

Biomass Gasification with Carbon Dioxide- Kinetic Studies

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ABSTRACT- The main intention of this study is to make a kinetic study on the reactivity of a specific type of biomass, from eucalyptus, under different atmospheres including air, nitrogen, carbon dioxide, and different mixtures between air and carbon dioxide. The main interest was to analyze the behavior of the biomass degradation, the derivative weight, and the heating flow under different gasification conditions and under different heating rates (10, 20, 50 and 100 °C/min). Also, a kinetic model was developed to simulate each TG test and also a preliminary model was done to help in the analyses of the DSC heat flow measurements. The mass loss models were developed assuming first-order reactions and restored to different pseudo-components to characterize the main components of the lignocellulosic biomass (Hemicellulose, cellulose and lignin). The results showed good correlation between the models and the experimental data. A model was also developed to simulate the heat flow of each test. The correlation for these models was not as accurate as the kinetic models but showed to be a promising route to follow.

INTRODUCTION

The current demand for energy in order to satisfy the human necessities is increasing every year. Today, the easiest way in order to fulfil this demand is with the use of fossil fuels, due to high availability and low price. But meeting this demand using fossil fuels has led to a series of environmental issues because these kinds of energies are harmful for the humanity and for the atmosphere. The amount of CO₂ and other greenhouse gases on the atmosphere has increased exponentially during the last century and the statistics show that this trend will continue to grow.

Giving an urgent solution has been a priority for the governments, who have started to see different solutions for alternative fuels that can lead to avoid having a dependence on fossil fuels. Biomass has turned into an interesting alternative in order to reduce the amount of emissions of greenhouse gases into the atmosphere. Biomass is known to absorb the solar energy in the photosynthesis process. This process involves the reaction of water and CO₂. When this material is used for combustion, the CO₂ that was absorbed is released back to the atmosphere, making this a carbon neutral process. Due to this feature, using biomass as a potential hydrocarbon replacement has become one of the paths to reduce carbon emissions, and studies have been increasing in the last period of time. Using the biochemical energy that is stored in the biomass is the main goal of the biomass processes, which can be done either by thermochemical processes or biochemical processes. This study is related to the thermochemical conversion process, in which one specific type of biomass that is common in Portugal (Eucalyptus) will be submitted to pyrolysis, combustion and gasification tests in order to make a kinetic study, which include how much the biomass decomposition process changes with different processes under different carrier gases.

Other studies have been done in order to find alternative processes that can use CO₂ as a potential feedstock, and deal with the vast amount of streams that are emitted daily. The idea is to have a possibility to recycle part of the emitted stream and use it for other purposes. One type of studies that have been carried out is using CO₂ in the gasification processes as a gasification media. Several studies have been

done using coal and some for biomass as a feedstock. For example, Ye et al.[1] made a study in which they used a low rank coal and made gasification tests with CO₂ and with steam, and found that the CO₂ gasification had a lower activation energy compared to steam, but the reactivity was higher. Marquez-Montesinos et al[2] used grapefruit skin char and made gasification experiments with steam and with CO₂. They reported that the activation energy was lower with CO₂ compared to steam, and they had a higher reactivity, due to a catalytic effect of minerals present on the biomass.

In this study, CO₂ will also be used as a gasification media for the tests, using pure CO₂, and also using mixtures between air and CO₂. The goal is to be able to compare how using CO₂ affects the kinetics of the biomass decomposition, and also to see how the heat that is required for the operation is affected by the presence of this gas, and its respective mixtures.

LITERATURE REVIEW

Lignocellulosic biomass has been a subject of many studies, to understand the behaviour of these under certain circumstances, the object of this study is to verify how the biomass degradation changes with respect to different factors, such as heating rate, or carrier gas.

For changes in respect to heating rates, several studies have been made, for example, Chen et al.[3] made a pyrolysis test using poplar wood, at different temperatures and heating rates. I was concluded that increasing the heating rate promoted the generation of CO and CH₄, and also enhanced the carbon content of biochar, while decreasing the water content of bio-oil. Barneto et al.[4] studied the effects of heating rate on 2 different biomasses. It was found that a slow heating rate produces more hydrogen than a fast heating rate. This could be related to the reactivity of the char produced in the first stage of the gasification process. Cetin et al.[5] studied the effects of pyrolysis pressure and heating rate on radiate pine char. In this study, it was concluded that with high heating rates the char particles melted. Also, the produced chars had less micropore network, because of the melting. Williams et al.[6] made a study of slow pyrolysis of pine wood changing heat rates from 5 to 80 °C/min. It was found that as the heating rate was increased from 5 °C/min to 80 °C/min, there was a shift to higher values of temperature values for the maximum rate of weight loss.

Carrier gas also plays an important role in biomass gasification, Butterman et al.[7] studied the gas evolution, mass decay behavior and energy content of several biomass and agricultural waste samples, doing steam and CO₂ gasification using thermogravimetric analysis and gas chromatography. It was found that carbon conversion was complete with 25% CO₂-75% steam mixture, compared to 90% conversion with pure steam in the temperature range of 800-1000°C. With 0-5% CO₂, there was an increase of CO concentration by a factor of 10, and a decrease in H₂ by a factor of 3.3 at 900 °C. Also, with 100% CO₂ there was a separation of cellulose from lignin at 380 °C in a 1 °C/min heating rate. The CO₂ has the ability to enhance the pore structure, providing an access for the CO₂ to gasify the solid. Jeremias et al.[8] used steam and CO₂ as a gasification agent for wood chips in a spouting fluidized bed. It found that mixtures of CO₂ and H₂O in the gasifying agent improves char conversion, and that the combined agents were effective decomposing the tars when lime based materials were used in the fluidized bed. The gasifying agents composed by a mixture of H₂O and CO₂ led to higher conversions of char to gas, and the tar was decomposed as well. Cheng et al[9]. Studied the behavior of CO₂ gasification of biomass (woodchips) in a fluidized bed. They found that when the CO₂-to-biomass ratio was increased, the mole fraction of CO in the producer gas increased, while the fraction of H₂ and CO₂ decreased. When the CO₂ percentage was 60%, the fractions of CO and CH₄ in the producer gas were maximum, as well as the lower heating value, being optimal. The increase of the moisture content and the particle size of the woodchips had a negative effect on the gasification performance, reducing the lower heating value, cold gas efficiency and CO₂ conversion ratio.

Finding the kinetic parameters of biomass degradation plays an important role in this study, so a few studies done in this field were investigated. Nedelchev et al.[10] made a review of the basic methods for non-isothermal analysis, and also made a study of kinetics of non-isothermal decomposition of calcium carbonate. Abbasi et al. [11] made an examination on the reliability on the of the kinetic parameters of the Coats-Redfern (CR) equation. They simulated TGA curves for reactions with different kinetic models, and found that the characteristics of CR approach to kinetic analysis of TGA data is

unsuitable for determination of kinetic parameters. Garrigos [12] made a kinetic study of biomass modelling for combustion and pyrolysis. She found the kinetic parameters for 5 different type of biomasses under oxidizing and non-oxidizing atmospheres at 4 different heating rates. Pokwizcal [13] made a study for thermochemical conversion of wooden chips, getting the kinetics information under different temperatures and carrier gases. Finally, a gasification simulation was done for the results obtained.

Heat flow studies were also required for this experimentation, for example, Haseli et al.[14] made a model to find kinetic parameters, particle pyrolysis and heat of reactions (temperature dependent) for a type of biomass. They took in account for variations the heat of reaction with the temperature, using 3 parallel reactions yielding gas, char and tar. Their model showed that the sensible heat released because of the biomass was responsible for the description of some experimental observations. Koufopoulos et al.[15] provided a model that describes the pyrolysis of a single solid particle of biomass. Their thermal properties in the model are linear functions of temperature and conversion, and were fitted with experimental data. The heat of reaction was represented by 2 values: endothermic (prevailing at low conversions), and exothermic (prevailing at high conversions). The pyrolysis was simulated with 2 parallel reactions and a third reaction for the secondary reactions between charcoal and volatiles.

EXPERIMENTALPROCEDURE

Biomass: The biomass used is a lignocellulosic material (eucalyptus). Table 1 shows the properties of this material:

Equipment: The equipment that was used for the experiment was a TA Instruments SDT 2960 simultaneous DSC-TGA apparatus. This equipment has a furnace that can be used up to 1500°C, and a couple of thermoelectric disks measuring heat flow, and a balance that records the weight of the sample during the experiment. In this disks 2 pans will be placed, one will carry the material for the experiment, and the second will be a blank pan that will be used as reference. The equipment has connection to 3 lines: a line that provides air, a line that provides nitrogen, and a line that provides CO₂. There is a digital flow meter that ensures that all the experiments were taken at the same flow

(20ml/min). The device is connected to a computer in which all the data is received and processed; giving as an output the data that was recorded (time, temperature, weight of sample, derivative weight, and heat flow). The system also delivers graphics of these curves for analysis.

Proximate analysis	
Parameter	Value
Moisture (%)	10,2
Volatile matter (dry %)	78,1
Fixed carbon (dry %)	17,5
Ash (dry %)	4,5

Ultimate analysis	
Parameter	Value
Carbon (%)	46,4
Hydrogen (%)	5,7
Nitrogen (%)	0,7
Sulfur (%)	nd
Oxygen (%)	42,3
Chlorine (%)	0,4
ash (%)	4,5

Table 1. Proximate and ultimate analysis of biomass.

Experimental method: The data analysis that was done in this study is divided into 2 parts: the first was a thermogravimetric analysis (TGA) and the second one is a differential scanning calorimetry (DSC) test. The material which is subject to a test is exposed to a controlled heating program in a controlled environment (highest temperature, gas flow, heating rate, type of heating gas). The TGA analysis provides information on profile of loss material and the rate in which the mass is lost. The DSC test shows the heat data of the process, if it was released or if it was absorbed during the experiment, and the temperature in which the event occurred. The experimentation steps are the following: Heat furnace to 40 °C, wait 10 minutes for stabilization, heat up from 40 °C until 900°C at given heating rate, isothermal at 900 °C for 10 minutes, cool off temperature to ambient temperature, finish experiment. The heating rates that were used for this study were 4: 10 °C/min, 20 °C/min, 50 °C/min and 100°C/min, and the carrier gases used for the experiments are: Nitrogen, Air, CO₂, 75% air-25% CO₂, 50% air- 50% CO₂, 25% air-75% CO₂.

RESULTS AND DISCUSSION

Biomass degradation profiles and derivative weight analysis: The biomass degradation profile was checked for every atmosphere tested and all the heating rates. It was found that for pyrolysis the heating rate presented a similar behaviour, the difference was that at a higher heating rate the volatiles were degrading at a higher temperature, and the char was not completely degraded. At the end of the test, char was still present on the residual weight (approx. 10-15% of the weight in all of the tests). For air combustion, there was no visible difference for mass loss difference between all the heating rates, except for the lignin degradation, in which at higher heating rates, the degradation was done at higher temperatures. As CO₂ was started to be mixed with air, it could be seen that the degradation temperature was higher than with air, due to the influence of CO₂ in the mixture, which acts like an inert gas. As more CO₂ was mixed, the degradation temperatures were higher as well. When CO₂ was used, the behaviour of the degradation profile was similar to the pyrolysis curves, until the gasification temperatures were reached, in which the gasification reactions took place, degrading the char that was formed at lower temperatures. Figure 1 shows the biomass degradation profiles for pyrolysis tests at different heating rates. Also, a derivative weight analysis was done for every carrier gas and all the heating rates. This analysis confirmed what was found on the first analysis. For pyrolysis, the highest heating rate was presented at the cellulose degradation stage. For combustion, it was seen that for high heating rates (50-100 °C/min), the lignin was degraded at low temperatures (below 500 °C), while they require higher temperatures to degrade at high heating rates. (Around 700 °C). When CO₂ was added to the mixture it was seen that it was required to have more temperature to degrade the biomass. At 50%-50% mixture of air and CO₂ it could be seen that at high heating rates there were gasification reactions as after 800°C there was a peak in the derivative weight curve. With CO₂ for all heating rates not all the biomass is degraded, as there was a char forming at low temperatures, but after 800°C, the char that was formed was consumed, as at these temperatures there were CO₂ gasification reactions taking place.

Figure 1 shows the example of the biomass derivative weight for the pyrolysis test at different heating rates.

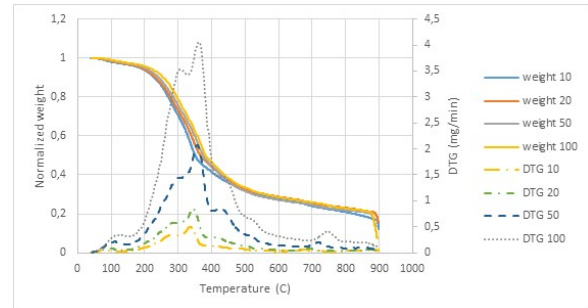


Figure 1. Biomass derivative weight profiles at different heating rates.

Heating rate analysis: A heating rate analysis was also done for all the carrier gases and all the heating rates. For pyrolysis tests, it was found that the behaviour was different at low and high heating rates. At higher temperatures (above 500 °C) the higher heating rates, it presented an exothermic behaviour, while at lower heating rates, presented an endothermic behaviour. For air combustion, it was concluded that all reactions were exothermic, and that the biggest amount of heat release (around 600 mW) was done at this stage. As CO₂ was mixed with air, the temperatures required for the reaction were also increased, and the amount of heat that was released was lower, due to the inert gas properties of the CO₂. For CO₂ gasification, it was seen that the behaviour was similar to pyrolysis. As there was an exothermic behaviour on high heating rates, and endothermic behaviour, but at 800°C there was a change in the behaviour of the reactions, as the CO₂ gasification reactions took place.

Figure 2 shows the heating rate profile for the pyrolysis test at different heating rates.

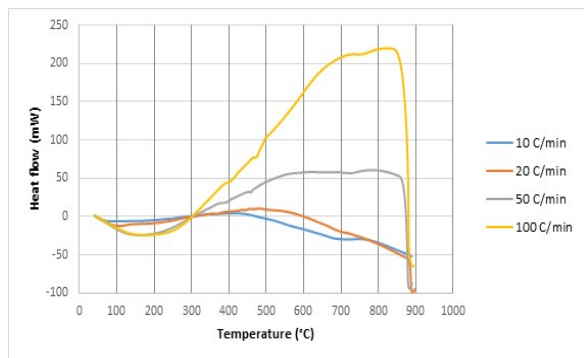


Figure 2. Pyrolysis heating rate profiles.

Specific heat of reaction analysis: A specific heat of reaction analysis, in which the heat flow is divided by the derivative weight, to calculate how much heat was released or absorbed by each mg of biomass that reacted, was done for all the different carrier gases. This allowed to make a qualitative approach and inferred on which different amount of components were being formed during the experiment. At the beginning it was showed that there was an endothermic behaviour, but this was due to the evaporation of the water that was inside the biomass sample. After this evaporation, the volatiles formation was taking place approximately above 300°C, the energy to form CO and CH₄ was reached. Finally, at 360 °C, CO₂ formation energy was achieved, and the process continued to grow until the end of the test, which inferred that all the gases were being formed. As CO₂ was added to the mixture of air, the amount of energy that was released decreased, but the reaction temperatures remained within the same range. Figure 3 shows the specific heat analysis that was done for the 50% air-50% CO₂ test.

Kinetic parameters fitting model: A kinetic model was built to simulate the biomass degradation of each sample, using the mass degradation with temperature increment, and using the least-square method to fit the model to the experimentation data, using the solver tool provided by excel. The models were done with the assumption that these were first order reactions that describe the degradation of the 3 main components of the lignocellulosic biomass (hemicellulose, cellulose and lignin).

between the experimental data and the simulated data.

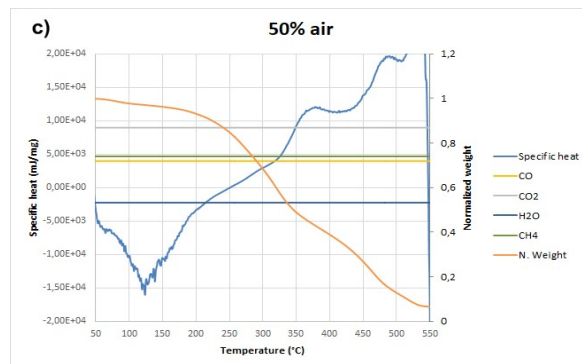


Figure 3. Specific heat analysis for 50% air-50% CO₂ test.

The models used different mass fractions as allocated to pseudo-components that would describe a part of the biomass decomposition reaction, until the reaction is completed. The description of some of the experiments required 4, others 5 pseudo-components to characterize the degradation profile, and in one case, 6 pseudo-components were necessary. For the biomass degradation profiles, the models had an excellent correlation compared to the experimental data (>0.994) in all of the cases, with better correlations on the low heating rates than in the higher rates, which is given as a lack of data to approach one model to the other, and also because there at high heating rates there are several reactions occurring at the same moments, overlapping the biomass degradation stages. At lower heating rates, there can be 3 degradation stages, first hemicellulose, then cellulose and finally lignin. At high heating rates, only 2 peaks are visible, in one of them, hemicellulose, cellulose and lignin reactions are overlapping on the other one, lignin reactions are taking place. From the models it can be seen that there is a variation between the different kinetic parameters of each one of the tests. When the data was being evaluated, it was seen that the pseudo-components were not related to one component but to different mixtures between the components that made very difficult to characterize and compare each one of the parameters between them.

Figure 4 shows a pyrolysis TGA curve simulated with the data from the experimental section. The figure shows the excellent correlation that is

		1	2	3	4	5	6	R ²
		CO ₂	k (1/min)	67,63946	0,087065	5,08E-07	0,033965	
Ea (kJ/mol)	12,9500106		16,9521348	55,3177654	6,62314347	25,2098043	60,668	0,998
Pyrolysis	k (1/min)	1,391	0,192	0,011	0,015	0,001	NA	0,999
	Ea (kJ/mol)	6,1312	18,8867	22,4299	9,8021	8,1221	NA	
100 % air	k (1/min)	11,51	0,22	0,000005	0,17	NA	NA	0,999
	Ea (kJ/mol)	6,83	26,34	45,45	8,86	NA	NA	
75% air- 25% CO ₂	k (1/min)	14,1	1,16	0,11	0,14	NA	NA	0,999
	Ea (kJ/mol)	4,83	11,14	32,17	8,04	NA	NA	
50% air- 50% CO ₂	k (1/min)	0,41	2,71	0,13	0,003	NA	NA	0,999
	Ea (kJ/mol)	5,44	10,74	25,09	20,85	NA	NA	
25% air- 75% CO ₂	k (1/min)	2,71	1,07	0,23	0,02	NA	NA	0,999
	Ea (kJ/mol)	4,37	17,93	7,21	13,33	NA	NA	

Table 2. Kinetic model fitting parameters for different gases.

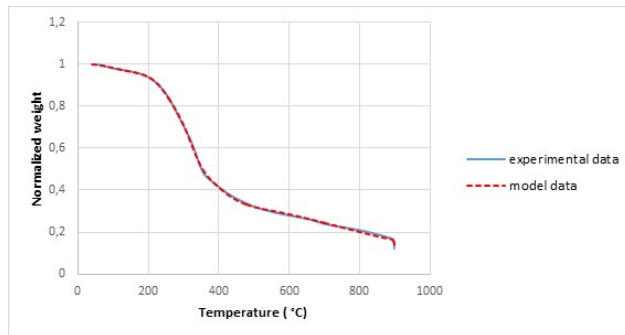


Figure 4. Biomass degradation profile of experimental and model information for pyrolysis at 10°C/min heating rate.

Table 2 depicts results for the kinetic parameters for Arrhenius equation for activation energy and pre-exponential factors estimated for the different atmospheres that were tested. The correlation factor was also included in this table.

Heat flow model: A model to characterize the heating rate behavior was also developed in order to describe the characteristics of the biomass heat flow at the different gases and at different heating rates for each gas. The least squares approximation was also used to do this test. The correlation coefficient (R^2) was also used to evaluate the correlation between the

experimental data and the simulated data. These models also were calculated using the same amount of pseudo-components that were used previously. So, for all the oxidizing tests, 4 pseudo-components were used, while that for pyrolysis, 5 components were used, and for CO₂ gasification, 6 components were used.

Figure 5 shows the correlation between the experimental data recorded and the modelled data. The correlation for this particular case was not very accurate. Table 3 shows a set of results for the modelling of air combustion.

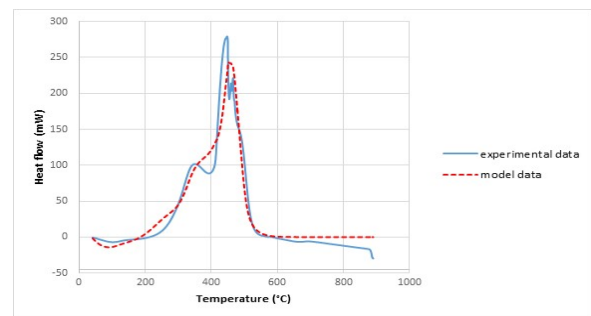


Figure 5. Heat flow experimental and model data for 100 % air combustion at a heating rate of 20 °C/min.

the model used for fitting does not give a good correlation on low heating rates, as it can be

	Air combustion	1	2	3	4	R2
10 °C/min	Heat of reaction (kJ/g)	-510,641	134,393	-195,874	-107,170	0,889
	Cp (J/K)	0,076	0,076	0,076	0,076	
20 °C/min	Heat of reaction (kJ/g)	-0,006	21,646	-241,902	-116,482	0,924
	Cp (J/K)	0,047	0,047	0,047	0,047	
50 °C/min	Heat of reaction (kJ/g)	-136,719	-23,634	-293343	-130,803	0,96
	Cp (J/K)	0,077	0,077	0,077	0,077	
100 °C/min	Heat of reaction (kJ/g)	-111,722	-1,173	25,266	-238,521	0,963
	Cp (J/K)	0,068	0,068	0,068	0,068	

Table 3. Air combustion heats of reaction model parameters for all heating rates with correlation factor.

seen on table 3, the correlation factor was the lowest at the smallest heating rate (10 °C/min), while at 20 °C/min the behavior was still having a small correlation. The correlation factor at high heating rates was better (around 0.96), while it's not the best expected, it is better compared to the scenario at lower heating rates. This is because at low heating rates each component has the time to degrade and its own heat of reaction is being recorded, while at high heating rates there are mixing reactions between each component, making a homogeneous reaction that is easier to characterize. This trend was seen on all the different tests that were done. For all the tests, it was decided to use one general C_p for each heating rate, this is why the results present the same C_p in one test. It can be observed that for the first pseudo component, there is always a negative value of heat of reaction, given because this component is representing the water evaporation, which is an endothermic process.

RECOMMENDATIONS

For next studies it can be recommended to separate the components of the lignocellulosic material, in order to be able to study them

[3] D. Chen, Y. Li, K. Cen, M. Luo, H. Li, and wood: Effect of heating rate and pyrolysis

separately and be able to have a proper kinetic characterization and a proper heat flow modelling. It is also recommended to have a device that is able to measure properly the components of the outlet gas after the reaction has taken place. This could help to identify properly the amount of components that are being formed as the experiment is taking place that could make identify the different reactions that are taking place in the reactor. Also, a more complex method could to identify the heat analysis can be recommended, as the one that was used in this study provided correlation rates that are not describing completely and accurately the behaviour of the biomass.

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