

Analysis of Tar Formation During Gasification and its Thermochemical Characterization

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ABSTRACT- 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 thermal 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 estimation of mass degradation of biomass sample from the TGA, to understand the behavior of the biomass when char was added and studied the conversion of each pseudo-component assuming first-order kinetic. Also, compared tar gasification in air and in CO₂ to see the effect of each gasifying agent. With CO₂ the tars degrade at a higher temperature (> 700 ° C) but this temperature still falls within the gasification temperature range of the gasifier. The kinetic parameters for the reactions were also obtained.

INTRODUCTION

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, this waste biomass can 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.

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, ethanol 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]. 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

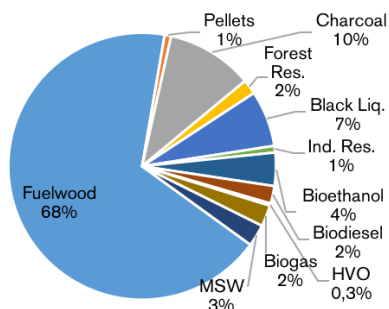


Figure 1 primary energy supply of biomass resources globally 2013 [2]

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 processing, 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.

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

LITERATURE REVIEW

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.[3] 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.[4]

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 [5]

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

Biomass is mainly considered as the organic matter from plant that is generated through photosynthesis and can be used for food, construction, medicine and energy. There are 3 main thermal/thermochemical ways of conversion of biomass to get energy we have combustion pyrolysis and gasification and among the by- product of the processes are tars which is our indirect purpose. in trying to investigate the thermal properties of the tars produced during one of this conversion processes, gasification. We will start with a brief description of these process.

Combustion- It 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,

combining power and heat generation in power and heat cycles.

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).[6]

Pyrolysis is defined as the thermal decomposition of organic materials in the absence of oxygen and halogens [7]. 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 [8].

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 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 [9]

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

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.

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 [10]. 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 [11]

Isoconversional method: These methods are quite reliable among the kinetic method used nowadays for the analysis of thermal data.[11], [12]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 [13]. 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 [14], [15]:

$$\frac{d\alpha}{dt} = \beta \left(\frac{d\alpha}{dT} \right) = A e^{\left(\frac{-Ea}{RT} \right)} f(\alpha) \quad (1)$$

Taking Log of both side from equation yields

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln \left(\beta \left(\frac{d\alpha}{dT} \right) \right) = \ln(Af(\alpha)) - \frac{Ea}{RT} \quad (2)$$

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.

$$g(\alpha) = \int_0^\alpha \left(\frac{d\alpha}{f(\alpha)} \right) = \frac{A}{\beta} \int_0^{T_\alpha} \exp \left(-\frac{Ea}{RT} \right) dT \quad (3)$$

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

$$g(\alpha) = \frac{AEa}{\beta R} \int_\alpha^\infty \left(\frac{\exp^{-x}}{x^2} \right) = \frac{AEa}{\beta R} p(x) \quad (4)$$

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

$$\log \left(\frac{\beta}{T_m^2} \right) = -\frac{Ea}{R} \left(\frac{1}{T_m} \right) - \ln \left[\left(\frac{Ea}{AR} \right) \left(\int_0^\alpha \left(\frac{d\delta}{f(\alpha)} \right) \right) \right] \quad (5)$$

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 [14].

Tars

Tars are a complex mixture that include phenols, polycyclic aromatic compounds (PAHs) and heterocyclic compounds.[16]. According to the ECN definition, tar comprises all organic components having a higher molecular weight than benzene.

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.[17]

EXPERIMENTS

The series of experiments involved in this project were divided into 3; the 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.

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.

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 texted 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

Gasification

Gasifier: The experimental facility is located at the university of Aveiro Portugal, it consists of a pilot scale 80 kWth bubbling fluidized bed reactor (BFB) made of AISI 310 SS with a reaction chamber of 0.25 m internal diameter and 2.3m height. The bottom bed height of 0.23m consist 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. A schematic diagram of the reactor is shown fig 2.

Feeder and feedstocks: The gasifier use 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).

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 the use of any 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.

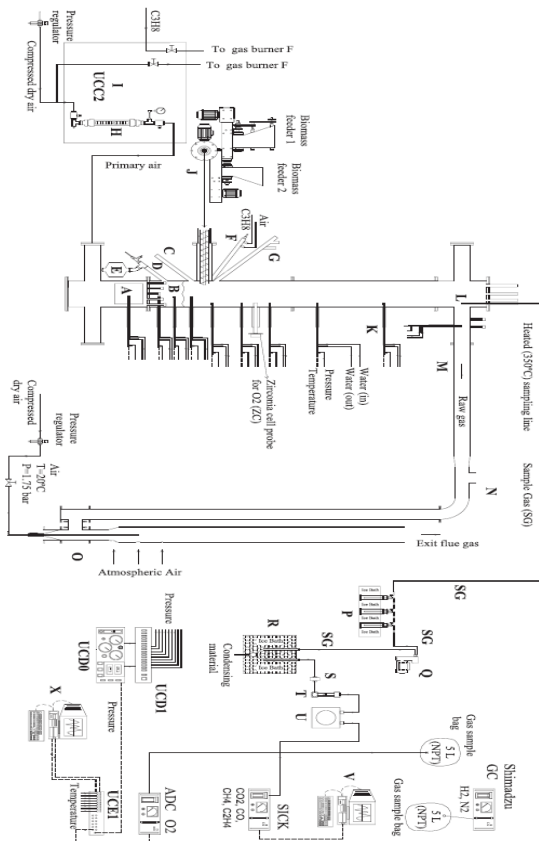


Figure 2: Schematic diagram of the pilot scale gasifier

Primary air heating system, B- Sand bed, C – Bed solids level control, D- Bed solids discharge, E – Bed solid discharge silo, F - Propane burner for preheating, G - Port for visual inspection of bed surface, H - Air flow meter (primary air), I - Control and command unit UCC2, J - Biomass feeder, K -Water-cooled probe for gas sampling, pressure and temperature monitoring, L - Raw gas sampling probe, M - Gas exhaust, N - Security exhaust pipe, O - Raw gas burner, P - Gas condensation unit with impingers for condensable gases (water, tars) removal, Q - Gas sampling pump, R - Gas condensation unit for moisture and other condensable gases removal, S - Filter for particle matter/aerosol removal, T - Gas flow meter, U - Dry gas meter, V - Computer for data acquisition from SICK analyzer, X - Computer for data acquisition and control system, UCD0, UCD1 - Electro-pneumatic command and gas distribution units, UCE1 - Electronic command unit, O2 - On-line gas analyzer for O2, SICK - On-line gas analyzer for CO2, CO, CH4, and C2H4, Shimadzu GC - Gas chromatograph.

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, as done earlier with biomass was carried out.

DISCUSSION OF RESULTS

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. As seen from the graph, the first thing to happen is moisture and some volatile components removal as depicted in fig 3A by the gradient drop and the small peak in fig 3B from around 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%.

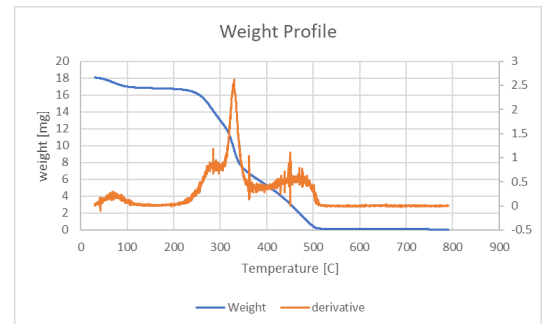


Figure 3: EA Combustion 800 C A) normalized weight. B) derivative

Combustion of biomass with chars

On combustion of the chars obtained with biomass the weight loss profile is shown 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 lignocellulosic materials, the third stage showing the oxidation of the residual chars..

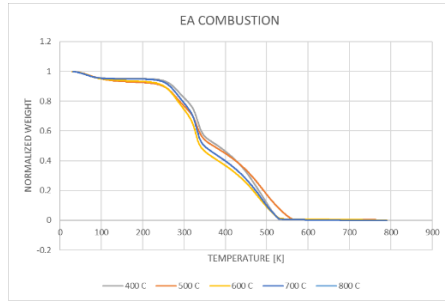


Figure 4:EA biomass combustion with chars

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.

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 10 and 11 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.

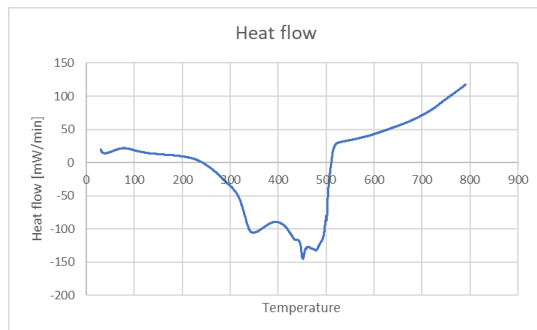


Figure 5:Heat flow EA 800

As shown on the graph above for the combustion of the sample at 800 ° C the reaction starts with the injection of heat into the system in the form of Cp 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, irrespective of what temperature the

char was obtained 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.

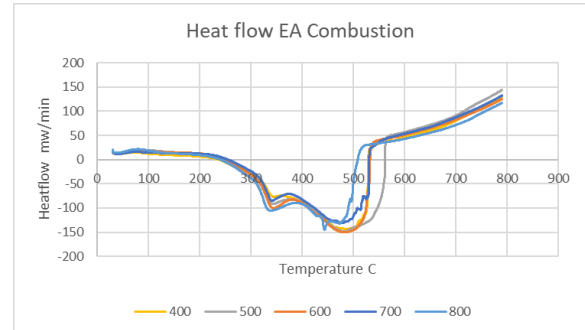


Figure 6:heat flow comparisons

Table 3:Exothermic peaks of the samples at 100 C/min

Sample Temperature	Final Temperature	Peak (mW/min)	Temperature (°C)
400		-73.85	339.11
		-144.29	488.46
500		-86.78	356.20
		-148.41	483.15
600		-100.27	344.98
		-150.07	487.23
700		-85.09	342.62
		-131.28	478.69
800		-102.89	358.54
		-144.21	450.70
		-131.87	178.81

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 show below for each of these.

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 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. 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.

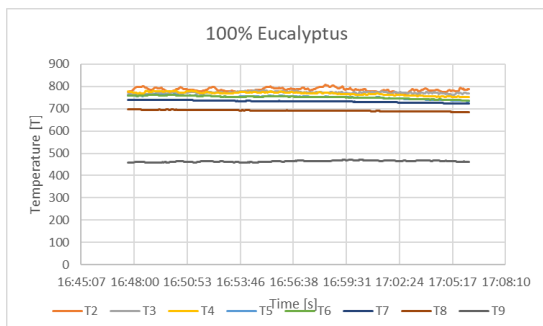


Figure 7: Gasification temperatures at different locations along the height of the reactor during gasification at 100% Eucalyptus .

Although the temperature profiles show a steady state behaviour, there are 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.

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.

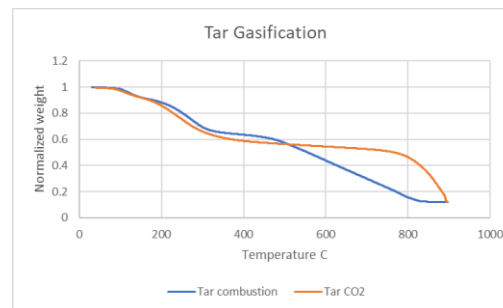


Figure 8- Tar Gasification Analysis

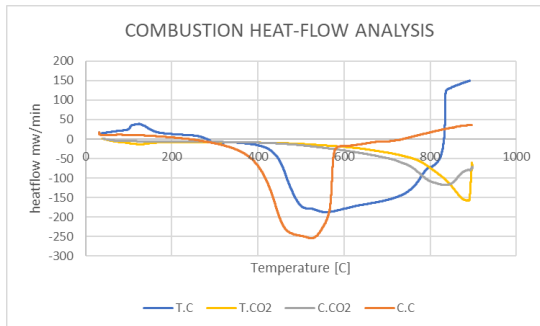
Tar combustion under different atmospheric condition

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.

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.

Energy Analysis: The following figure 9 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 9- 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.

Kinetic model fitting.

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. these models obtained are accurate and appropriately describes 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.

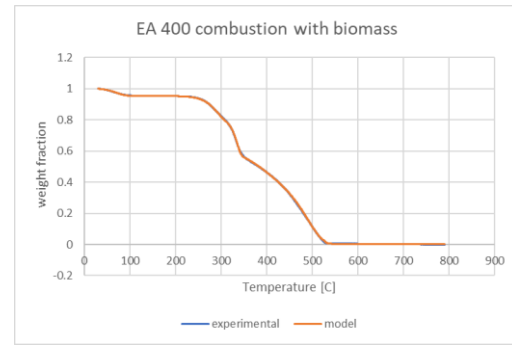


Figure 10: Model fitting for combustion of EA samples with biochar

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 order to get a single model describing the gasification of this specific Eucalyptus biomass with or without bio-char.

Kinetic parameters

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

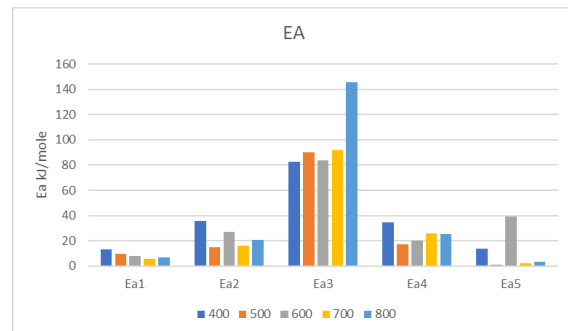


Figure 11: Apparent activation energy of the biomass samples

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

CONCLUSION

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.

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. 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.

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. The models show that tars degrade or breakdown at a higher temperature when gasified with CO₂ as compared to air.

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