predominantly two peaks from the decomposition of the tars which could be tagged representing the light component and the heavy components of tars, as explained in literature earlier there are mix of aromatic hydrocarbons. The models show that tars degrade or breakdown at a higher temperature when gasified with CO₂ as compared to air.

The Apparent activation energies and kinetic rates observed in the model would be of great use in design modifications for gasifiers to reduce the production of the tars during the gasification process.

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